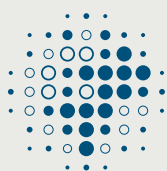




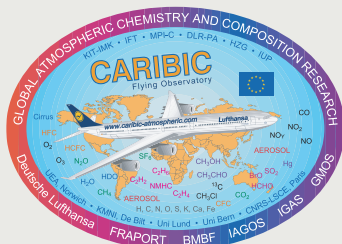
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STABLE ISOTOPE COMPOSITION OF ATMOSPHERIC CARBON MONOXIDE: A MODELLING STUDY

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Abstract

Stable isotope composition of atmospheric carbon monoxide: A modelling study. This study aims at an improved understanding of the stable carbon and oxygen isotope composition of the carbon monoxide (CO) in the global atmosphere by means of numerical simulations. At first, a new kinetic chemistry tagging technique for the most complete parameterisation of isotope effects has been introduced into the Modular Earth Submodel System (MESSy) framework. Incorporated into the ECHAM/MESSy Atmospheric Chemistry (EMAC) general circulation model, an explicit treatment of the isotope effects on the global scale is now possible. The expanded model system has been applied to simulate the chemical system containing up to five isotopologues of all carbon- and oxygen-bearing species, which ultimately determine the $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ isotopic signatures of atmospheric CO. As model input, a new stable isotope-inclusive emission inventory for the relevant trace gases has been compiled. The uncertainties of the emission estimates and of the resulting simulated mixing and isotope ratios have been analysed. The simulated CO mixing and stable isotope ratios have been compared to in-situ measurements from ground-based observatories and from the civil-aircraft-mounted CARIBIC-1 measurement platform.

The systematically underestimated $^{13}\text{CO}/^{12}\text{CO}$ ratios of earlier, simplified modelling studies can now be partly explained. The EMAC simulations do not support the inferences of those studies, which suggest for CO a reduced input of the highly depleted in ^{13}C methane oxidation source. In particular, a high average yield of 0.94 CO per reacted methane (CH_4) molecule is simulated in the troposphere, to a large extent due to the competition between the deposition and convective transport processes affecting the CH_4 to CO reaction chain intermediates. None of the other factors, assumed or disregarded in previous studies, however hypothesised to have the potential in enriching tropospheric CO in ^{13}C , were found significant when explicitly simulated. The inaccurate surface emissions, likely underestimated over East Asia, are responsible for roughly half of the discrepancies between the simulated and observed ^{13}CO in the northern hemisphere (NH), whereas the remote southern hemisphere (SH) compositions suggest an underestimated fractionation during the oxidation of CO by the hydroxyl radical (OH). A reanalysis of the kinetic isotope effect (KIE) in this reaction contrasts the conventional assumption of a mere pressure dependence, and instead suggests an additional temperature dependence of the ^{13}C KIE, which is driven by changes in the partitioning of the reaction exit channels. This result is yet to be confirmed in the laboratory.

Apart from ^{13}CO , for the first time the atmospheric distribution of the oxygen mass-independent fractionation (MIF) in CO, $\Delta^{17}\text{O}$, has been consistently simulated on the global scale with EMAC. The applicability of $\Delta^{17}\text{O}(\text{CO})$ observations to unravelling changes in the tropospheric CH_4 -CO-OH system has been scrutinised, as well as the implications of the ozone (O_3) input to the CO isotope oxygen budget. The $\Delta^{17}\text{O}(\text{CO})$ is confirmed to be the principal signal for the CO photochemical age, thus providing a measure for the OH chiefly involved in the sink of CO. The highly mass-independently fractionated O_3 oxygen is estimated to comprise around 2% of the overall tropospheric CO source, which has implications for the $\delta^{18}\text{O}$, but less likely for the $\Delta^{17}\text{O}$ CO budgets. Finally, additional sensitivity simulations with EMAC corroborate the nearly equal net effects of the present-day CH_4 and CO burdens in removing tropospheric OH, as well as the large turnover and stability of the abundance of the latter. The simulated CO isotopologues nonetheless hint at a likely insufficient OH regeneration in the NH high latitudes and the upper troposphere / lower stratosphere (UTLS).

Zusammenfassung

Stabile Isotope des atmosphärischen Kohlenmonoxids: eine Modellstudie. Diese Studie hat ein besseres Verständnis der stabilen Kohlenstoff- und Sauerstoffisotope im Kohlenmonoxid (CO) der globalen Atmosphäre zum Ziel und stützt sich auf numerische Simulationen. Zunächst wurde ein neues Markierungsverfahren für eine umfassende Parameterisierung von Isotopeneffekten bei der Berechnung der chemischen Kinetik in das Simulationssystem MESSy (Modular Earth Submodel System) eingebaut. Als Teil des Chemie-Klimamodells EMAC (ECHAM/MESSy Atmospheric Chemistry) wurde damit eine explizite Beschreibung von Isotopeneffekten in der globalen Atmosphäre möglich. Das erweiterte Modellsystem wurde zur Simulation des chemischen Systems mit bis zu 5 Isotopologen aller Kohlen- und Sauerstoff enthaltenden Stoffe verwendet, die die Isotopensignatur ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$ und $\Delta^{17}\text{O}$) des atmosphärischen CO bestimmen. Als Modelleingangsgröße wurde ein neues Emissionskataster aller relevanten Spurengase erstellt, welches auch die Information der stabilen Isotope enthält. Die Unsicherheit der Emissionen und der daraus resultierenden Ungenauigkeit der simulierten Spurenstoff- und Isotopenmischungsverhältnisse wurde analysiert. Die simulierten CO Mischungs- und Isotopenmischungsverhältnisse wurden mit in-situ Messungen an Bodenstationen und mit Messungen der verkehrsflugzeuggetragenen CARIBIC-1-Messplattform verglichen.

Die systematische Unterschätzung des $^{13}\text{CO}/^{12}\text{CO}$ -Verhältnisses früherer, vereinfachter Modellstudien kann nun teilweise erklärt werden. Die EMAC-Simulationen bestätigen nicht die Schlussfolgerung früherer Studien, die für CO einen geringeren Beitrag der im ^{13}C stark angereicherten Methanoxidsquelle vorschlugen. Insbesondere wird eine hohe Ausbeute von durchschnittlich 0.94 CO aus jedem reagierenden Methanmolekül (CH_4) in der Troposphäre simuliert, zu einem großen Teil bedingt durch die Konkurrenz zwischen Depositions- und konvektiven Transportprozessen, die die Zwischenprodukte der Reaktionskette von CH_4 zu CO beeinflussen. Keiner der anderen Faktoren, die in früheren Studien berücksichtigt wurden oder unberücksichtigt blieben, jedoch das Potential vermuten lassen, troposphärisches CO in ^{13}C anzureichern, konnte durch explizite Simulation als signifikanter Beitrag identifiziert werden. Die ungenauen, über Ostasien sehr wahrscheinlich unterschätzten, Bodenquellen sind verantwortlich für ungefähr die Hälfte der Abweichung zwischen simuliertem und beobachtetem ^{13}CO in der Nordhemisphäre (NH), während die Zusammensetzungen in der abgelegenen Südhemisphäre (SH) eher auf eine unterschätzte Fraktionierung während der CO-Oxidation mit dem Hydroxylradikal (OH) deuten. Eine neue Analyse des kinetischen Isotopeneffektes (KIE) in dieser Reaktion deckt sich nicht mit der konventionellen Annahme einer reinen Druckabhängigkeit, sondern legt stattdessen eine zusätzliche Temperaturabhängigkeit des ^{13}C KIE nahe, die durch eine Änderung der Partitionierung im Reaktionsausgangskanal bedingt wird. Dieses Ergebnis muss allerdings durch Laborstudien noch bestätigt werden.

Neben ^{13}CO wurde zum ersten Mal auch die Verteilung der massenunabhängigen Sauerstofffraktionierung (MIF) im atmosphärischen CO, $\Delta^{17}\text{O}$, konsistent auf globaler Skala mit EMAC simuliert. Die Anwendbarkeit von $\Delta^{17}\text{O}(\text{CO})$ -Beobachtungen zur Entschlüsselung von Veränderungen im troposphärischen CH_4 -CO-OH-System wurde eingehend untersucht, ebenso die Auswirkungen des Beitrags von Ozon (O_3) zum Sauerstoffisotopenbudget von CO. Es konnte bestätigt werden, dass $\Delta^{17}\text{O}(\text{CO})$ das Hauptsignal des photochemischen Alters von CO darstellt und sich als Maß für OH eignet, welches die Hauptsenke von CO ist. Der stark massenunabhängig fraktionierte Sauerstoff aus O_3 trägt mit circa 2% zur gesamten troposphärischen CO Quelle bei, was zwar Auswirkungen auf das $\delta^{18}\text{O}$ CO-Budget hat, nicht aber auf das von $\Delta^{17}\text{O}$. Zusätzliche Sensitivitätssimulationen mit EMAC bestätigten schließlich die in etwa gleich großen Nettoeffekte der gegenwärtigen atmosphärischen Mengen von CH_4 und CO beim Abbau von troposphärischem OH und zugleich dessen große Umsätze und sein stabiles Vorkommen. Die simulierten CO-Isotope weisen gleichwohl auf eine wahrscheinlich unzureichende OH-Neubildung in den hohen Breiten der Nordhemisphäre und in der oberen Troposphäre / unteren Stratosphäre (UTLS) hin.

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«Essentially, all models are wrong, but some are useful.»

George E. P. Box

1

Introduction and overview

Comprised of two elements whose abundance is essential for the existence of life as we know it (Epelbaum *et al.*^[2013]), carbon monoxide (CO) is as a trace gas that challenges atmospheric scientists for over six decades since it was discerned as an atmospheric constituent in solar spectrum by Migeotte^[1949]. A conjunction of multiple *in-situ* and surface sources, enormous turnover, large spatiotemporal variations and a moderately short lifetime renders the CO atmospheric budget hitherto difficult to reckon: Since the early attempts undertaken by Junge *et al.*^[1971] and Seiler^[1974], the uncertainties in tropospheric source estimates of about $\pm 40\%$ have reduced by merely a factor of three, despite vastly more observational data available to date. The momentous efforts in unravelling atmospheric CO are rather to be enumerated through the encouraging contributions of D. Bates, C. Junge, C. Seiler, P. Warneck, B. Weinstock, L. Jaffe, P. Novelli, L. Yurganov, M.A.K. Khalil *et al.* to the ambient observations and budget estimates, bolstered by the pioneering studies of P. Crutzen, S. Wofsy, J. Logan *et al.* which proved modelling indispensable for their adequate interpretation.¹ A milestone in atmospheric chemistry, namely the elucidation of the central role of OH radicals in cycling of reduced gases by Levy^[1971], was to a certain degree propelled by an unexplained sink of CO in the troposphere inferred by Weinstock^[1969], who attributed it to the reactions of CO with OH radicals, and was first to postulate that the latter are to be sustained by the regenerative chain mechanisms. The early model-aided analysis by Crutzen^[1974] corroborated the prevalence of the OH reactions with CO and methane in the troposphere.

Since the times when CO was known merely as toxic gas emanating during incomplete combustion of various fuels, *e.g.* from car exhaust, many sophisticated approaches and observational platforms were established to study its cycle. Crowned by the remote sensing techniques (first time conducted onboard Space Shuttle, Reichle *et al.*^[1999]), nowadays they ironically witness the diminishing role of CO as a tracer of road transport, foremost owing to the application of catalysts that reduce vehicular emissions. An inimitable and primordial instrument is provided to us by Nature through isotopes, the rare counterparts of the abundant ¹²C and ¹⁶O that comprise less than 2% of terrestrial carbon and oxygen. Stable ¹³C, ¹⁷O and ¹⁸O and radioactive ¹⁴C atoms create five more usable and independent tracers: Any chemical or physical transformation, likewise the emissions from various sources, alter the abundance of each CO isotopologue in a unique manner. It is remarkable that the early ‘regular’ studies on CO were followed by the isotope-inclusive approaches quickly thereupon. A seminal inquiry was conducted by Stevens *et al.*^[1972], who demonstrated the capacity of simultaneous application of two isotope signatures to distinguishing various CO sources, and identified pronounced, uncorrelated seasonal variations in ¹³CO and C¹⁸O tropospheric abundances. To adequately interpret these, crucial missing pieces of the isotope CO puzzle (mainly the estimates of various source signatures and concomitant isotope effects) were to be collected subsequently by H. Smit, J. Conny, D. Lowe, K. Lassey, T. Röckmann, G. Saueressig *et al.*, however, the entire scientific subject of atmospheric CO isotopes would not subsist without the cardinal advancements in the laboratory work and especially the ambient observations and their interpretation pursued by C. Stevens and C. A. M. Brenninkmeijer.¹

¹ Most of the studies implied here are cited below in the “References” section (p. 313) of this manuscript.

A handful of progressive modelling studies dedicated to atmospheric CO isotopes exist to date, thanks to the contributions of B. Weinstock, R. Müller, M. Manning, P. Bergamaschi, L. Emmons, P. Jöckel and their co-workers.¹ On the other hand, no substantial insights were attained in the stable isotope-inclusive modelling and interpretation of carbon monoxide since the study of Manning *et al.*^[1997], who uncovered a peculiar problem: Observations in the southern hemisphere unambiguously indicated the impossibility of closing the tropospheric CO budget without involving rather strong assumptions on one of the main CO sources, *viz.* the photochemical oxidation of methane. Rather indiscernible in the ‘regular’ modelling studies, this discrepancy is obvious in ¹³CO to date. Throughout the subsequent fifteen years, our modelling capabilities have expanded drastically, clearing some of the obstacles that were insurmountable in the earlier model realisations. At present, a substantially more detailed representation of the relevant atmospheric chemical and physical processes, as well as new data on isotope kinetics and sources’ composition are available. Although *le diable est dans les détails*², these are not the only reasons that prompted the current research.

For instance, the initial futile attempts to reconcile ¹³CO in this study have led to the development of the additional diagnostics, special sensitivity studies and, deductively, to revisiting of some well-established conventional approaches in modelling of CO stable isotopes. Secondly, the unique observational data from the upper troposphere from the CARIBIC platform were to be analysed and matched with the simulated isotope CO for the first time. Finally, an ultimate goal of consistently simulating $\Delta^{17}\text{O}(\text{CO})$, the mass-independent (anomalous) oxygen isotope fractionation (MIF) in atmospheric CO, a characteristic heretofore not estimated in the global circulation models, was pursued. In addition to these primary objectives, this thesis covers yet as much important aspects of kinetic isotope modelling, estimation of uncertainties and methodology of the CO isotope composition analysis. To aid the reader, the contents of the chapters are briefly described seriatim and outlined in the diagram below.

Outline of the chapters in this manuscript

Scope	Chapter Topics or subjects	
Model development	2	Isotope kinetic chemistry modelling p. 5
Model parameterisation and setup	3	C/O isotope transfer and kinetic effects p. 29
	5	EMAC model and emission setup p. 107
Observational data analysis	4	Surface station and CARIBIC data p. 67
Model application and discussion	3	Simulations with CAABA (box) p. 55
	6	Simulations with EMAC (3D) p. 139

A sizeable part of this study is devoted to the model development and set-up, owing to the comprehensiveness of the modelling system employed. In particular, the two subsequent chapters present an elaboration of the ‘core’ kinetic chemistry components that enable simulating the stable carbon and oxygen isotope chemistry. Reviewing both, the computational and isotope aspects of chemical kinetics, Chapter 2 introduces an optimisation technique dedicated for simulating large, comprehensive and computationally expensive chemical mechanisms comparable to the one employed in the current study. Some specific issues are covered:

- What are the crucial aspects of the isotope exchange in a kinetic system?
- Which universal indicators are to be used to identify a simulation with inadequate isotope kinetics?
- How to efficiently simulate a set of few additional isotopologues in a chemical mechanism of few hundreds species and reactions, implemented in a large atmospheric-chemistry global circulation model?

² *The devil is in the details (fr.).*

Chapter 3 assembles and reviews all available to date information relevant to the carbon and oxygen isotopes chemical interchange, such as kinetic isotope effects and transfer peculiarities. Thus compiled isotope chemistry parameterisation is probed in a box-model study focussing on a few particular questions:

- Are the simulated tropospheric (isotope) chemical interchanges adequate?
- What are the decisive components for the CO isotope composition variations?
- What additional information can one infer from such simulations?

In Chapter 4, a review of the observational data on atmospheric CO stable isotopes is given, followed by an effort to compile the consistent seasonal climatologies of the mixing and isotope ratio variations from the observations obtained in diverse timeframes and conditions. Some aspects that were not addressed earlier are targeted, *e.g.*:

- Do we see similar trends in the isotope and mixing ratios of tropospheric CO?
- How representative are certain locations for the background conditions and isotope signals in CO?
- Why does the Keeling-plot approach, a tool widely used for identifying the isotope signatures of the trace gas sources, appears apt for $C^{18}O$ but not for ^{13}CO variations?

Apart from the surface station data, Chapter 4 also glances over the CARIBIC data that offer a unique perspective on CO isotopes from the UTLS region.

The last two chapters of this thesis are dedicated to the modelling studies with EMAC, the second generation of the ECHAM5/MESSy Atmospheric Chemistry model (Jöckel *et al.*^[2010]). Thus, Chapter 5 details the components and base configuration of EMAC used in the current study, as well as the necessary extensions applied in order to perform consistent, stable C and O isotope-inclusive simulations with a general circulation model. A separate inquiry is undertaken about the isotope ratios imposed on the applied trace gas emissions. The novel questions addressed are:

- What other (non-chemical) isotope effects are to be expected in EMAC, how influential are these?
- Which assumptions are crucial in estimating the isotope signatures of the given sources?
- What are the errors associated with the sources (either *in-situ* of surface emissions), and how do the uncertainties in their atmospheric abundances/influxes intertwine with those in the concomitant isotope ratios?

The quintessence of the analysis, model development and simulation efforts exerted in this study is accommodated in Chapter 6, which also contains most of the discussion. Thus, given in the first place, a scrupulous re-analysis of the previous modelling studies on CO isotopes aims at their particularities and potential shortcomings. That is:

- May the slight differences in the applied parameterisations result in substantially dissimilar interpretations of the isotope CO budget?
- If so, could this lead to misconstruing of some characteristic model *vs.* observations discrepancies?

The second part of Chapter 6, in turn, details the goals and results of the simulations to provide the answers to the above given questions, and to raise a few new ones hopefully. For instance, the problematic of closing the ^{13}CO budget spotted by Manning *et al.*^[1997] can be resolved, however a corroboration of the proposed alternative requires further laboratory research. Tackling CO isotopes involves recurring to some notorious and novel questions of the atmospheric chemistry, *e.g.*:

- How sensitive is the atmospheric abundance of OH to the perturbations in the CO or CH_4 burden?
- How responsive is $\Delta^{17}O(CO)$ to the changes in OH?

The answers provided by EMAC, when opposed to the studies employing simplified chemistry schemes or conventional isotope equilibrium models, are rather interesting. The overarching aim of this study is, however, to newly demonstrate the isotopes of CO running the full gamut of atmospheric applications, from identification of the pollution sources to tracing complex chemical and physical processes.

2

Modelling of the isotope kinetic chemistry with MECCA-TAG

In this chapter, the kinetic chemistry tagging technique approach developed in the course of this study is introduced (Sect. 2.2) conjointly with a panoptic review of the isotope-specific aspects of the kinetic chemistry modelling (Sect. 2.3). Subsequently, the approximations applied and adaptation of the tagging technique to stable isotope chemistry modelling are considered in Sect. 2.4. At last, Sect. 2.5 is focusing on the model configuration and evaluation, with illustrative examples followed by a performance analysis.

2.1 Overview

Historically, process- and budget-level isotope-enabled atmospheric chemistry models diverged, embodying rather different aspects of the isotope chemistry in a particular modelling application. The process-oriented studies comprise comprehensive chemistry schemes accounting for isotopes and related isotope effects in full detail. This approach resolves certain peculiarities of the isotopic chemistry, but typically *induces computational strain*. At first, one is compelled to simulate a greatly enlarged chemical mechanism (*i.e.* set of species and equations, whose numbers grow as the isotopologues and isotopomers are considered separately). At second, some of the simplifications commonly used in kinetic chemistry modelling may be not applicable for isotopes, thus limiting usage of reduced chemical schemes. Consequently, the modelling domain is usually limited, *e.g.* to a column- or a box-model, frequently assisting only laboratory work.³ Nonetheless, the main complication of isotope chemistry modelling lies in the intricacies of isotope composition transfer. Although normally not discerned in regular chemistry reaction mechanisms, different isotopes end up in different reaction products, thus forming “isotopically” *different kinetic pathways*. For example, there are isotope exchange reactions that affect the isotopic ratios of reacting species, but not their concentrations.⁴ Another aspect of isotope chemistry is that the isotopic composition is usually measured as the atomic ratio of the rare isotope to the abundant one, whereas the reaction kinetics is calculated on the basis of molecular concentrations. The removal of a particular isotope atom from the molecule during chemical reaction (for example, D or H during the oxidation of CH₄ to HCHO) alters its isotope ratio differently.⁵

³ For instance, Yung *et al.*^[1991] at an early stage applied a one-dimensional photochemical model to study the heavy ¹⁸O isotope enrichment in stratospheric CO₂. They showed that a model calculation with an incorporated complex chemistry mechanism can account for the observed enrichment, and attributed its origin to the chemical exchange with ozone mediated by O(¹D), supporting the hypothesis of the chemical origin of the effect. In a subsequent study, Yung *et al.*^[1997] refined the model by using an expanded chemical scheme that accounted for ¹⁷O, the enrichment of which in O₃ does not follow that for ¹⁸O in the expected mass-dependent manner. The refined chemical mechanism (accounting for two rare isotopes, plus selected isotopomers) grew many times larger. The authors remarked that the calculations could be improved using a 2D model, yet greater computational accuracy was needed for isotopic species.

⁴ A model study illustrating the significance of oxygen isotope exchange in the atmosphere was done by Lyons^[2001], who elaborated the novel mechanism including oxygen isotope exchange reactions. His column-model simulations predicted both, tropospheric and stratospheric ozone-impelled isotope enrichments for oxygenated short-lived radicals as well as notable mass-independent enrichment for stratospheric water through OH. The latter was shown to originate from the isotope exchange with NO_x, signifying a notable influence of the isotope exchange on the result. Zahn *et al.*^[2006] incorporated this result in an extensive study on multiple isotopes in stratospheric H₂O, which required a comprehensive mechanism for hydrogen and oxygen isotopes encompassing a large set of kinetic isotope effects (KIEs) and isotope exchange reactions. They emphasised important peculiarities in isotope modelling, such as the *inapplicability of the “chemical families” concept*. For instance, in common (non-isotopic) cases the conversion of one family member to another does not affect the abundance of the whole family; however, if in the course of the conversion chain the exchange with another isotope reservoir takes place, it alters the isotopic composition of the entire family. The HO_x (=HO₂+OH) family is an example of such, as HO₂ obtains its composition from molecular oxygen during the conversion from OH.

⁵ Pieterse *et al.*^[2009] refer to the importance of this counting effect in their study on hydrogen isotope chemistry.

The above mentioned complications are, nevertheless, commonly neglected in the budgeting studies. The isotopic composition here serves as an additional constraint on the budget of a species composed of contributions from a set of emission classes, each associated with a given isotopic signature. The modelling domain covers scales from zero-dimensional box-models to three-dimensional atmospheric transport models with implicit (*i.e.* isotopic signatures and effects are *approximated* from a set of chemical tracer values) or explicit chemistry calculation schemes (*e.g.*, Gros *et al.*^[2002], Cuntz *et al.*^[2003]). A large number of atmospheric modelling studies use isotope variations, *e.g.* in CO₂, CH₄ or N₂O, to assess the interhemispheric, troposphere-stratosphere and biosphere exchange (see, for instance, Allan *et al.*^[2001], Boering *et al.*^[2004], Lassey *et al.*^[1993], Liang *et al.*^[2008], Liang and Yung^[2007], McCarthy *et al.*^[2003], Quay *et al.*^[1991]). The key features of such studies are the use of relative timescales of the atmospheric transport/mixing processes and isotope ratio variations of a given tracer together with the facility to account for the isotope effects. To illustrate this, the isotopic composition of carbon in methane is relatively easy to parameterise since it has virtually no in situ sources (*i.e.* as a product of a chemical reaction). Thus, the isotopic composition is easily derived by combining direct (surface) emission, transport and removal terms. Applying this concept in a similar manner for the species which in-situ sources cannot be neglected, most implicit-chemistry transport models incorporate simplified isotopic chemistry parameterisations. These account for the main chemical sources and sinks of the species in so-called “net reactions” (without consideration of the intermediates) accompanied by terminal KIEs (*i.e.* upon entering/exiting a “net reaction” chain). Unfortunately, such a concept is not very well-suited for species that have multiple in situ sources or for “net reactions” involving intermediates whose behaviour varies in different chemical and physical regimes. Recalling the examples above, it is difficult to accurately account for the isotopic exchange of a particular intermediate with other disjointed reservoirs, as well as for the other individual and non-chemical processes that alter the isotopic composition. These may be transport (*e.g.* the advection term is governed by the chemical gradient of the intermediate, but not the lump of them) or removal processes accompanied by KIEs.

Unfortunately, the limitations introduced by approximations often preclude further application of the model results, whereas a detailed chemistry scheme would be of benefit. At present, models explicitly calculating chemistry hold the potential of providing detailed isotope chemistry treatment. This has been shown by numerous studies, but not yet applied within atmospheric chemistry global circulation models (AC-GCM) that are capable of handling comprehensive chemistry mechanisms. The advantage of the coupled AC-GCM system is also its capability to account for physical processes affecting isotope ratios individually per species. The holdup in development of such systems can probably be attributed to the large computational demands and painstaking technical implementation of the detailed isotope chemistry. The motivation of the work presented in the current chapter is to give an isotope extension to the comprehensive kinetic chemistry model implemented in the AC-GCM used further in the current study, to overcome the computational issues and facilitate the model configuration. These aspects are resolved in the *tagging technique* proposed here (described in the following), which is generic and is well-suited for various kinetic chemistry investigations; it is intrinsically apt for stable isotope modelling as well.

2.2 The kinetic chemistry system tagging technique

2.2.1 The tagging framework

The *tagging technique* described here is intended to serve as a diagnostic method applied to simulated kinetic chemistry systems only. The concept of tagging implies that a given characteristic (not necessarily measurable in reality, but an imaginary “tag”) is assigned to the molecules of a given subset of simulated chemical species. In other words, a “tag” is an additional property of a “tracer” describing the species (as defined *e.g.* by Jöckel *et al.*^[2008]), to trace certain processes. For instance, one can add a tag of the species “origin” to trace its atmospheric transport pathways and contribution of the sources to regional pollution. Similarly, the information related to the chemical composition interchange can be obtained by tracing the distribution of the “tags” transferred in chemical reactions from one species to another. For instance, one can tag a single species to assess its individual contribution to the budget of the others. Another prominent application is the isotopic tagging, when the presence of the rare isotope in the molecule constitutes indeed a natural intrinsic “tag”. This isotope tagging is discussed below.

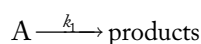
We first declare the studied kinetic system as being *regular*. It incorporates the chemical *mechanism*, being a set of compartments (species) of molecules that interact via different pathways (chemical reactions) characterised by certain transfer speeds (reaction rates). The mechanism defines the resulting numerical system of ordinary differential equations (ODEs) with the species' concentrations as unknowns that must be solved (numerically integrated) to find the evolution of the species' concentrations in time from their given initial values. In this work, MECCA, the Module Efficiently Calculating the Chemistry of the Atmosphere (Sander *et al.*^[2005], Sander *et al.*^[2011]) is employed as the regular kinetic system and extended by a flexible tagging procedure. MECCA is an atmospheric chemistry sub-model based on a kinetic pre-processor (KPP, Sandu and Sander^[2006]). KPP provides a set of robust and efficient chemistry kinetic system solvers allowing the simulation of chemical mechanisms of various complexities. MECCA is currently interfaced via the MESSy interface (Modular Earth Submodel System, Jöckel *et al.*^[2005]) to the photochemical 0-D (box) model CAABA/MECCA (Sander *et al.*^[2011]) and to the 3D atmospheric chemistry AC-GCM EMAC (ECHAM5/MESSy atmospheric chemistry, Jöckel *et al.*^[2006], Jöckel *et al.*^[2010]). The tagging technique for MECCA presented here is implemented as the sub-sub-model MECCA-TAG according to the MESSy standard (Jöckel *et al.*^[2005]).

Due to the nature of its application, tagging is not intended to provide additional information on the significance of the various chemical pathways in the mechanism (as, for example, in Lehmann^[2004]), which forms a different diagnostic method. Nevertheless, all chemical pathways (*i.e.* reactions) in the studied mechanism are accounted for to trace the net species' exchange. Although the number of different "tags" as such is not limited, the approach presented here is restricted to molecules that have not more than one single "tag" attached. All species' molecules are partitioned this way to disjoint subsets termed *tagging classes*. Molecules with the same "tag" belong to the same and only class. This allows one to define the (tagging) modelling problem as such that it still deals with quantitative (statistical) characteristics, namely the number of molecules of a certain class, rather than considering the tagging of each individual molecule. By definition, the total abundance of a species is represented by the sum of its molecules of all classes. Consequently, the resulting quantitative information one obtains is the *share* of each class in the entire budget of every species.

2.2.2 The modelling problem

The tagging technique is designed to meet two criteria that define its applicability in complex and costly simulations. First, it should add minimum possible computational overhead to the entire simulated system. Second, it should be diagnostic (*i.e.* decoupled) in such a way that the regular system remains unaltered and produces (numerically) identical results while being tagged. However, as it is pointed out below, the simultaneous realisation of these two objectives forms a challenge. For a subset of *tagged species* one needs to formulate an approach that parameterises the chemical interaction of the molecules of each class in addition to the regular mechanism. The natural approach to this is to form a new kinetic system whose mechanism replicates only the set of necessary reactions, and includes sets of species representing each class of tagged species. To give an example, consider a subset of N species tagged into M classes. To create the kinetic tagging system, we pick out all *tagged reactions* in which these N tagged species act. Then we replicate these reactions M times in a new mechanism for every set of species of each class. If the number of tagged reactions equals R , the resulting mechanism should include in total N times M species and R times M reactions. Furthermore, by imposing the initial conditions from the regular system and additionally the species' classes distributions, we integrate the tagged system simultaneously with the regular one.

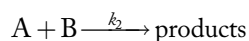
Unfortunately, in most cases it is not sufficient to replicate only the tagged reactions and species. To illuminate this, let us regard two reactions of different order. A unimolecular reaction



describes the decomposition of a species A . The reaction rate v_1 in $[\text{molecules cm}^{-3} \text{ s}^{-1}]$ is expressed as

$$\frac{d[A]}{dt} = -v_1 = -k_1 \cdot [A] \quad (\dagger)$$

and depends only on the concentration $[A]$ and the first-order rate coefficient k_1 $[\text{s}^{-1}]$. A bimolecular reaction



describes the interaction of species A and B with the rate v_2 which depends on the concentration of both reactants and the second-order rate coefficient k_2 , in units of $[\text{molec}^{-1} \text{ cm}^3 \text{ s}^{-1}]$:

$$\frac{d[B]}{dt} = \frac{d[A]}{dt} = -v_2 = -k_2 \cdot [A][B] \quad (\ddagger)$$

Now suppose that species A is tagged. It is clear that the rates of those reactions replicating the unimolecular reaction in the tagged system are to be determined by concentrations of the respective “class” of species A. However, a problem arises with the bimolecular reaction when species B is *not* tagged and hence its concentration is unknown, if only tagged species are replicated. We have to somehow add species B and all reactions it participates in to the new system. This will inevitably cause the same problem with non-tagged species paired in reactions with B, and so on. Finally, one may end up copying a large part of the regular mechanism plus enlarging the tagged part with M times more species and reactions between them.

Another perplexing case arises when both, A and B are tagged. How should one parameterise the way the educts of different classes react and contribute to the common products? Again, a natural way is to consider all possible combinations of possible reactants, class by class. This would require to add another 2^M reactions for each bimolecular reaction of two different species and some $M(M+1)/2$ reactions for any self-reacting species. Finally, albeit that the resulting tagging system is diagnostic and decoupled from the regular one, its kinetic mechanism grows to a great extent. For comprehensive mechanisms (which include many reactions and species to tag) the tagged system will become unwieldy, too large, and hence computationally impracticable to be simulated in 3-dimensional models.

Here, an approximate solution to the problem, which permits omitting species that are not tagged, is proposed and described. The basic idea of the approach is to utilise the reaction rates v that are customarily calculated in course of the integration of the regular system. Indeed, in the above example, processing of the species A does not require the information about the concentration [B], if the rate v_2 is already known. However, at this stage the specific kinetic system formulation intervenes. The decoupled regular system is inaccessible while it is being integrated; one cannot retrieve the momentary value of v_2 but only its integral over a certain period of time. Nonetheless, as we will discuss, the latter can actually still be utilised under a number of assumptions. In addition, we will reconsider the species’ composition exchange in higher order reactions on the basis of pair exchange for the purpose of dealing clearly with the mentioned transfer ambiguities. This also allows effective optimisations to the final tagging kinetic system. Foremost, the reader is referred to Table 2.1 (pp. 8–9) for the summary of the used notations.

Table 2.1 Notation used

Symbol	meaning, [units]	example or definition
N_S	number of tagged species	
C	subset of tagged species	$C = \{C_1, \dots, C_{N_S}\}$
N	particular species index in the tagged species subset	$n = 1, \dots, N_S$
c_n	n^{th} tagged species concentration, [molecules cm^{-3}]	if C_n refers to CO, $c_n = [\text{CO}]$
N_R	number of tagged reactions	
R	subset of tagged reactions	$R = \{R_1, \dots, R_{N_R}\}$
r	tagged reaction index	$r = 1, \dots, N_R$
k_r	r^{th} reaction rate coefficient [s^{-1}] or [$\text{molec}^{-1} \text{cm}^3 \text{s}^{-1}$]	
v_r	r^{th} reaction rate, the product of the educt(s) concentration(s) and specific reaction rate coefficient k_r , [molecules $\text{cm}^{-3} \text{s}^{-1}$]	see Eqs. (†), (‡) (p. 7)
P_r	subset of tagged products in r^{th} reaction	for example reaction ^{a)} and a set of tagged carbonaceous species: $P_R = \{\text{CH}_3\text{O}_2; \text{HCHO}\},$ for oxygen-bearing species: $P_R = \{\text{CH}_3\text{O}_2; \text{HCHO}; \text{OH}; \text{H}_2\text{O}\}$
e, p	species indices referring to current reaction educts, products	for example reaction ^{a)} and a set of tagged carbonaceous species: e refers to CH_3OOH p refers to $\text{CH}_3\text{O}_2, \text{HCHO}$
s_{rp}	r^{th} tagged reaction p^{th} product stoichiometric coefficient	for example reaction ^{a)} $s_{\text{CH}_3\text{O}_2} = 0.7, s_{\text{HCHO}} = 0.3$
q_n	specific stoichiometric weighting of the species C_n ; for the isotopic tagging: number of atoms of selected chemical element (atomic number Z) in C_n	if n refers to CH_3O_2 , – for carbon $q_n = 1$ – for oxygen $q_n = 2$

Table 2.1 Notation used

Symbol	meaning, [units]	example or definition
ψ_r^{-p}	r^{th} reaction branching ratio, a fraction of the contribution of the educt C_e to the product C_p	for example reaction ^{b)} $\psi_r^{\text{O}_2 \rightarrow \text{O}_3} = 2/3$, $\psi_r^{\text{O}^{(3)\text{P}} \rightarrow \text{O}_3} = 1/3$
τ	regular mechanism (KPP) integration time step [s]	
A_r	r^{th} reaction approximated rate [molecules $\text{cm}^{-3} \text{s}^{-1}$]	$A_r = \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} v_r dt$
J	tagged system rate matrix of the size N_s by N_s elements [molecules $\text{cm}^{-3} \text{s}^{-1}$]	if n refers to CO, e refers to HCHO: $\mathbf{J}_{n,n}$ is the total sink rate of CO $\mathbf{J}_{n,e}$ is the pair rate of $\text{HCHO} \rightarrow \text{CO}$ $M = 2$ for $^{12}\text{C}/^{13}\text{C}$ isotopes, $M = 3$ for $^{16}\text{O}/^{17}\text{O}/^{18}\text{O}$ isotopes $m = 1 \dots M$
M	number of tagging classes (number of isotopologues considered in case of isotopic tagging)	
m	tagging class index	
${}^m C_n$	tagged mechanism n^{th} species m^{th} class species	${}^m C = \{{}^m C_1, \dots, {}^m C_{N_s}\}$
${}^m c_n$	tagged mechanism n^{th} species m^{th} class species concentration	$C_n = \{{}^m C_n\}$
${}^m f_n$	share of m^{th} class species in total n^{th} species molecular abundance	$c_n = \sum_{m=1}^M {}^m c_n, \quad {}^m f_n = \frac{{}^m c_n}{\sum_{l=1}^M {}^l c_n}$
i	minor isotopologue index	$i = 1 \dots M-1$
$\text{maj} C_n, \text{min}, i C_n$	isotopically tagged mechanism n^{th} species major and i^{th} minor isotopologues	$\text{maj} C_n$ is equivalent to ${}^1 C_n$ $\text{min}, i C_n$ is equivalent to ${}^{1+i} C_n$, $i = 1 \dots M-1$
$\text{maj} c_n, \text{min}, i c_n$	isotopically tagged mechanism n^{th} species major and i^{th} minor isotopologues concentration	if C_n refers to CO, for oxygen isotopes: major isotopologue: $\text{maj} c_n = [\text{C}^{16}\text{O}]$, minor isotopologues: $\text{min}, 1 c_n = [\text{C}^{17}\text{O}]$, $\text{min}, 2 c_n = [\text{C}^{18}\text{O}]$
$\text{maj} f_n, \text{min}, i f_n$	respective shares of the major and i^{th} minor isotopologue molecules in n^{th} species total molecular abundance; $\text{maj} f_n$ is equivalent to ${}^1 f_n$ $\text{min}, i f_n$ is equivalent to ${}^{1+i} f_n$, $i = 1 \dots M-1$	$\begin{cases} \text{maj} f_n = \text{maj} c_n \cdot \varsigma, & \text{min}, i f_n = \text{min}, i c_n \cdot \varsigma \\ \varsigma \equiv \left(\text{maj} c_n + \sum_{i=1}^{M-1} \text{min}, i c_n \right)^{-1} \end{cases}$
$\text{abu}, i \chi_n, \text{rare}, i \chi_n$	respective shares of abundant and rare isotope atoms (of the same atomic number Z) in minor isotopologue $\text{min}, i C_n$	$\begin{cases} \text{rare}, i \chi_n = \text{min}, i f_n \cdot (q_n)^{-1} \\ \text{abu}, i \chi_n = \text{rare}, i \chi_n \cdot (1 - q_n) \end{cases}$
$\text{min}, \mathbf{J}$	copy of the rate matrix J with some changed elements accounting for KIE for i^{th} minor isotopologue in the isotopically tagged system [molecules $\text{cm}^{-3} \text{s}^{-1}$]	see Eq. (2.23) in Sect. 2.4.1 (p. 19)
${}^i R$	The isotopic ratio of the i^{th} rare isotope (see also Sect. 3.2, p. 30)	${}^i R(C_n) = \frac{\text{min}, i c}{\text{maj} c \cdot q_n + (q_n - 1) \cdot \sum_{i=1}^{M-1} \text{min}, i c}$
${}^e, i \alpha_r$	KIE fractionation factor for $\text{min}, i C_e$ isotopologue educt in r^{th} reaction	$^{13}\text{CH}_3 \alpha_{\text{CH}_4 + \text{OH}} = k^{13}\text{CH}_4 + \text{OH} / k^{12}\text{CH}_4 + \text{OH}$
${}^a, i \beta_r$	isotope exchange reaction fractionation factor for $\text{min}, i C_a$ isotopologue	$^{18}\text{OH} \beta_{\text{OH} \rightleftharpoons \text{NO}_2} = k^{\text{N}^{16}\text{O}_2 + ^{18}\text{OH}} / k^{\text{N}^{18}\text{O}^{16}\text{O}^{18}\text{OH}}$
$\lambda_r^{a \rightarrow b}$	probability of rare isotope transfer from species C_a to C_b in the isotope exchange reaction r	$\lambda_r^{a \rightarrow b} = \frac{q_b}{q_a + q_b}$
${}^i I_r^{a \leftrightarrow b}$	the rate of i^{th} rare isotope atom transfer from C_a to C_b species in the isotope exchange reaction r [molecules $\text{cm}^{-3} \text{s}^{-1}$]	see Eq. (2.25) in Sect. 2.4.1 (p. 19)
${}^i \gamma_a$	net rate of gain (loss) of i^{th} rare isotope atoms by C_a species due to all isotope exchange reactions it participates in [molec. $\text{cm}^{-3} \text{s}^{-1}$]	${}^i \gamma_a = - \sum_{r \in \text{IEX}} {}^i I_r^{a \leftrightarrow b}$

Notes:

^{a)} example reaction: $\text{CH}_3\text{OOH} + \text{OH} \longrightarrow 0.7 \cdot \text{CH}_3\text{O}_2 + 0.3 \cdot \text{HCHO} + 0.3 \cdot \text{OH} + \text{H}_2\text{O}$ ^{b)} example reaction: $\text{O}_2 + \text{O}^{(3)\text{P}} \longrightarrow \text{O}_3$

2.2.3 Definitions and assumptions

We denote a subset of tagged species picked from the regular mechanism as

$$C = \{C_n\}, \quad n = 1, \dots, N_S$$

and a subset of reactions between them as

$$R = \{R_r\}, \quad r = 1, \dots, N_R,$$

where N_S and N_R are the total number of tagged species and reactions, respectively. Any reaction of R can be unimolecular (thermal decomposition, photolysis or radioactive decay) or multi-molecular (bimolecular or ter-molecular reactions). For the purpose of tagging, it is important to discriminate how many tagged species are present among the *educts* (the reacting species). For a reaction with a single tagged educt, the composition transfer can be formulated as:



The notation of Eq. (2.1) resembles the common chemical reaction notation, but we mention only the tagged educts and products and apply the reaction rate v_r instead of the rate coefficient. So far, we will suppose v_r to be a defined momentary value in units of [molecules cm⁻³ s⁻¹]. In essence, Eq. (2.1) signifies that in course of the reaction R_r all its products P_r (*i.e.*, a set of species C_p) are being created from the educt species C_e at rate v_r . The coefficients s_{rp} designate the stoichiometric coefficients of the respective products.

Now consider a reaction of two tagged educts:



Here, the molecules of educts C_e and C_n are transferred with the same rate v_r and become distributed among the products. In fact, Eq. (2.2) can be rewritten as the composition of two single-educt reactions:

$$\begin{cases} C_e \xrightarrow{v_r} \sum_{p \in P_r} \psi_r^{e \rightarrow p} \cdot s_{rp} C_p \\ C_n \xrightarrow{v_r} \sum_{p \in P_r} \psi_r^{n \rightarrow p} \cdot s_{rp} C_p \end{cases}, \quad (2.3)$$

where each pair of branching ratios $\psi_r^{n \rightarrow p}$ and $\psi_r^{e \rightarrow p}$ regulates the transfer of the molecules to the particular product C_p from C_n and C_e , respectively. To maintain the balance in (2.3) with respect to (2.2), the sum of the ratios must be equal to unity for each product p :

$$\psi_r^{n \rightarrow p} + \psi_r^{e \rightarrow p} = 1$$

The ratios ψ are the additional information required for the tagging. For example, one can dispense the explicit creation of a certain product C_p from C_n by setting $\psi_r^{n \rightarrow p} = 1$ and $\psi_r^{e \rightarrow p} = 0$, accordingly. When the exact transmission of the molecules from the educts to the products is not known, the following setting is proposed:

$$\psi_r^{e \rightarrow p} = \frac{q_e}{q_e + q_n}, \quad \psi_r^{n \rightarrow p} = \frac{q_n}{q_e + q_n} \quad (2.4)$$

where q_n and q_e are the number of the selected isotope atoms in the educts. Thus the branching ratios in Eq. (2.4) define a proportional (isotope) content share of both educts in the products composition.

An illustrative example for the formulations above is given for the reaction of quenching and interaction of O(¹D) with O₂:



First, we rewrite this bimolecular reaction as a composition of two simpler reactions, *i.e.*

$$\begin{cases} \text{O}_2 \xrightarrow{v_{\text{O}_2 + \text{O}(\text{}^1\text{D})}} \psi_{\text{O}_2 \rightarrow \text{O}(\text{}^3\text{P})} \cdot \text{O}(\text{}^3\text{P}) + \psi_{\text{O}_2 \rightarrow \text{O}_2} \cdot \text{O}_2 \\ \text{O}(\text{}^1\text{D}) \xrightarrow{v_{\text{O}_2 + \text{O}(\text{}^1\text{D})}} \psi_{\text{O}(\text{}^1\text{D}) \rightarrow \text{O}(\text{}^3\text{P})} \cdot \text{O}(\text{}^3\text{P}) + \psi_{\text{O}(\text{}^1\text{D}) \rightarrow \text{O}_2} \cdot \text{O}_2 \end{cases} \quad (2.6)$$

Given the proportional share of the educts composition in the products, the transfer ratios for each educt-product pair, according to Eq. (2.4), are

$$\begin{aligned}\psi_{\text{O}_2 \rightarrow \text{O}(^3\text{P})} &= \psi_{\text{O}_2 \rightarrow \text{O}_2} = \frac{2}{3} \\ \psi_{\text{O}(^1\text{D}) \rightarrow \text{O}(^3\text{P})} &= \psi_{\text{O}(^1\text{D}) \rightarrow \text{O}_2} = \frac{1}{3}\end{aligned}\quad (2.7)$$

Alternatively, to specify the explicit transfer of the composition from $\text{O}(^1\text{D})$ to $\text{O}(^3\text{P})$, one defines the ratios as

$$\begin{aligned}\psi_{\text{O}_2 \rightarrow \text{O}(^3\text{P})} &= 0, & \psi_{\text{O}_2 \rightarrow \text{O}_2} &= 1 \\ \psi_{\text{O}(^1\text{D}) \rightarrow \text{O}(^3\text{P})} &= 1, & \psi_{\text{O}(^1\text{D}) \rightarrow \text{O}_2} &= 0\end{aligned}$$

In this elementary example, the products' stoichiometric coefficients s_{rp} are all equal to unity.

Eq. (2.3) also shows that if C_e and C_n were species of different classes, each of them would create the products of their own class. As a result, if any higher order reaction of R having multiple tagged educts can be “decomposed” into a set of single educt reactions, we can consider the class to class exchange between particular educt species instead of dealing with combinations of the educts of different classes. This is important for the subsequent approximations that are introduced.

The use of formulation (2.3) and reaction rates v enables one to reduce the total number of reactions needed to be introduced in the kinetic mechanism of the tagged system. The subset R may contain more than one reaction in which a particular pair of species undergoes exchange. Instead of replicating all of them, we can create one pair reaction:

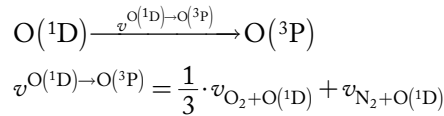
$$\begin{aligned}C_e &\xrightarrow{v^{e \rightarrow p}} C_p \\ v^{e \rightarrow p} &= \sum_{r \in R^{e \rightarrow p}} \psi_r^{e \rightarrow p} \cdot s_{rp} \cdot v_r\end{aligned}\quad (2.8)$$

in which $R^{e \rightarrow p}$ is the subset of reactions where species C_e produces C_p and $v^{e \rightarrow p}$ is the pair reaction rate. For the comprehensive mechanisms, this step may lighten the numerical complexity of the tagged system by transforming the set of tagged reactions to the equivalent set of maximum $2 \cdot N_s$ pair reactions (thus reducing the system of ODEs to solve).

An example for a pair reaction rate is illustrated, similarly to the reaction (2.5), by the quenching of $\text{O}(^1\text{D})$ to $\text{O}(^3\text{P})$ with molecular nitrogen:



In (2.9), the transfer of the oxygen is unambiguous, thus $\psi = 1$. The final $\text{O}(^1\text{D})$ to $\text{O}(^3\text{P})$ pair reaction encompassing reactions (2.5) and (2.9) plus assuming the transfer from (2.7) is:



The pair reaction rate is always proportional to the concentration of the educt C_e (e.g. $\text{O}(^1\text{D})$ in the above example). Subsequently, if Eq. (2.8) were replicated in the tagging system, then the reaction rate of each class' replica is proportional to the share of this class. This result, together with the “class to class” concept from Eq. (2.3), founds the formulation of the tagged system kinetic mechanism proposed below.

We assume that a subset C of species is tagged into M classes. Thus, in the tagged kinetic system mechanism we introduce sets of species termed as tagging classes ${}^m C$:

$${}^m C = \{{}^m C_n\}, \quad n = 1, \dots, N_s, \quad m = 1, \dots, M$$

such that every regular species C_n is represented class-by-class in the tagged system as:

$$\begin{aligned}C_n &\equiv \{{}^1 C_n, \dots, {}^M C_n\}, \\ c_n &= \sum_{m=1}^M {}^m c_n\end{aligned}\quad (2.10)$$

where lowercase c_n and ${}^m c_n$ denote the concentration of the species C_n and ${}^m C_n$, respectively. Note that these species belong to the different (*i.e.* regular and tagged) simulated mechanisms. Further, for every class m and a pair of exchanging species, we define the pair reaction in the tagging mechanism:



The rates ${}^m v^{e \rightarrow p}$ must satisfy the following condition to account properly for the total transfer:

$$\sum_{m=1}^M {}^m v^{e \rightarrow p} = v^{e \rightarrow p}$$

This ensures that the amounts of reacted molecules in the regular and tagged systems are equal. Recalling from Eq. (†) (p. 7) that the reaction rate is proportional to the concentration of the educt, for Eqs. (2.8) and (2.11) we can relate the rates $v^{e \rightarrow p}$ and ${}^m v^{e \rightarrow p}$ as

$$\begin{aligned} \frac{dc_e}{dt} &= -v^{e \rightarrow p} = c_e \cdot k^{e \rightarrow p} , \\ \frac{d{}^m c_e}{dt} &= -{}^m v^{e \rightarrow p} = {}^m c_e \cdot k^{e \rightarrow p} , \end{aligned} \quad (2.12)$$

where $k^{e \rightarrow p}$ plays the role of a first-order reaction rate coefficient. In fact, $k^{e \rightarrow p}$ is a “superposed” rate coefficient of all single- and multi-tagged educt reactions of reacting C_e , as resulting from the assumptions we considered. Since there is no difference between the molecules of the regular species C_e and any tagging class species ${}^m C_e$, the coefficient k is identical for them. Rearranging Eq. (2.12) with respect to $k^{e \rightarrow p}$ and retaining from Eq. (2.10) that the concentrations ${}^m c_e$ are additive to the concentration c_e , we compute the final m^{th} class rate ${}^m v^{e \rightarrow p}$ as:

$${}^m v^{e \rightarrow p} = v^{e \rightarrow p} \cdot \frac{{}^m c_e}{\sum_{l=1}^M {}^l c_e} , \quad (2.13)$$

which means that we set the reaction rate of a class proportional to its share in the entire budget of the reacting species.

Altogether Eqs. (2.3), (2.10), (2.11) and (2.13) define the tagging system kinetic mechanism that uses reaction rate values v_r provided by the regular system and additional exchange information in the form of branching coefficients ψ_r .

So far, the reaction rates v_r are considered as the instantaneous values obtained from the regular system. However, as it was mentioned above, when tagging is applied to MECCA (the kinetic chemistry modelling system employed), these momentary rates are not accessible due to the specifics of the kinetic pre-processor (KPP, see p. 7). Solving the regular kinetic chemistry mechanism, KPP can provide only the integral of the particular reaction rate over a given period, namely the integration step. During the integration, KPP advances the solution of the regular system by an internally adjusting time stepping procedure; the appropriate length of the external integration step may vary from seconds to hours, depending on the simulated system. Therefore, the final pair rates (Eq. (2.8)) have to be derived *a posteriori* from the integral value of v_r . In a first approximation, the estimated reaction rate A_r can be assumed to be constant throughout the integration time step:

$$\begin{aligned} A_r &= \frac{1}{\tau} \int_{t_0}^{t_0+\tau} v_r dt, \\ v^{e \rightarrow p} &= \sum_{r \in R^{e \rightarrow p}} \psi_r^{e \rightarrow p} \cdot s_{rp} \cdot A_r \end{aligned} \quad (2.14)$$

Here A_r is an average value of the regular reaction rate v_r over the time step of length τ . Such a primitive approximation ensues from the fact that the exact evolution of the reaction rates in the regular system during its internal integration procedure is not known. To obtain a better approximation or estimate, one needs to account for the specifics of the regular mechanism and kinetic solver, which is beyond of the scope of this approach. We will rely on the fact that reaction rates constancy neither violates mass transfer/conservation in the system, nor affects the ratios of totals per class (*i.e.* total mass of the molecules of all species of a certain class related to the total mass of molecules in the tagged system). Notwithstanding, the use of (2.14) may introduce artificial species' composition (namely class to class ratios) exchanges. These may happen in the case of concurrent significant changes of reaction rates and the reacting species composition during the internal integration. Indeed, the

constant reaction rates approximation holds well for cases in which either the species composition *or* the rates of reactions they are removed by, are approximately constant. To clarify the reasoning underlying this statement, we consider the following example sketched in Figure 2.1.

A set of species is tagged into 2 classes with “blue” and “red” tags. Initially, species B and R possess exclusively “blue” and “red” molecules respectively, whilst species P and E are empty. Now assume that during the integration step the chemical regime changes radically in the middle of it. It happens that B reacts to P during the first half of the integration step, filling it up with “blue” molecules. Then B stops, but R starts to move to P, colouring it to a certain “purple” mixture of “red” and “blue” molecules. Concomitantly, in the first half of the integration step, P spills into E. What will be the resulting colour of E by the time the integration is finished? It is completely blue. Now suppose that reaction rates do not change, they are assumed to be constant averages. During the integration, B and R simultaneously react to P colouring it straight with purple. What would be the resulting colour of E? In this case, it is purple. Because P changes its colour, the constancy of the rate between P and E makes the difference. Consequently, the constant rate approximation is correct for the transfer of either equal portions of a variable composition *or* equal composition at variable rates.

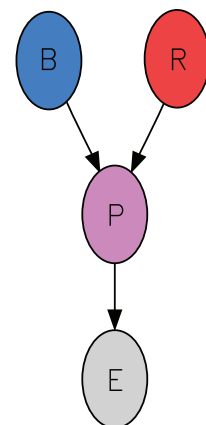


Figure 2.1 Illustration to the rate approximation example (see text).

The magnitude of deviation of the approximated system is proportional to the length of the regular system integration step τ . In the ideal case, differences disappear as the integration step becomes so small that the rates in the regular system become virtually constant. However, for the range of applied KPP integration steps (from seconds within the box-model to tens of minutes within the AC-GCM), the corresponding rate changes appear to be still admissible to achieve a necessary satisfactory precision. We derive the actual precision by comparing the tagged system to the reference “doubled” system described below. The crucial point is the adequate choice of the regular system’s integration step that should be short enough to adequately circumvent the mentioned difficulties for each particular mechanism dealt with.

2.2.4 Integration of the tagged system

The following sketches the numerical implementation of the tagged system originating from the assumptions formulated above. The systems are integrated in sequence, *i.e.* the tagged system is being integrated over the same time step in immediate succession to the regular system’s integration. During each integration step, the regular kinetic solver advances the species’ concentrations in the regular system to the new values and provides the integrals of the reaction rates v_r which are used to derive the approximated rates A_r . Further, by using A_r , the concentrations of the class species ${}^m C$ are advanced within the tagged system according to:

$$\begin{aligned}
 J_{p,e} &\equiv \sum_{r \in R^{e \rightarrow p}} \psi_r^{e \rightarrow p} \cdot s_{rp} A_r, \quad e \neq p \\
 J_{e,e} &\equiv -\sum_{r \in R^e} A_r + \sum_{r \in R^{e \rightarrow e}} \psi_r^{e \rightarrow e} \cdot s_{rp} A_r \\
 \begin{cases} \frac{d {}^m \mathbf{c}}{dt} = \mathbf{J} \times {}^m \mathbf{f}, \\ {}^m f_n \equiv \begin{cases} \frac{{}^m c_n}{\sum_{l=1}^M {}^l c_n}, & \text{if } \sum_{l=1}^M {}^l c_n \neq 0 \\ 0, & \text{otherwise} \end{cases} \end{cases} \end{aligned} \tag{2.15}$$

Here the bold-faced symbols are used for matrices and vectors. Thus, ${}^m \mathbf{c}$ is the class concentration vector, ${}^m f_n$ is the class fraction (share) in the total budget of C_n . The indices e, p refer to the educt and product species, r is the reaction index, and m is the class index. For the sake of notation convenience, we use the vector product of the “rate matrix” $\mathbf{J}$ of the size N_s by N_s elements by a vector of species’ m^{th} class fractions ${}^m \mathbf{f}$. Each diagonal element $J_{e,e}$ contains the net reaction rate for a certain species C_e , whereas each off-diagonal element $J_{p,e}$ contains the pair reaction rate (Eq. (2.8)) for species C_e to C_p . The matrix $\mathbf{J}$ resembles the Jacobian matrix with respect to its structure, since the position and value of each element determines the direction and rate of the molecules’ transfer between the species, or its removal.

The resulting ODE system defined by Eq. (2.15) requires considerably less computational operations for its integration compared to a straightforwardly replicated mechanism. The rate matrix $\mathbf{J}$ within the current formulation consists of elements that remain constant while the solution is being advanced; hence, during the integration iteration the amount of transferred molecules of each class m is determined only by its fraction mf_n . The rate matrix is evaluated only once before the integration starts and used to advance every set of class species. This is particularly useful for tagging into a large number of classes. To compare, the straightforward replication of the regular mechanism (see Sect. 2.2.2) would require the calculation of at least $N_R \cdot N_S \cdot M$ reaction rates to advance all classes of tagged species, whereas in the formulation (2.15) this number reduces to $N_S \cdot N_S$, and usually $N_S < N_R$. In consequence, the greater the complexity of the simulated mechanism, the greater the expected gain in speed.

Despite its simplicity, approach (2.15) as a rule inherits numerical complications from the regular system, particularly its stiffness. The implementation of the integration scheme for Eq. (2.15) in the MECCA-TAG includes a selection of different solvers (including the opportunity to plug-in a user-defined integrator) incorporating specifically those schemes that can cope with stiff systems. The latter are based on several approaches (Bloch^[1991], Eriksson *et al.*^[2003], Press *et al.*^[1992]) adapted for the needs of tagging, but are not detailed here. Generally, every solver employed for the tagging integration ensures that the solution of the ODE (2.15) is asymptotically stable. Ordinarily, different solving methods lead to slightly different equilibrium solutions for tagging, *i.e.* *classes fractions*, depending on the precision chosen. That is similar to what one discovers simulating the *species concentrations* in regular chemistry with different solvers. The regular chemistry (hence, the approximated reaction rates as well) is calculated by KPP for instance with the Rosenbrock solvers that have excellent stability properties (Sandu and Sander^[2006]). The tagging integration intrinsically produces (again, within the given precision) the same total concentrations as in the regular mechanism. One finds also, that errors in simulated *class fractions*, due to the tagging integration itself, are negligibly small compared to those introduced by the rates approximation in Eq. (2.14). Hence, only the regular mechanism integration time step length τ is decisive for the tagging precision.

To recapitulate, the presented method comprises an optimised kinetic chemistry mechanism tagging technique that is: 1) diagnostic and decoupled from the regular system, 2) simplifies calculations using the reaction rates calculated by the regular system solver, and 3) uses a computationally lighter integration method (constant coefficients ODE system). This method can be applied to a comprehensive chemical mechanism for various tagging purposes. The tagging is diagnostic in the sense that it helps to diagnose the regular kinetic chemistry and does not affect the solution of the regular kinetic system. However, this method itself is based on prognostic equations.

2.3 Modelling of isotope-enabled kinetic systems

Modelling of isotope chemistry-enabled systems requires a special treatment of the composition exchange between species as compared to the ordinary molecular case. The specific characteristic of any isotopically differentiated compartment is its *isotopic ratio* ZR , which is not always equal to the molecular ratio of the isotopologues representing it. Simulating isotopic chemistry requires that the isotopic ratios are correctly altered by the different kinetic processes and transfer between species.

Concerning tagging for simulating isotope ratios one has, apart from the standard chemical interaction, to account for isotope effects (kinetic and equilibrium isotope fractionation). Moreover, it is often the case that for ensuring the correct isotopic signature to be passed on from educts to products in the regular chemical reactions, the transfer of the rare and abundant isotopes has to be parameterised explicitly. To the author's knowledge, in many approaches, essential peculiarities are inadequately treated in the isotope-modelling literature. Below some shortcomings, along with the current approach towards the isotope-enabled chemistry mechanism modelling and its realisation in MECCA-TAG, are discussed. For the concepts and formulation related to isotopes and isotopic effects, the reader is also referred to Sect. 3.2 (p. 30) and reviews referenced therein.

2.3.1 Isotope tagging assumptions

The case of *isotopic tagging* of the kinetic chemistry mechanism involves the separation of all species of interest (those containing the isotope element of the atomic number Z) into a number of classes equal to the

number of possible isotopologues considered. Although a more detailed, complete parameterisation is possible (e.g. consideration of isotopomers and multiple substituted isotopologues), the tagging presented here is restricted to the existence of only one isotopologue of a certain isotopic substitution of the element Z ; an extension to a larger number of isotopologues (plus isotopomers) can be achieved analogously. Rejection of isotopologues with more than one minor isotope substitution, as well as isotopomeric differences is a simplification applied partly based on the following arguments:

- The abundance of the rare isotopes for the abundant elements (H, C, N, O) is sufficiently low to neglect the presence of doubly (or more) substituted molecules.
- Given low abundances, the differences introduced by isotope effects have no significant effect on the chemical system as a whole. In contrast, for chlorine isotopes, whose relative abundances are ~24% and ~76% for ^{37}Cl and ^{35}Cl , respectively, we would have a case where isotope effects affect bulk chemistry.
- Non-stochastic internal isotopic distribution is neglected (thus excluding special cases such as ozone where the central O atom has a different abundance of ^{17}O and of ^{18}O compared to the terminal position of oxygen atoms) since it has a minor effect on the species isotopic composition in terms of kinetic exchange.⁶ Nevertheless, the separation of certain important species into different isotopomers (for instance, symmetric and asymmetric O_3) can be introduced. On the other hand, the general reduction of isotopomeric differences greatly reduces the number of species (and reactions they act in) to be simulated, and hence computational costs.

Resulting from these assumptions, we set the number of tagging classes M to be equal to the number of considered isotopic substitutions of the element Z , or the number of considered isotopologues. The molecules of different classes contain either only abundant isotopes (giving the *major* isotopologue) or containing a singly substituted rare isotope (giving the *minor* isotopologues):

$$\begin{aligned} C &= \{C_n | Z \text{ in } C_n\} \\ C_n &\equiv \{^{\text{maj}}C_n, ^{\text{min},1}C_n, \dots, ^{\text{min},M-1}C_n\} \\ c_n &= ^{\text{maj}}c_n + \sum_{i=1}^{M-1} ^{\text{min},i}c_n \end{aligned}$$

where C is a subset of species containing element Z . The superscripts of C and c indicate the major or any minor isotopologues. Incidentally, any minor isotopologue possessing more than one atom of the selected element Z is a molecule containing always *one rare* isotope of Z , with the remainder of the isotopes being the abundant ones. Thus, for species of the same isotopic composition (i.e. isotopic ratio $^Z R$) the molecular fractions of the minor isotopologues are proportional to the number of the atoms q_n of the element Z these species contain. For example, for isotopic carbon in CO ($q_{\text{CO}} = 1$) and C_5H_8 ($q_{\text{C}_5\text{H}_8} = 5$) of the same ratio $^{13}\text{C}R$, the fraction of molecules containing ^{13}C differs by a factor of five.

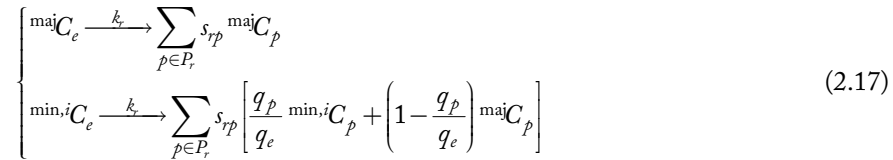
2.3.2 Isotope composition transfer

In the kinetic system, the transfer of the composition between species in course of the reaction must occur without violation of the mass conservation. Normally, reaction stoichiometry for Eq. (2.1) satisfies the following condition:

$$q_e = \sum_{p \in P_r} s_p q_{rp} \quad , \quad (2.16)$$

where q_e and q_p are the number of the atoms of a given isotope Z in the educt and products used to define the stoichiometric coefficients s_p (for example, see Sect. 2.2.3). For the correct mass transfer, Eq. (2.16) must hold, if the weightings q are substituted by the number of atoms of any element Z in the respective species. Moreover, for the correct transfer of isotopic composition, the respective quantity of the rare and abundant atoms must be preserved as well, in order to preserve the isotopic ratio of the transferred portion of atoms. Recalling the definition of the major and minor isotopologues, we state the correct system representing Eq. (2.1) for each isotopologue as:

⁶ With regard to the isotope composition of the species related to CO scrutinised in the current study.

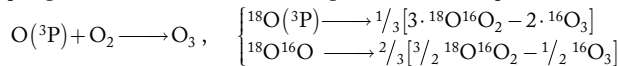


Here, superscripts of C indicate major and i^{th} minor isotopologues, respectively; i is the minor isotopologue index ($1 \leq i \leq M-1$). Similarly to Eqs. (2.2) and (2.3), any high-order reaction can be represented as a composition of multiple reactions of the kind of Eq. (2.17). So far, we have not yet accounted for any (kinetic) isotope effect in Eq. (2.17).

The first term in squared brackets describes the probability of the rare isotope to be transferred to the current product, while the second term describes the creation of the major isotopologues from the abundant isotopes of the educt, eliminating discrepancies caused by neglecting of the doubly (or more) substituted isotopologues. Indeed, in case q_p is smaller than q_e the term $(1 - q_p/q_e)$ is positive and accounts for the major isotopologue of C_p constructed from excessive abundant atoms left after the decomposition of C_e and redistribution of its atoms to the minor isotopologues. When q_p equals q_e the term cancels, thus describing the straight transfer of the composition. In the case of q_p being larger than q_e the mentioned term has a negative sign, physically describing the amount of molecules that has to be taken from the major isotopologue pool to complete at least one valid minor isotopologue of the C_p species. The “probability” q_p/q_e in all cases is greater than zero, meaning that the minor isotopologue is created unconditionally.

The system (2.17) preserves both, the mass and the isotopic ratio in course of the reaction: the number of transferred rare isotopes is conserved, whereas the deficiency or excess of the abundant atoms is eliminated at the expense of the major isotopologue pool.⁷ Virtually, we perform the repartitioning of the transferred reacted atoms to the valid isotopologues; such scheme satisfies the requirements introduced in Sect. 2.3.1. It is essential

⁷ We elucidate the isotope transfer in the system (2.17), considering the reaction of the minor isotopologue (second line). At the left hand side (LHS), an isotopologue possessing q_e isotopes of the element of interest is reacting. We consider the case when q_e is greater than unity; hence, the reacting isotopologue carries one rare and (q_e-1) abundant isotopes. For example, for the rare ^{13}C -isotopologue of propene (C_3H_6), $q_e = 3$ and the isotopologue composition is $^{13}\text{C}^{12}\text{C}_2\text{H}_6$. Now, consider a case when the right hand side (RHS) has a single product C_p , with the number of the isotopes q_p . The stoichiometry condition (2.16) requires that $s_{rp} = q_e/q_p$. Three cases are possible then: (1) $q_e = q_p$, i.e. number of isotopes is equal in the educt and the product, and $s_{rp} = 1$; (2) $q_e > q_p$, i.e. the product species pool receives one rare and (q_p-1) abundant isotopologues; (3) $q_e < q_p$, i.e. the educt is incorporated into the product. For the case (1), the transfer of the rare and abundant isotopes is unambiguous. In the cases (2) and (3), the stoichiometric coefficient is not equal to unity to create the same number of isotopes redistributed in the product molecules. Noteworthy, the LHS has only one rare isotope, thus only one rare isotope can be created at the RHS. The additional coefficient q_p/q_e next to the product minor isotopologue in the RHS ensures that; thus not more than one rare isotope is transferred as a part of one minor isotopologue. As an artificial example for the case (2), if a ^{13}C -propene isotopologue produces formaldehyde molecules (HCHO), then $s_{\text{HCHO}} = 3$ and only one of these HCHO carries ^{13}C isotope, the rest two acquire the abundant ^{12}C from propene: $^{13}\text{C}^{12}\text{C}_2\text{H}_6 \rightarrow 3 (^{1/3} \text{H}^{13}\text{CHO} + ^{2/3} \text{H}^{12}\text{CHO})$. The case (3) is somewhat intricate. Imagine, for the example only, that now HCHO produces propene. The stoichiometric coefficient in this case is $s_{\text{C}_3\text{H}_6} = 1/3$, i.e. one needs to assemble three carbons from the formaldehyde molecules to create C_3H_6 . However, we allow the minor isotopologue of propane to carry not more than one ^{13}C isotope, thus the rest isotopes have to be ^{12}C . These can be taken only in form of propene major isotopologues, so that the overall isotopic ratio of the propene pool is preserved. Conclusively, for this example of case (3), it follows: $\text{H}^{13}\text{CHO} \rightarrow 1/3 (3 ^{13}\text{C}^{12}\text{C}_2\text{H}_6 - 2 ^{12}\text{C}_3\text{H}_6)$. Again, the coefficients require that only one minor isotopologue is being created, and it is completed with the abundant isotopes from the major isotopologues. A more realistic example of the case (3) is the bimolecular reaction of the production of the ozone isotopologues from minor isotopologues of $\text{O}(^3\text{P})$ and O_2 , considering ^{16}O and ^{18}O isotopes:



Here, the bimolecular reaction decomposition (Eq. (2.3)) is used with the branching ratios (Eq. (2.4)), so that effective stoichiometric coefficients become $s_{\text{O}(^3\text{P})} = 1/3$ and $s_{\text{O}_2} = 2/3$, respectively. This argumentation can be straightforwardly extended to the cases when the RHS has more than one product. Finally, we calculate the number of rare and abundant isotopes at the LHS and RHS in the general formulation (2.17). First, we count the number of RHS rare isotopes only, i.e.

$$n_{\text{rare}} = \sum_{p \in P_r} s_{rp} \frac{q_p}{q_e} = \frac{1}{q_e} \sum_{p \in P_r} s_{rp} q_p = 1$$

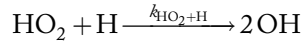
assuming one rare isotope in each minor isotopologue and recalling the stoichiometry condition (2.16). Similarly, the number of the abundant atoms at the RHS is

$$n_{\text{abu}} = \sum_{p \in P_r} s_{rp} \left[\frac{q_p}{q_e} (q_p - 1) + \left(1 - \frac{q_p}{q_e} \right) q_p \right] = \frac{(q_e - 1)}{q_e} \sum_{p \in P_r} s_{rp} q_p = (q_e - 1)$$

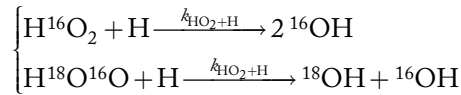
taking into account that the major and minor isotopologue of the products have q_p and (q_p-1) abundant isotopes, respectively. Thus, the total number of transferred isotopes is q_e , of which one is rare.

(for any isotope kinetic chemistry modelling system) to verify that such repartitioning of the composition is parameterised correctly, otherwise the system either starts to violate mass conservation or introduces inadmissible conversion of the rare isotope atoms into abundant or vice versa. Obviously, formalism (2.17) relies on the assumption that the probability of each reactant atom to constitute every product is equal; diverging cases should be considered individually (e.g. by applying a concept analogous to that introduced for Eqs. (2.2) and (2.3)).

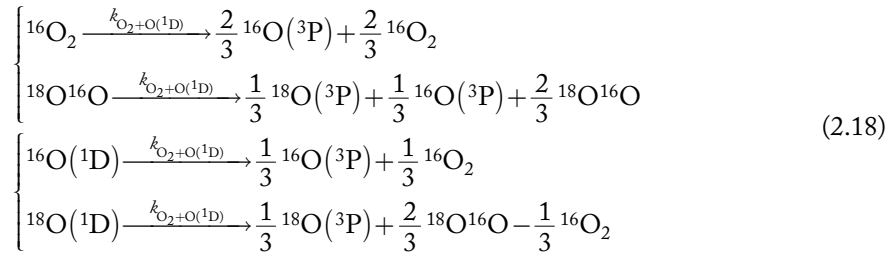
The following examples clarify the above. Consider an oxygen isotopic tagging case (using ^{16}O and ^{18}O) in a reaction of a peroxy molecule (HO_2 radical) to give two single oxygen-bearing molecules (OH radicals):



The transfer of the oxygen composition from the HO_2 to OH reservoir is:



Thus, each minor HO_2 isotopologue creates both, major ^{16}OH and minor ^{18}OH . Similarly, consider a more complex case of the isotope tagging of the reaction of $\text{O}(^1\text{D})$ with O_2 (Eq. (2.5), decomposition (2.6) and transfer conditions (2.7) from Sect. 2.2.3):



The fractional stoichiometric coefficients in Eq. (2.18) are a result of the combination of the branching ratios ψ and the mass/isotopic ratio balance condition (Eq. (2.17)). One can ascertain that the number of rare and abundant isotope atoms on the left and right side are equal. The negative sign of the term in the last equation means that two ^{16}O isotopes are taken from the major isotopologue pool in form of one $^{16}\text{O}_2$ molecule in order to build every two $^{18}\text{O}^{16}\text{O}$ isotopologues.

2.3.3 Kinetic isotope effect

Due to changes in physical properties caused by isotopic substitution, the reaction rate coefficients of the minor isotopologues differ (generally only slightly) from those of the major isotopologue. These kinetic isotope effects (KIEs) in irreversible reactions can be attributed to various causes, like differences in zero point energy *etc.*, and are often quantitatively characterised with fractionation factors α that equal the ratio of the reaction rate coefficients of the minor isotopologue over that of the major one.⁸ Accounting for KIEs, the reaction rate coefficient in Eq. (2.17) is modified for the minor isotopologue:

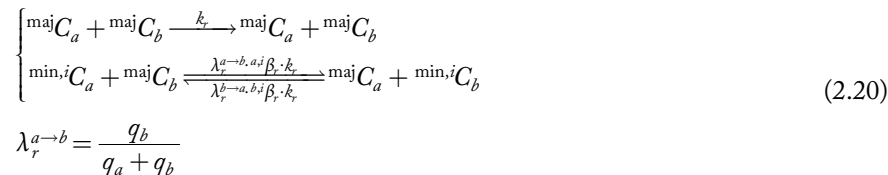
$$\text{min},i C_e \xrightarrow{k_r \cdot \epsilon_r^i \alpha_r} \sum_{p=1}^P \psi_r^{e \rightarrow p} \cdot s_{rp} \left[\frac{q_p}{q_e} \cdot \text{min},i C_p + \left(1 - \frac{q_p}{q_e} \right) \cdot \text{maj} C_p \right] \quad (2.19)$$

where the $\epsilon_r^i \alpha_r$ designate the fractionation factors for the i^{th} minor isotopologue of C_e , respectively. Each minor isotopologue in Eq. (2.19) may create both, minor and major isotopologues which belong to the different tagging classes. Such would require essential changes to the parameterisation (Eq. (2.15)) since *previously disjoint classes start to exchange their composition*. Moreover, the KIE alters the reaction rates such that they are no longer strictly proportional to the respective class' share, as we derived in Eqs. (2.12) and (2.13). To resolve these complications, we further (in Sect. 2.4.1) reformulate Eq. (2.15) in terms of exclusive *atomic* tagging (*i.e.* the consideration of atomic fractions of the rare and abundant isotope atom in the species composition), which makes calculations easier. Nonetheless, the rate of the reaction of each isotopologue is determined by its *molecular* fraction.

⁸ See Sect. 3.2 (p. 30) on terms and definitions for the isotopes used in the current study. Note that, as it is intuitively preferable, the definition for α used here does not follow the IUPAC recommendation (McNaught and Wilkinson^[1997]).

2.3.4 Isotope exchange reactions

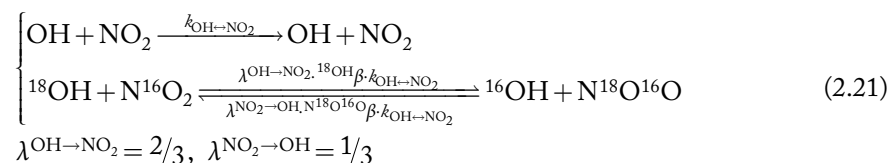
A minor isotopologue of one species can exchange its rare isotope with the abundant isotope of another species' major isotopologue (*e.g.* $\text{H}_2^{18}\text{O} + ^{16}\text{OH} \rightleftharpoons \text{H}_2^{16}\text{O} + ^{18}\text{OH}$). When this exchange reaction is sufficiently fast, isotopic equilibrium is obtained. In terms of isotopic tagging, the onward (*i.e.* left to right in the example reaction above) isotope exchange is the conversion of the minor (H_2^{18}O) to major (H_2^{16}O) isotopologues of one reagent and *vice versa* (*i.e.* major ^{16}OH to minor ^{18}OH) for another at a given rate. Noteworthy, the backward (conformably, right to left) isotope exchange may have a different rate (compared to the onward reaction), owing to the KIEs. Therefore, the general description of an isotope exchange reaction is:



The first equation in (2.20) introduces the reference reaction rate k_r to which the pair of isotope exchange reaction rates is related to; a, b are the indices of exchanging species and $^{a,i}\beta_r, ^{b,i}\beta_r$ denote the kinetic fractionation factors for the i^{th} minor substitution of C_a and C_b in the pair. The ratios λ incorporated in the reaction rates are analogous to those introduced in Eqs. (2.3) and (2.4), but describe the probability of one species' minor isotopologue to transfer its rare atom thus creating the minor isotopologue of the partner. The particular derivation of $\lambda_r^{a \rightarrow b}$ shown above relies on the assumption that the isotopomeric differences do not play a role in the exchange; every rare isotope of C_a has equal probability to be exchanged with each abundant isotope of C_b . In some studies (for example, by Johnston *et al.*^[2000]) the onward reaction rate is explicitly reported; then for the backward reaction, λ and β are expressed relatively to the onward reaction rate with $\lambda_r = \lambda_r^{b \rightarrow a} / \lambda_r^{a \rightarrow b}$ and $\beta_r = ^{b,i}\beta_r - ^{a,i}\beta_r$, respectively, while for the onward reaction they both equal to unity.

The rates of each reaction in Eq. (2.20) are determined by the abundance of the different (major and minor) isotopologues of both species and thus cannot be correctly approximated in the tagged system as being linearly proportional to the reference reaction rate v_r (equals $k_r \cdot c_a \cdot c_b$). The use of Eq. (2.13) would slightly (since $\text{maj}c_a \gg \text{min},i c_a$) change the reaction rates, thus introducing an additional kinetic effect when product $\lambda \cdot \beta$ differs for onward and backward directions. In fact, the linearisation (Eq. (2.13)) can be used in case the mentioned artificial KIE is insignificant compared to the effect of the species composition exchange in the ordinary reactions. Nevertheless, further we apply proper adjustments to the tagging scheme to treat isotopic exchange in a non-linear way.

To illustrate the formulation (2.20), consider an example of the oxygen isotope exchange between OH and NO_2 :



The probability of $2/3$ in the onward exchange reaction rate of Eq. (2.21) signifies the statistical expectation of the ^{18}O isotope exchange between OH and NO_2 . Conformably, the backward reaction probability is by a factor of two smaller, because when minor $\text{N}^{18}\text{O}^{16}\text{O}$ swaps one of its oxygen atoms with ^{16}OH , we expect that only in half of the cases the rare ^{18}O isotope becomes exchanged.

2.3.5 Conservative characteristics of an isotopic system

To assess whether the parameterisation of the described effects in the chemistry isotope modelling system is adequate, we consider some of its invariable characteristics. The following features must be observed in a closed system (*i.e.*, when the mechanism is isolated so that no removal or introduction of the molecules from outside of it is allowed, and reactions have no misbalanced stoichiometry):

- 1) the total atomic mass and also the ratio of the rare to abundant isotope(s) masses is preserved;
- 2) the previous characteristic is insensitive to the presence of KIEs and isotope exchange reactions, changes of macro parameters (*e.g.* pressure or temperature), and changes of the species abundances;

- 3) if there are no kinetic isotope effects introduced in the system, and all compartments have the same initial isotopic composition, then no isotope ratio change is expected for any species despite alterations in its abundance.

If these characteristics are not reproduced, the system obviously introduces improper conversion of the rare isotope atoms into abundant ones or vice versa. The third condition points directly to incorrect isotopic transfer in the regular reactions. Note that usually the isotope ratio in the system is a very sensitive characteristic. For example, the reference test simulations with isotope-enabled MECCA mechanisms (see below, Sect. 2.5.2) show that for a typical ratio of the stable carbon isotopes corresponding to 0‰ (with respect to the carbon V-PDB⁹ standard ratio), a deviation of the $\delta^{13}\text{C}$ value of the total carbon in the system (characteristic 1) larger than merely 10^{-10} permil (equivalent to the concentrations calculation precision of absolute and relative tolerance values of 10 molecules/cm³ and 10^{-3} , correspondingly) is a sign of potential error.

2.4 MECCA–TAG isotope modelling specifics

The following section is devoted to extending the molecular tagging technique we introduce to account for the isotope chemistry specifics outlined above. We describe also some additional processing of the species budgets required for diagnostic tagging when it is applied to modelling systems like MECCA. Unless stated otherwise, the notation follows the one used in the preceding sections.

2.4.1 Formulation of the isotope-inclusive tagged system

The alterations to the tagged system are to deal with the additional processing of the classes representing minor isotopologues and their interaction with the major isotopologues class. To formulate the isotopically tagged system, we recur the considerations described in Sects. (2.2.3) and (2.2.4) and the specifics of the isotopic transfer from Eq. (2.17). For the major isotopologues containing only abundant isotope atoms, the integration proceeds in the same way as in Eq. (2.15), using their molecular fractions $\text{maj}\mathbf{f}$:

$$\begin{aligned} J_{p,e} &\equiv \sum_{r \in R^{e \rightarrow p}} \psi_r^{e \rightarrow p} \cdot s_{rp} A_r, \quad p \neq e \\ J_{e,e} &\equiv -\sum_{r \in R^e} A_r + \sum_{r \in R^{e \rightarrow e}} \psi_r^{e \rightarrow e} \cdot s_{rp} A_r \\ \left\{ \begin{aligned} \frac{d \text{maj}\mathbf{c}}{dt} &= \mathbf{J} \times \text{maj}\mathbf{f} \\ \text{maj}f_n &\equiv \frac{\text{maj}c_n}{\text{maj}c_n + \sum_{i=1}^{M-1} \text{min}_i c_n} \end{aligned} \right. \end{aligned} \quad (2.22)$$

The rate matrix terms include the branching ratios ψ (Eq. (2.4)) derived with respect to the atomic content of the selected isotope and composition transfer. Using the already calculated “major” rate matrix $\mathbf{J}$, we form the “minor” matrices whose elements include the correction terms that account for the kinetic isotope effects for the minor isotopologues:

$$\left\{ \begin{aligned} \text{min}_i J_{p,e} &= J_{p,e}, \quad C_p, C_e \notin C_{KIE}, \quad \text{else} \\ \text{min}_i J_{p,e} &= J_{p,e} - \sum_{r \in R_{KIE}^{e \rightarrow p}} \psi_r^{e \rightarrow p} \cdot s_{rp} A_r \cdot (1 - \epsilon_r^i \alpha_r), \quad e \neq p \\ \text{min}_i J_{e,e} &= J_{e,e} + \sum_{r \in R_{KIE}} A_r \cdot (1 - \epsilon_r^i \alpha_r) \end{aligned} \right. \quad (2.23)$$

The C_{KIE} and R_{KIE} refer to the subsets of species and reactions experiencing kinetic isotope fractionation, respectively. The correction terms for the production and loss elements are of opposite signs to properly account for the absolute value of the current reaction rate contributing to the corresponding production and loss “one-way” rates. The correction terms for each reaction are calculated just once before the integration.

⁹ The Vienna Pee-Dee Belemnite (abbreviated as V-PDB) is the standard ratio used for reporting $\delta^{13}\text{C}$ values throughout this study (see Sect. 3.2, p. 30).

The elements of the rate matrices are referring to the molecular exchange rates, *i.e.* the number of molecules of the particular class transferred per unit of time. Recalling the isotopic composition transfer rules (Sect. 2.3.2) we need to consider the transfer of the rare and abundant isotopes from the minor isotopologues separately. For that, we introduce rare and abundant atom fractions χ of the minor isotopologue that are proportional to its molecular fraction and atomic content:

$$\begin{aligned} \min,i f_n &\equiv \frac{\min,i c_n}{\text{maj}c_n + \sum_{i=1}^{M-1} \min,i c_n}, \\ \text{rare},i \chi_n &\equiv \frac{1}{q_n} \cdot \min,i f_n, \\ \text{abu},i \chi_n &\equiv \frac{(q_n - 1)}{q_n} \cdot \min,i f_n, \end{aligned} \quad (2.24)$$

where q_n is the number of atoms of the selected isotope in the molecule C_n . Thus, for instance, for the oxygen composition of NO_3 ($q_n = 3$) we account for one rare ($\text{rare}\chi = 1/3$) and two abundant ($\text{abu}\chi = 2/3$) oxygen isotopes in the minor isotopologue. According to the definitions (Sect. 2.3.1), one transferred rare isotope implies that one minor isotopologue has ended up in the product, a substitution of the molecular fraction of the minor isotopologues with the atomic one properly accounts for the transfer of minor isotopologue molecules:

$$\begin{cases} \frac{d \min,i \mathbf{c}}{dt} = \min,i \mathbf{J} \times \text{rare},i \chi \\ \frac{d \text{maj} \mathbf{c}}{dt} = \mathbf{J} \times \text{maj} \mathbf{f} + \sum_{i=1}^{M-1} [\min,i \mathbf{J} \times \text{abu},i \chi - \min,i \mathbf{c} \cdot (\mathbf{q} - \mathbf{1})] \end{cases} \quad (2.25)$$

The bracketed term in Eq. (2.25) accounts for the redistribution of the abundant atoms in the products in order to create valid isotopologues: the positive part equals the total amount of abundant isotopes reacted via minor isotopologues, while the negative denotes the fraction that is taken to complete the minor isotopologue molecules. If the set of tagged species consists only of those having one isotope, the mentioned term cancels out and Eq. (2.25) becomes identical to the one for the molecular system (Eq. (2.15)).

Finally, we need to account for the isotopic exchange as it is the pertinent process inducing interchange between major and minor classes. From Eq. (2.20) one derives the net rate of the major-to-minor isotopologues conversion of the exchanging species:

$$\begin{aligned} r &\in R_{\text{EX}}^{a \leftrightarrow b} \\ i I_r^{a \leftrightarrow b} &= \frac{1}{\tau} A_r (\lambda_r^{a \rightarrow b, i, a} \beta_r \cdot \min,i f_a^{\text{maj}} f_b - \lambda_r^{b \rightarrow a, i, b} \beta_r \cdot \min,i f_b^{\text{maj}} f_a) \\ i I_r^{a \leftrightarrow b} &= -i I_r^{b \leftrightarrow a} \end{aligned} \quad (2.26)$$

For the pair of reagents C_a, C_b exchanging in the subset of reactions R_{EX} , the conversion rate I has the same magnitude; indeed, the net effect of the isotope exchange reaction is equal to the effect of the process when one reagent swaps its rare atoms with abundant ones of the partner until species are in isotopic disequilibrium (*i.e.* I is non-zero). Summing the contributions of all isotope exchange reactions in which a certain species participates, we form isotope exchange component vectors ${}^i \gamma$:

$${}^i \gamma_n = - \sum_{r \in R_{\text{EX}}^n} i I_r^{n \leftrightarrow p} \quad (2.27)$$

where R_{EX}^n is the subset of isotope exchange reactions of the species C_n , p is the index of a particular reaction r exchange partner. Every element of ${}^i \gamma_n$ equals the net rate of onward (or backward, when negative) “conversion” of the major isotopologue $\text{maj}C_n$ into the minor $\min,i C_n$ due to all isotope exchange reactions in which species C_n takes part. Further, ${}^i \gamma$ is added to Eq. (2.25):

$$\begin{cases} \frac{d \min,i \mathbf{c}}{dt} = \min,i \mathbf{J} \times \text{rare},i \chi + {}^i \gamma \\ \frac{d \text{maj} \mathbf{c}}{dt} = \mathbf{J} \times \text{maj} \mathbf{f} + \sum_{i=1}^{M-1} [\min,i \mathbf{J} \times \text{abu},i \chi - \min,i \mathbf{c} \cdot (\mathbf{q} - \mathbf{1}) - {}^i \gamma] \end{cases} \quad (2.28)$$

The resulting system (2.28) is integrated in the same way as (2.15) inheriting its optimisation features. Some extra work is required to process the minor isotopologues’ abundant isotopes’ transfer term and the iso-

tope exchange (*i.e.* calculation of the vectors $\mathbf{y}$ in every iteration), although the latter is much less expensive compared to the processing of the ordinary kinetic exchange.

2.4.2 Budget corrections

In case there are kinetic isotope effects introduced in the mechanism, different reaction rates for certain isotopologues will result in a slight but systematic deviation of the tagged species budgets in the tagged system compared to those in the regular mechanism. To avoid integration over this propagating divergence a correction of the species budgets is necessary. It is performed by scaling the class species budgets to the total budget of the regular mechanism, while the newly obtained isotopic composition remains unaffected:

$$\begin{aligned} \text{maj}c_n^{(t_0+\tau)} &\leftarrow \text{maj}f_n \cdot c_n^{(t_0+\tau)}, \\ \text{min},i c_n^{(t_0+\tau)} &\leftarrow \text{min},i f_n \cdot c_n^{(t_0+\tau)} \end{aligned} \quad (2.29)$$

The arrows indicate that the left-hand-side is re-defined. The correction is performed after the integration of both, regular and tagged, systems is finished at the time $(t_0+\tau)$. The fractions $\text{maj}f_n$ and $\text{min},i f_n$ are calculated as given in (2.22) and (2.24) from not yet corrected values of $\text{maj}c_n$ and $\text{min},i c_n$. It is possible to reformulate the KIE fractionation factors to achieve the same products' composition as from Eq. (2.29) without the correction. This may be done by assigning the following fractionation factors to each (including the major) isotopologue reaction rate:

$$\begin{aligned} \epsilon, \text{maj} \alpha_r &= \left(\text{maj}f_e + \sum_{i=1}^{M-1} \text{min},i f_e \cdot \epsilon, i \alpha_r \right)^{-1}, \\ \epsilon, \text{min},i \alpha_r &= \epsilon, i \alpha_r \cdot \text{maj} \alpha_r \end{aligned} \quad (2.30)$$

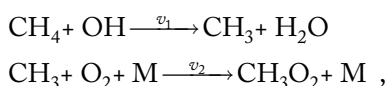
Here, the notation follows that of Eq. (2.19) and $\epsilon, \text{maj} \alpha_r$ and $\epsilon, \text{min},i \alpha_r$ denote new fractionation factors for the major and minor isotopologue(s) reactions. The amount of produced molecules equals to those in the regular mechanism, whilst the effect on the reagents' ratios change is of the same KIE magnitude of $\epsilon, i \alpha_r$. Unfortunately, a reformulation like Eq. (2.30) involves recalculation of the corresponding pair rates (elements of $\mathbf{J}$) for every isotopologue class in every iteration of the integration of (2.28), which may increase computational effort considerably. Since for typical integration step lengths (see Sect. 2.2.3) the discrepancies to be eliminated by Eq. (2.30) do not significantly change the chemistry, it is advisable to choose the *a posteriori* option (Eq. (2.29)) which is obviously faster and does not interfere with the main function of the isotopic tagging, namely to transfer and preserve the isotopic ratios.

2.4.3 Accounting for a specific composition source

It is common practice in kinetic chemistry modelling, that complex reactions involving several intermediate steps are approximated (or "lumped") using one net reaction of a certain rate by omitting (usually short-lived) intermediates. Nevertheless, the latter can exchange their composition with other species in course of the reaction chain, which is of importance for the isotope chemistry and thus needs to be accounted for. For example, the reaction of methane oxidation may be parameterised in the regular mechanism as (O_2 is omitted among the reactants):



which is a superposed sequence of two specific reactions, namely:



Virtually, v_{net} equals v_1 since the rate-determining step of this sequence is the reaction of methane with the hydroxyl radical ($v_1 \ll v_2$ at typical atmospheric concentrations of OH and O_2). The methyl radical reacts with molecular oxygen, which gives its signature to the methylperoxy radical, whereas the water molecule incorporates its oxygen atom from OH. As a result, atmospheric oxygen resets the CH_3O_2 signature, thus determining the composition of all its subsequent products, whilst OH contributes to the composition of the atmospheric water (Dubey *et al.*^[1997]). Notably, this does not ensue from the approximated formulation (*).

To account for such a particular sourcing in the tagged system (Eq. (2.28)), a simple change of the corresponding production term in the rate matrix $\mathbf{J}$ in Eq. (2.22) is required. It is noteworthy that the source specification violates the isotopic composition transfer balance; it is introduced to account for the correct isotopic source signatures in those comprehensive mechanisms that include reactions of high complexity. At atmospheric conditions in the presence of highly abundant species, like atmospheric water or molecular oxygen, this approach is a valid approximation. For any precise setup (*e.g.* a laboratory experiment reproduction within a box-model) it is adamant that all intermediates are accounted for.

2.5 MECCA–TAG evaluation and examples

2.5.1 Doubling technique

As an alternative to the diagnostic tagging, a reference method (hereafter referred to as “doubling”) is introduced here and is implemented in the MECCA-DBL sub-submodel. The doubling is – alike tagging – a diagnostic, but not a decoupled method. It embodies the expansion of the regular mechanism by additional doubled species for each tagged regular species together with additional reactions they act in. In the *explicit doubling* setup, the original species and reactions are replaced by the doubled ones. In the *implicit* setup, additional reactions become virtual. In other words, they include only the doubled species thus leaving the regular mechanism reactions unchanged. Other, non-tagged, educts in virtual reactions are replicated as reaction products thus becoming catalysts: only the doubles are produced or consumed. The high-order reactions are decomposed using Eq. (2.3) to a set of single-order reactions. To account optionally for a particular composition source (see Sect. 2.4.3) in the doubled system, a set of additional reactions with the rate proportional to the source species’ class fraction is introduced. In the case of isotopic doubling, the isotope-specific transfer and exchange reactions are formulated exactly as in Eqs. (2.17) to (2.20). Similar to the tagging case, the implicitly doubled mechanism requires the doubled species budget correction (see Sect. 2.4.2) when kinetic isotope effects are introduced. The explicitly doubled mechanism replaces the original one and thus does not need to be corrected for KIE influence.

Both doubling setups yield the same result (within the numerical precision), whereas the implicit doubling introduces no changes to the regular reactions and allows simultaneous doubling of several different *configurations* (*i.e.* given sets of tagged species, reactions and number of classes). In addition, the implicit setup enables a comparison of the results obtained by doubling and tagging methods implemented within the same simulated chemical mechanism (which is more preferable due to the independence of the result on the numerical precision of the simulated system). Tables 2.2a and 2.2b present examples of implicit and explicit doubling, respectively, of the regular mechanism for the isotopic tagging described above.

The doubling usually enlarges the simulated kinetic system extensively. Therefore, using this reference method (which is computationally very expensive) in application to comprehensive mechanisms is practical only for assessing the adequacy and accuracy of the tagging approach. Nevertheless, for less resource-demanding applications (*e.g.* box- or column-model), doubling extends MECCA to a fully fledged isotope-enabled kinetic chemistry model.

Table 2.2a Example of implicit isotopic doubling of the regular chemical mechanism

Regular mechanism	Doubled mechanism (additions to regular)
Species (in MECCA species list)	
$\{C_n\}$	$\{\text{maj } C_n, \text{min}, 1 C_n, \dots, \text{min}, M-1 C_n\}$
Equations (in MECCA reactions list)	
(regular reaction)	
$C_e + C_n \xrightarrow{k_r} \sum_{p \in P_r} s_p \cdot C_p$	$\left\{ \begin{array}{l} \text{maj } C_e + (C_n) \xrightarrow{k_r} (C_n) + \sum_{p \in P_r} \psi_r^{e \rightarrow p} \cdot s_{rp} \text{maj } C_p \\ \text{min}, i C_e + (C_n) \xrightarrow{\epsilon^i \alpha_r \cdot k_r} (C_n) + \sum_{p \in P_r} \psi_r^{e \rightarrow p} \cdot s_{rp} \left[\frac{q_p}{q_e} \text{min}, i C_p + \left(1 - \frac{q_p}{q_e} \right) \text{maj } C_p \right] \\ \dots^a \end{array} \right.$
(reaction with the specified particular source) ^{b)}	
$C_e + C_n \xrightarrow{k_r} \sum_{p \in P_r} s_p \cdot C_p$	$\left\{ \begin{array}{l} (C_n + C_e) \xrightarrow{\text{maj } f_r \cdot k_r} (C_n + C_e) + \sum_{p \in P_r^{i \rightarrow p}} \psi_r^{s \rightarrow p} \cdot s_{rp} \text{maj } C_p \\ (C_n + C_e) \xrightarrow{\epsilon^i \alpha_r \cdot \text{min}, i f_r \cdot k_r} (C_n + C_e) + \sum_{p \in P_r^{i \rightarrow p}} \psi_r^{s \rightarrow p} \cdot s_{rp} \left[\frac{q_p}{q_s} \text{min}, i C_p + \left(1 - \frac{q_p}{q_s} \right) \text{maj } C_p \right] \end{array} \right.$
$C_s \longrightarrow C_p$	$\left\{ \begin{array}{l} \text{maj } C_e + (C_n) \xrightarrow{k_r} (C_n) \\ (C_e) + \text{maj } C_n \xrightarrow{k_r} (C_e) \\ \text{min}, i C_e + (C_n) \xrightarrow{\epsilon^i \alpha_r \cdot k_r} (C_n) \\ (C_e) + \text{min}, i C_n \xrightarrow{\epsilon^i \alpha_r \cdot k_r} (C_e) \end{array} \right.$
(isotope exchange reaction) ^{c)}	
$C_a \xrightleftharpoons{k_r} C_b$	$\left\{ \begin{array}{l} \text{min}, i C_a + \text{maj } C_b \xrightarrow{\lambda_r^{a \rightarrow b, i, a} \beta_r \cdot k_r} \text{maj } C_a + \text{min}, i C_b \\ \text{maj } C_a + \text{min}, i C_b \xrightarrow{\lambda_r^{b \rightarrow a, i, b} \beta_r \cdot k_r} \text{min}, i C_a + \text{maj } C_b \end{array} \right.$

Notes:

Notation as before. Bracketed species are those from the regular mechanism used as virtual catalysts. Here the reaction rate constant k_r is featured instead of the reaction rate v_r .

^{a)} For this bimolecular reaction only one pair of equations in which C_n is used as a catalyst is shown, another pair for C_e is to be written in analogous way; thus one reaction of two tagged species of M isotopologues requires $2 \cdot M$ reactions to be added.

^{b)} The isotopic composition of the specific source C_s is accounted via its isotopologues molecular fractions f_i incorporated in the reaction rate coefficient. Each particular source requires an additional set of M equations. The educts are destroyed separately in an additional set of virtual equations.

Table 2.2b Example of explicit isotopic doubling of the regular chemical mechanism

Regular mechanism	Doubled mechanism (replacement of regular)
Species (in MECCA species list)	
$\{C_n\}$	$\{\text{maj } C_n, \text{min}, 1 C_n, \dots, \text{min}, M-1 C_n\}$
Equations (in MECCA reactions list)	
(regular reaction)	
$C_e + C_n \xrightarrow{k_e} \sum_{p \in P_r} s_p \cdot C_p$	$\left\{ \begin{array}{l} \text{maj } C_e + \text{maj } C_n \xrightarrow{k_e} \sum_{p \in P_r} s_p \text{ maj } C_p \\ \text{min}, i C_e + \text{maj } C_n \xrightarrow{\epsilon, i \alpha_e \cdot k_e} \sum_{p \in P_r} s_p \left[\psi_r^{n \rightarrow p} \cdot \text{maj } C_p + \psi_r^{e \rightarrow p} \left(\frac{q_p}{q_e} \text{ min}, i C_p + \left(1 - \frac{q_p}{q_e} \right) \text{maj } C_p \right) \right] \\ \text{maj } C_e + \text{min}, i C_n \xrightarrow{n, i \alpha_e \cdot k_e} \sum_{p \in P_r} s_p \left[\psi_r^{e \rightarrow p} \cdot \text{maj } C_p + \psi_r^{n \rightarrow p} \left(\frac{q_p}{q_n} \text{ min}, i C_p + \left(1 - \frac{q_p}{q_n} \right) \text{maj } C_p \right) \right] \\ \text{min}, i C_e + \text{min}, j C_n \xrightarrow{(\epsilon, i), (j, n) \alpha_e \cdot k_e} \sum_{p \in P_r} s_p \left[\psi_r^{e \rightarrow p} \left(\frac{q_p}{q_e} \text{ min}, i C_p + \left(1 - \frac{q_p}{q_e} \right) \text{maj } C_p \right) + \right. \\ \left. \psi_r^{n \rightarrow p} \left(\frac{q_p}{q_n} \text{ min}, j C_p + \left(1 - \frac{q_p}{q_n} \right) \text{maj } C_p \right) \right] \\ \dots^a \end{array} \right.$

Notes:

Notation as before. The isotope exchange and particular composition source reactions are parameterised identical to the implicit doubling case. Similarly, the doubled species are used as the catalysts in virtual reactions.

^{a)} Shown example of bimolecular reaction of two doubled species presents only reactions of major and i^{th} minor isotopologues and a pair of i^{th} and j^{th} minor isotopologues. Considering all possible combinations of reactants' isotopologues, the total number of replicated reactions for M isotopologues amounts to 2^M .

2.5.2 Test case simulations

To verify whether both the tagging and the doubling approaches can correctly reproduce the isotopic composition, several simulations have been performed with the CAABA/MECCA box-model for the carbon-12/13 and oxygen-16/17/18 tagging configurations. As the criterion of proper reproduction by tagging, the absolute differences of the simulated isotopic ratios of selected species for tagging and doubling were required to be within $\Delta^Z R = 10^{-9}$. For carbon, this is equivalent to a change of less than 10^{-4} permil in $\delta^{13}\text{C}$, for oxygen it is equivalent to deviations of $5 \cdot 10^{-4}$ and $2.5 \cdot 10^{-3}$ permil for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, respectively. This limit is a trade-off between the precision and speed of the tagged system, and is at least orders of magnitude below experimental precision. At the same time, the test simulations showed a good run-time performance and reveal that tagging offers a remarkable speedup compared to the doubling, due to the optimisations used (see next Sect. 2.5.3). In addition to the accuracy evaluation, it is necessary to verify that the kinetic isotope system is adequate, *i.e.* complies with the criteria outlined in Sect. 2.3.5, and maintains composition exchange correctly. Both, oxygen and carbon isotope tagging, MECCA-TAG/DBL sub-submodels were found to successfully pass the series of such test simulations of which one is exemplified in the following.

A simple, but representative test was performed on the prototype mechanism derived from the complete MECCA chemistry mechanism (similar to that applied by Jöckel *et al.*^[2006] on a global scale) but excluding the NMHC chemistry. The resulting mechanism is schematically depicted in Figure 2.2 and has the following properties:

- The mechanism contains intermediate and non-intermediate species (CH_4 as a source and CO_2 as reservoir) and two artificial source species (C_X , C_Y).
- The species exchange their isotopic composition via different reactions (the rates are taken from the original MECCA reactions list), some species are recycled.
- A kinetic isotope effect for the $\text{CO} + \text{OH}$ reaction is used equivalent to an enrichment of +6.5‰ in $\delta^{13}\text{C}(\text{CO})$ at 1 bar (Röckmann *et al.*^[1998a]).

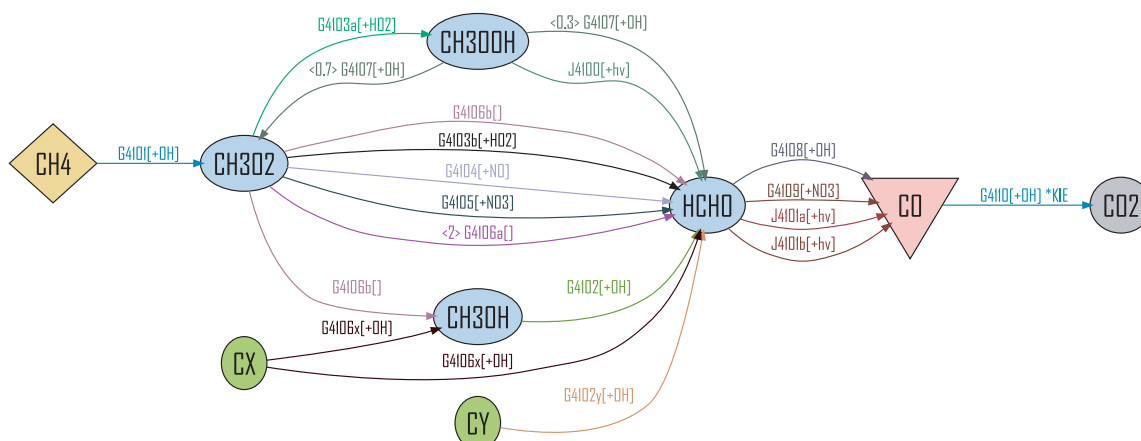


Figure 2.2 Schematic representation of carbon interchanges in the prototype mechanism. Intermediates are shown in blue; methane, carbon dioxide and two artificial species (CX, CY) are non-transient in-situ C source species. Pathway captions refer to the MECCA reaction number (for the reference, see Appendix A) and second reactant.

The prototype mechanism was configured for the CAABA box-model. A set of six simulations, in which the species' isotopic composition was traced, was carried out to check the isotopic composition exchange between the species as follows:

- all species were initialised with the same isotopic composition of -20‰ in $\delta^{13}\text{C}$ (setups 1, 2);
- the principal source of carbon in the system was either methane (3, 4) or artificially added CX and CY species (5, 6) with corresponding values of $\delta^{13}\text{C}(\text{CH}_4) = -52\text{‰}$ and $\delta^{13}\text{C}(\text{C}_\text{X}, \text{C}_\text{Y}) = -32\text{‰}$;
- the CO+OH reaction kinetic isotope effect was disabled (1, 3, 5) or enabled (2, 4, 6);
- the system was closed, except for setups 5 and 6, where methane was absent and CX and CY were continuously emitted into the box;
- simulations were performed with a parameterised seasonal cycle determining the photolysis rates and the OH concentration.

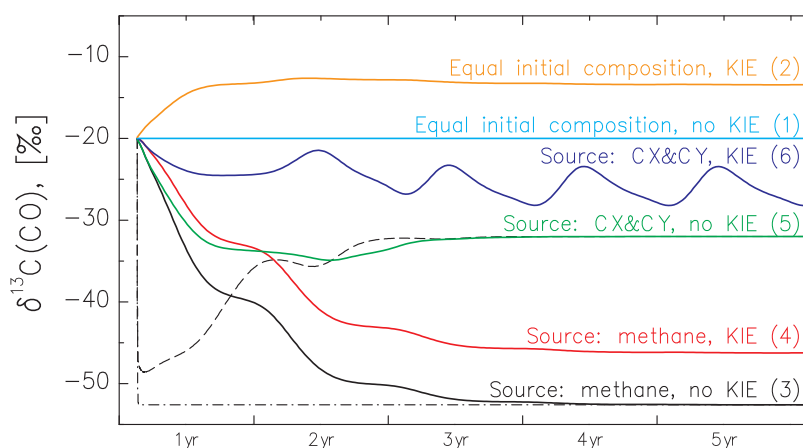


Figure 2.3 Carbon monoxide isotopic composition evolution (solid lines) for different simulation setups (1-6) with the prototype mechanism (Figure 2.2). Dashed and dash-dotted lines denote the formaldehyde composition for setups 5,6 and 3,4, respectively.

The simulated isotopic composition of CO (Figure 2.3) in all cases adequately reflects the dominating source signature as well as the kinetic isotope effect. Thus, the evolution of $\delta^{13}\text{C}(\text{CO})$ in setup 2 reflects the superposition of the CO source and sink enrichment, yielding a typical sink effect equilibration time at ~ 9 months. The sink fractionation is also noticeable in the results of setups 3 and 4, developed, however, on top of markedly slower equilibration of the CO reservoir with the composition from the highly ^{13}C -depleted CH_4 source. Interestingly, in setup 6 (with dominating “VOC-like” source from CX and CY), the system exhibits a noticeable KIE feedback via the OH channel. More OH available in summer results in CO enriched in ^{13}C due to the oxidation reaction KIE, while less OH in winter leads to the takeover of the transfer of lighter composition of CX and CY through HCHO (*i.e.* the KIE “competes” with the precursor signature). A noticeably larger magnitude of the isotope composition variation is explicable by the low CO abundance (and hence the more pronounced oxida-

tion KIE signal). This is caused by the much smaller (compared to methane, see setup 4) source of carbon from C_X and C_Y , whose reaction to the intermediates (methanol and formaldehyde) also proceeds via the oxidation by OH. Excluding the non-closed system setups (5 and 6), the total carbon content and isotopic ratio of the system were found to be conserved.

2.5.3 Performance analysis: Tagging versus doubling

To estimate the benefit of the optimised tagging technique, the performance of both methods (tagging and doubling) was compared in a series of box-model simulations with kinetic chemistry mechanisms of various complexity. Table 2.3 lists selected MECCA mechanisms, which were “tagged” and “doubled” to simulate a stable carbon isotope chemistry configuration (thus accounting for two additional isotopologue classes). Each mechanism was repeatedly simulated in box-model setups for regular (MECCA), doubled (MECCA-DBL) and tagged (MECCA-TAG) cases and subsequently compared using the wall-clock time spent for a one month simulation period.

For the integration of the regular and doubled mechanisms the third-order Rosenbrock solver (ROS3) with adaptive time stepping was used; it is provided by the KPP package in MECCA and is very powerful in handling stiff problems efficiently. The integration of the tagging mechanism (Eq. (2.28)) was performed with a simple solver based on a modified Runge-Kutta algorithm with adaptive time-step control (RKA). The latter is not very well suited for systems of high stiffness, yet in other cases usually shows a decent performance due to its robustness (Press *et al.*^[1992]). Although MECCA-TAG incorporates other more complex solvers, this analysis is to show that even the RKA implemented in the tagged system offers a remarkable speed gain in the competition with the highly efficient ROS3.

To make the comparison more representative, two distinct simulation regimes, namely “free” and “forced”, were chosen. In the “free” regime the initial conditions (species abundances and classes ratios) are set once before the simulation starts while the system remains closed (*i.e.* no introduction or removal of the molecules is allowed) during the simulation. As a consequence, the system proceeds towards an equilibrium state in both, abundance and isotopic signature. In the “forced” regime some species are permanently emitted into the box thus keeping the system in a perturbed state. These two regimes are the extremes of conditions of the chemistry grid-boxes processed in an AC-GCM, *e.g.* ranging from grid-boxes positioned at the surface layer (with emissions as part of the boundary conditions) and at the levels where the perturbation is smaller due to smoother species gradients and weaker mixing terms. For the presented simulations, the “forced” regime integration required more computational time because of the higher stiffness of the ODE system to be solved in contrast to the “free” regime. Comparing the overall results, one gets a rough estimate of the chemistry mechanism performance to be expected in 3D applications.

Table 2.3 Comparison of selected MECCA mechanisms

Abbr.	Number of simulated species (reactions)			Remarks, reference ^{a)}
	Regular mechanism	Amount of tagged	Doubled mechanism	
M6	26 (51)	8 (15)	42 (81)	Minimum (C_1) carbon chemistry, used in the simulation presented in Sect. 2.5.2.
M9 ^{c)}	42 (84)	13 (27)	68 (138)	
M7 ^{b)}	65 (145)	47 (109)	159 (363)	
EVAL ^{b) c) e)}	100 (253)	60 (140)	220 (533)	Used in EMAC evaluation simulation (see Jöckel <i>et al.</i> ^[2006] , Appendix B), used in the simulations presented in Sect. 3.5.
AR ^{b) c) d) e)}	132 (342)	69 (170)	270 (682)	Complete gas-phase reactions set

Notes:

^{a)} For a general MECCA mechanisms reference, see Sander *et al.*^[2005], also Sect. 3.1 and Appendix A.

^{b)} Includes higher hydrocarbons (C_2 to isoprene) species and reactions.

^{c)} Includes stratospheric reactions set.

^{d)} Includes halogen chemistry (excluded in other mechanisms).

^{e)} Includes sulphur and chlorine chemistry.

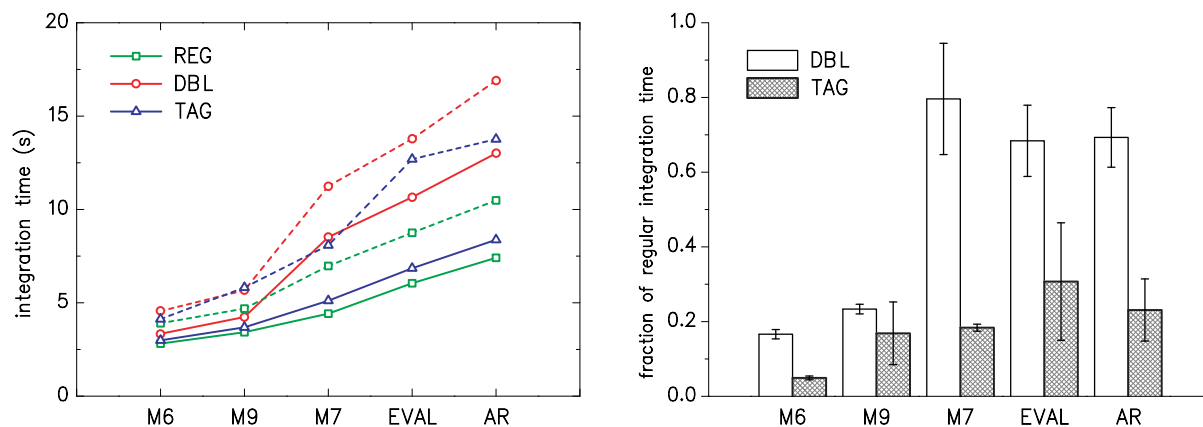


Figure 2.4 Left: Total time spent to integrate the regular, doubled and tagged systems. Solid and dashed lines denote “free” and “forced” regimes, respectively (see text for details). Right: The average additional time required for the doubled and tagged systems as a fraction of the regular mechanism integration time. The vertical lines on the top of the bars represent the variability due to the different regimes.

In Figure 2.4 (left) the simulation times for the different mechanisms and regimes are shown; the average complexity of the mechanisms increases along the abscissa. Figure 2.4 (right) also depicts the estimated average additional time (expressed as a fraction of the regular mechanism integration time) required to process the doubled and tagged systems. In general, the tagged system outperforms doubling, as expected. Speed gains of a factor 3 and larger are achieved when simulating the M6, M7 and AR mechanisms; for the former two the time saved is to a certain extent proportional to the fractions of the tagged species and reactions. The least speed gain was achieved with M9, which includes sulphur chemistry accounting additionally for carbonaceous species involved in the reactive chemistry, which is inefficiently simulated with RKA in the “forced” regime. The same difficulty appears if higher hydrocarbons were included. For the EVAL mechanism the required CPU-time increased by 30% for tagging and by 70% (80% for M7) for doubling. The mechanism including all gas-phase reactions (AR) requires comparable CPU-times as EVAL, with slightly better results for the tagging, likely due to a more efficient handling of the halogen chemistry by RKA.

Evidently, each mechanism has its own individual characteristics that may be considered individually for a better optimisation strategy. To note, for the molecular tagging case the integration time is expected to be ~30% less compared to the isotopic tagging; the latter needs one kinetic exchange derivative calculation more, operating with atomic fractions of the species. The overall performance of the tagging technique, however, is very promising, especially in perspective of the tagging of the complex chemistry mechanisms in 3D model environments.

2.5.4 MECCA-TAG/DBL implementation in MESSy

The realisation of the MECCA-TAG and MECCA-DBL sub-submodels allows the simultaneous simulation of an arbitrary number of *tagging configurations* (*i.e.* sets of tagged species and reactions). For the tagging, this concept is of a great use when more than one tagging configuration is needed to be simulated with the same regular chemistry mechanism. A particular example is a single AC-GCM simulation with various separate stable isotope configurations that tag the same incorporated regular chemistry mechanism.¹⁰ It is stressed again that none of each configuration interferes with the others or with the regular mechanism, thus remaining purely diagnostic.

The setup of a particular configuration is controlled by the configuration file, which contains all necessary information to perform the full (isotopic) tagging of a given mechanism of desired complexity. The configuration files are used for both, the tagging and the doubling sub-submodels that utilise the same pre-processing routines. The latter parse the selected MECCA chemistry mechanism (*i.e.* the species and reactions files) and tagging configuration files and automatically generate the sub-submodels code plugged into the destination simulation code. Parsing routines significantly facilitate the model setup, additionally checking for possible overlooked inconsistencies (like missing species or mass imbalance in any of the tagged reactions) and providing composition interchanges charts (an example is given in Appendix B, p. 239). The tagged reactions are

¹⁰ This concept is exploited further in 3D simulations performed within the current study (see Chapters 5 and 6).

also routinely diagnosed for unaccounted sources of the isotopologues in the mechanism (with respect to the approximations described in Sect. 2.4.3), which helps greatly to deal with large mechanisms and their parts including reactions with multiple “lumped” products.¹¹ The parsing routine codes are written in Pascal (it offers greater flexibility in handling string and text information compared to Fortran) and built with the Free Pascal Compiler (<http://www.freepascal.org/>). The execution of the code is controlled (switched on/off) via the MECCA conventional Fortran95 namelist.

The implementation of the MECCA-TAG/DBL is in conformity with the MESSy standard (Jöckel *et al.*^[2005]). This implies the relocation of the code parts to the dedicated layers of the MESSy interface structure according to their functionality. The interface part of MECCA-TAG is responsible for passing the kinetics information from MECCA to the MECCA-TAG kinetics driver. The latter prepares the pair rates for all tagged species and invokes the integration and processing of each particular configuration. Each of the tagging configurations resides (see Figure 2.5) in the submodel core layer (SMCL) thus being independent from the basemodel. The driver is called from within the submodel interface layer (SMIL) after the call to the regular MECCA integration. The interface layer routines (which are basemodel-dependent) at the BMIL layer contain subroutines processing I/O and other maintenance and provide the interface to other MESSy submodels and base models. Being in fact an extension of MECCA, MECCA-DBL utilises its infrastructure routines. MECCA-TAG and MECCA-DBL are being included in the latest releases of the MESSy-based box-model CAABA/MECCA (Sander *et al.*^[2011]) thus providing diagnostic and isotope modelling extensions to this model.

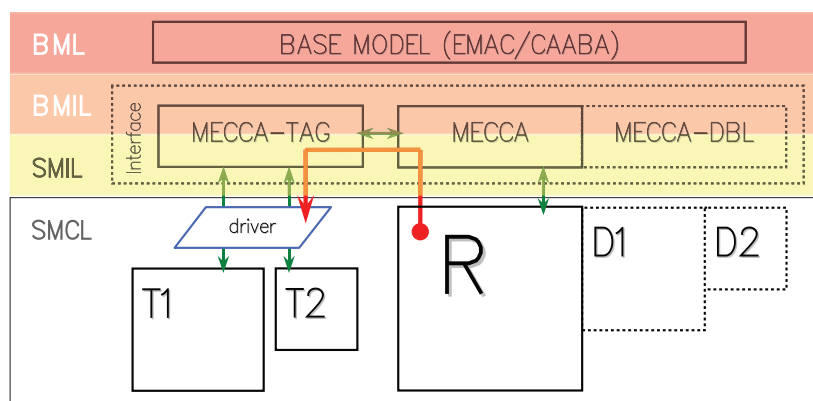


Figure 2.5 Schematic of the MECCA-TAG and MECCA-DBL principal structure (SMCL level is detailed). The regular simulated mechanism (R) provides one-way information on the tagged reaction rates and species budgets to the MECCA-TAG driver. Further each configuration (T1, T2) uses approximated rates to advance the tagged species. Additional species and reactions of the doubling configurations (D1, D2) are added to the regular mechanism, thus MECCA-DBL is just an extension of MECCA.

¹¹ An example is the isoprene oxidation mechanism (MIM) which is part of MECCA and regarded in Chapter 3.

3

Stable carbon and oxygen isotope kinetic chemistry parameterisation

This chapter is devoted to the specifics of the kinetic isotope chemistry parameterisations developed for MECCA in the course of this study. The emphasis is put on the chosen set of relevant carbon and oxygen isotope kinetic effects (Sect. 3.4) and isotope transfer pathways specified in either regular (irreversible) or equilibrium isotope exchange reactions (Sects. 3.3 and 3.3.3, respectively). Subsequently, the results of the evaluation study on the modelling of the species carbon and oxygen isotope compositions with the atmospheric box-model CAABA are presented in Sect. 3.5.

3.1 Overview

The complete chemical mechanism implemented in MECCA contains a “conglomerate” of the various sets of chemical reactions describing diverse aspects of the atmospheric chemistry. MECCA provides the ability to select a functional set of the chemical reactions that suits the particular scientific need, *i.e.* the model configuration. The complete gas phase chemical mechanism comprises the stratospheric chemistry of ECHAM4/CHEM (Steil *et al.*^[1999]) and tropospheric chemistry including the non-methane hydrocarbons chemistry (Pöschl *et al.*^[2000], von Kuhlmann *et al.*^[2003], von Kuhlmann^[2001]). The latter is hereafter referred to as MIM (Mainz Isoprene Mechanism) and comprises species up to C₅ (isoprene, C₅H₈). MIM is supplementary reviewed elsewhere (Taraborrelli^[2009], Butler *et al.*^[2008]). The sulphur and halogen chemistry extension of the mechanism (Kerkweg^[2005], Kerkweg *et al.*^[2008]) is based on the work described in detail in Sander and Crutzen^[1996], von Glasow *et al.*^[2002]. MECCA utilises only principle variables such as temperature, pressure and air density for calculating the chemical reaction rates; the rates required for the photolysis reactions (so-called *J*-values) are provided by an external submodel which depends on the model domain (see details in Sect. 5.1.2, p. 108). A detailed overview of MECCA and its mechanism is presented in Sander *et al.*^[2005], Sander *et al.*^[2011] and in supplementary material therein. More details and the current state of the submodel development are available at the MECCA website¹².

The overall MECCA mechanism incorporates a few hundreds of species and reactions they participate in.¹³ Essentially, the isotope kinetic chemistry parameterisation described below is the extension of the regular chemistry mechanism in view of the following aspects:

- Regular isotope exchange information, *i.e.* how the isotopes of interest of reacted species are distributed among the products in regular reactions (see Sect. 3.3.1 and 3.3.2) is added. The majority of MECCA reactions is given in the bimolecular form (Eq. (‡), p. 8), which is often subject to *individual* specification of the isotope transfer, if the plain redistribution of the composition among the products (like exemplified in Sect. 2.3.2) is not a valid assumption. In general, to explain the complex composition transfers in MECCA, the information from the master chemical mechanism¹⁴ (MCM, Saunders *et al.*^[2003], Jenkin *et al.*^[1997]) is used, unless another reference is given. MCM is an explicit, detailed chemistry mechanism that is expected to sufficiently explain transfers. The reduced MIM chemistry has been derived from MCM. The complete list of reactions and transfers is given in

¹² <http://www.rolf-sander.net/messy/mecca>

¹³ The mechanism used in this study is detailed in Appendix A (p. 225). Throughout this chapter, relevant reactions are referred to using “internal” MECCA reaction labels given in Tables A.1 and A.2 (*ibid.*).

¹⁴ <http://mcm.leeds.ac.uk/MCM>

Appendix A. Additionally, the isotope transfer is detailed in the species interchanges charts inset in Appendix B.

- Additional isotope exchange reactions, whose presence is not relevant for the regular chemistry, but crucial for adequate reproduction of the isotopic composition of the species are introduced (see Sect. 3.3.3).
- Available to date information on kinetic isotope effects escorting relevant reactions is specified. Some model studies (for example, Zahn *et al.*^[2006]) approximate the unknown KIEs using certain assumptions which are applicable in case the mechanism of the chemical reaction is relatively simple (*e.g.* if the reaction rate is proportional to the collision frequency of a particular isotopologue, or the zero-point energy differences result in a proportionality of the reaction rates to the reactants' reduced masses). Unfortunately, the majority of chemical reactions pertains to the complex kind, thus chemical KIEs are much more intricate phenomena and often even the most advanced sophisticated theoretical models show poor agreement with measured values. In this study, the values obtained from the laboratory studies are generally included, omitting uncertain or approximated KIEs where possible.

The aspects itemised above include all the information required for the full isotope extension of the chemical mechanism. The latter is accomplished in MECCA by means of the tagging approach (described in Chapter 3) and implemented in the sub-submodel MECCA-TAG. Applying the terminology from the tagging, we hereafter term the required information for the selected isotope extension as the *isotope tagging configuration*. Thus, the carbon and oxygen isotope tagging configurations are described in the course of this chapter. Before proceeding with the description of the isotope parameterisations, the notation and necessary terms used for isotopes are discussed in the following subsections.

3.2 Used terms and definitions for the isotopes

There are various reference standards, terms and definitions conventionally used in the literature to express the isotopic compositions and effects. To avoid confusion occasionally arising from different notations, all the relevant values reported in this study are converted and expressed exclusively in the terms regarded below. The terms referring to the molecular differences induced by the isotope substitution are following those from the IUPAC definitions (McNaught and Wilkinson^[1997]), namely:

- *Isotopologue*: a molecular entity that differs only in isotopic composition (number of isotopic substitutions), *e.g.* CH₄, CH₃D, CH₂D₂ are the isotopologues of methane.
- *Isotopomers*: from "isotopic isomers", are the set of different isotope position configurations of a selected isotopologue. Hence, ¹⁵N¹⁴N¹⁶O, ¹⁴N¹⁵N¹⁶O are the isotopomers of N₂O, so are CH₂DCH=O and CH₃CD=O for acetaldehyde.

The notation of the isotope composition and effects is conventional, as follows:

- The isotopic ratio ^{*i*}*R* is the *atomic* abundance ratio of any *i*th rare isotope to the abundant isotope in the sample, *e.g.*

$$^{13}\text{C}_R(\text{CO}) = \frac{^{13}\text{C}}{^{12}\text{C}}, \quad ^{18}\text{O}_R(\text{CO}) = \frac{^{18}\text{O}}{^{16}\text{O}} \quad \text{in CO}$$

- The delta-notation is used to express the difference of a given sample isotopic ratio ^{*i*}*R* relative to the reference standard material ratio ^{*i*}*R*_{st}:

$$\delta^i = \left(\frac{{}^iR}{{}^iR_{\text{st}}} - 1 \right) \quad (3.1)$$

For the δ¹³C stable isotope carbon composition, the Pee-Dee Belemnite (abbreviated as V-PDB) standard ratio of 11237.2×10⁻⁶ (Craig^[1957]) is applied. The stable isotope oxygen enrichments are reported relative to the Vienna Standard Mean Ocean Water (V-SMOW) standard ratios of 2005.20×10⁻⁶ for ¹⁸O (Gonfiantini^[1978], Coplen^[1994]) and 386.72×10⁻⁶ for ¹⁷O (Assonov and

Brenninkmeijer^[2003]) isotopes, respectively.¹⁵ The relative enrichments are typically small for carbon and oxygen tracers, hence δ values are customarily reported on the permil (‰) scale.

- The isotopic fractionation *constant* ε (or, alternatively, *enrichment*) expresses the difference of one compartment's isotopic ratio relative to that of another. It is often used to describe isotopic composition changes due to various processes (*e.g.* soil uptake fractionation, KIE, etc.), for example:

$$^{18}\text{O}\varepsilon(\text{H}_2\text{O}) = \left(\frac{^{18}\text{O}R(\text{H}_2\text{O})_{\text{vapour}}}{^{18}\text{O}R(\text{H}_2\text{O})_{\text{liquid}}} - 1 \right) \quad (3.2)$$

describes the enrichment of the ^{18}O isotope of the water vapour relative to the liquid phase due to the kinetic vapour pressure isotope effect. Essentially, reporting the fractionation is only a matter of a concise formulation of which compartment gets enriched (depleted), with relation to which source compartment, and owing to which process.

- The isotopic fractionation *factor* α determines how much faster/slower the reaction with the minor isotopologue goes relative to the reaction with the major isotopologue:

$$^i\alpha = \min,^ik / ^{\text{maj}}k, \text{ e.g. } ^{13}\text{C}\alpha = ^{13}\text{C}k / ^{12}\text{C}k, \quad (3.3)$$

where $\min,^ik$ and $^{\text{maj}}k$ are the reaction rates corresponding to the i^{th} minor and major isotopologues, respectively. Note that this definition differs from the IUPAC-recommended definition for α , which defines the ratio of the reaction rate coefficients of the isotopically light (lower atomic mass) to the rate coefficient of the heavy (higher atomic mass) species (Coplen *et al.*^[2002]). Alternatively, the isotope fractionation due to the KIE may be expressed in terms of enrichment, relating the composition of the product to that of the reactant in Eq. (3.2), that is

$$^i\eta_{\text{reactant}} = \left(\frac{^{\text{maj}}k}{\min,^ik} - 1 \right) = \frac{1 - ^i\alpha}{^i\alpha}. \quad (3.4)$$

Thus, η describes the depletion (in rare isotope) of the portion of reacted molecules with respect to the reactant's composition. If the reaction is accompanied by the KIE of the magnitude α smaller than unity, the reacting species becomes enriched in the rare isotope, sharing the depleted composition with the products, *i.e.* the enrichment is positive. Conversely, the inverse isotope effect ($\alpha > 1$) depletes the reactant composition, whilst the products acquire an enriched composition, and the enrichment is negative.

- The “capital delta” notation is used to express the deviation of the multiple minor isotope composition from a general, largely observed correlation ensuing from their mass differences. For example, in most processes involving oxygen the magnitude of enrichment (or depletion) in ^{17}O isotope is found to be roughly half of that for ^{18}O , relating proportionally to the excess of their masses over lighter ^{16}O , respectively. Certain chemical reactions, however, are found to violate the mass-dependent relationship (*e.g.*, significantly deflecting enrichments in ^{17}O and ^{18}O from the ~2:1 ratio, respectively), promoting so-called mass-independent isotope fractionation (MIF). Quantitatively the degree of MIF is described similar to the regular enrichment:

$$\Delta^{17}\text{O} \equiv \frac{(\delta^{17}\text{O} + 1)}{(\delta^{18}\text{O} + 1)^\beta} - 1, \quad (3.5)$$

where β determines the slope of the line on which the data points of the mass-dependently fractionated compositions fall in the three-isotope plot (Assonov and Brenninkmeijer^[2005]). The value β for

¹⁵ Quoted ^{13}C RV-PDB and ^{17}O RV-SMOW standards are nominally outdated since the last re-determination of the carbon isotope ratio of the NBS 19 reference material used to define the “hypothetical” V-PDB scale introduced after the former PDB primary material was exhausted (see Chapter 40 in de Groot^[2004], also Zhang *et al.*^[1990]). Owing to the differences between the former (*i.e.*, assigned from PDB) and revised scales, a change in isotope composition corresponding to 1‰ in $\delta^{13}\text{C}$ on the PDB-scale is ~1.176 permeg larger on the V-PDB scale, which implies *ex post facto* different absolute abundances derived using the same $\delta^{13}\text{C}$ values reported. Furthermore, changes to ^{13}C RV-PDB reciprocally affect the absolute value of ^{17}O RV-SMOW due to the peculiarities of its analytical determination (see Assonov and Brenninkmeijer^[2003], Brand *et al.*^[2010]). The modelling results presented here are sensitive to the choice of these standards, since all simulated compositions (*e.g.*, of atmospheric abundances, emission fluxes) are defined through them. Nonetheless, errors introduced by adopting outdated values are negligible compared to uncertainties introduced by the other factors in the model, *e.g.* laboratory estimates of the isotope effects magnitudes or emission strengths and signatures.

mass-dependent processes is close to 0.5 but varies individually for a particular species and fractionation mechanism. In this study regarding oxygen isotopes, for universality, the value of $\beta = 0.528$ derived for the meteoric waters (Barkan and Luz^[2005], Brand *et al.*^[2010]) is used for all species. Regarding the atmospheric tracers (whose isotope ratio deviations are not large), the relation above is sometimes linearly approximated as

$$\Delta^{17}\text{O} \cong \delta^{17}\text{O} - \beta \cdot \delta^{18}\text{O} . \quad (3.6)$$

A graphical example of $\Delta^{17}\text{O}$ is shown in Figure 3.1 (p. 34). The magnitude of an anomalous, or mass-independent KIE can also be expressed in terms of enrichment, relating the corresponding fractionation factors similarly to that in Eq. (3.5), for example:

$$\Delta^{17}\text{O}\eta = \frac{({}^{18}\text{O}\alpha)^{\beta}}{{}^{17}\text{O}\alpha} - 1 . \quad (3.7)$$

Analogously to the regular KIE enrichment, the “anomalous” fractionation constant $\Delta^{17}\text{O}\eta$ quantifies the depletion of the reacting molecules in $\Delta^{17}\text{O}$ with respect to the reacting species’ composition, if the reaction proceeds with KIEs of magnitudes ${}^{17}\text{O}\alpha$ and ${}^{18}\text{O}\alpha$ for ${}^{17}\text{O}$ and ${}^{18}\text{O}$ isotopologues, respectively. Thus, a reaction with positive $\Delta^{17}\text{O}\eta$ induces positive $\Delta^{17}\text{O}$ values in the reactant. The uncertainties in $\Delta^{17}\text{O}$ propagating from the uncertainties in $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are calculated using the relation (assuming errors in $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ being uncorrelated):

$$\begin{aligned} \langle \Delta^{17} \rangle &= \sqrt{\left(\frac{\partial \Delta^{17}}{\partial \delta^{18}} \right)^2 \cdot \langle \delta^{18} \rangle^2 + \left(\frac{\partial \Delta^{17}}{\partial \delta^{17}} \right)^2 \cdot \langle \delta^{17} \rangle^2} = \\ &= (\delta^{18}+1)^{-\beta} \sqrt{\beta^2 \cdot \left(\frac{\delta^{17}+1}{\delta^{18}+1} \right)^2 \cdot \langle \delta^{18} \rangle^2 + \langle \delta^{17} \rangle^2} \end{aligned} \quad (3.8)$$

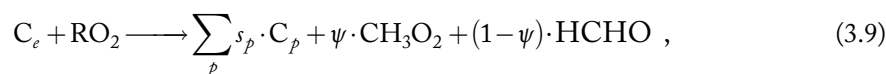
For the sake of lucidity, the angle brackets $\langle \rangle$ here denote the uncertainty of the respective δ or Δ value; the oxygen symbol is omitted. The formulation (3.8) can be straightforwardly used for the $\Delta^{17}\text{O}\eta$ value by substituting the δ -terms with the corresponding η -terms. When fractionation factors are considered, (δ^i+1) and $\langle \delta^i \rangle$ terms are to be replaced with ${}^i\alpha$ and $\langle {}^i\alpha \rangle$ terms for every isotope, respectively.

The reader is referred additionally to the literature (Brenninkmeijer *et al.*^[2003], Schauble^[2004], Johnson *et al.*^[2002], Kohen and Limbach^[2006], Criss^[1999], Kaye^[1987]) for an extensive review of the isotopic effects and their application in atmospheric studies.

3.3 Isotope composition transfer

3.3.1 Carbon interchanges

The chemical transfer of the carbon composition between the atmospheric tracers is a relatively unsophisticated process to be described readily. Usually, the carbonaceous molecules oxidise to the respective products transferring the source carbon further into the oxidation chain. The oxidation of the higher carbons may be escorted by the decomposition (breaking) of the source molecule into smaller fragments. In this case, statistically the distribution of the composition among the products should follow the reaction stoichiometry and isotope mass balance. This is intrinsically handled by the MECCA-TAG/DBL isotope tagging, on the assumption that the isotopomeric differences can be neglected (Sect. 2.3.1, p. 14). The exceptional cases in MIM describe mutual reactions of VOCs¹⁶, in particular the reactions of the higher VOCs with reactive peroxy radicals (RO_2). The latter reactions can be generalised as



¹⁶ Referenced in the mechanism as G4206, G4215a, G4215b, G4216, G4306, G4314, G4401 and G4410 (hereinafter the reaction labels refer to Tables A.1 and A.2 in Appendix A, p. 225).

where C_e denotes the higher-carbon NMHC/VOC educt, C_p are the produced carbon-degraded VOCs and RO_2 is usually the methyl peroxy radical (CH_3O_2). The formulation (3.9) incorporates possible pathways of the reaction via the branching ratio ψ . The latter determines the combination of the stoichiometric coefficients s_p for the higher carbon products (these can be different for each of the reaction branches) and whether formaldehyde or CH_3O_2 is created concomitantly. The correct carbon transfer scheme for Eq. (3.9) suggests the balanced transfer of the C_e composition to the products C_p and a direct transfer of RO_2 carbon to either formaldehyde or CH_3O_2 . Hence RO_2 carbon is either recycled or removed to the HCHO pool.

The reaction¹⁷ of the peroxy acetyl radical (PA) and ethylperoxy radical (EtO_2) is the sole exception of the rule (3.9) in MIM. EtO_2 is assumed to produce acetaldehyde (CH_3CHO), while PA carbon proceeds to either acetic acid (CH_3COOH), or is shared equally between CH_3O_2 and CO_2 (D. Taraborrelli, pers. comm.).

3.3.2 Oxygen interchanges

In contrast to the carbon exchange, oxygen transfer between the species is rather intricate. Carbon and oxygen in the molecular transformations ‘resemble the driver and the passenger of a bicycle: whereas the former is riding to the end of the journey, the latter often readily leaps from his seat to let another oxygen passenger enjoy the ride instead.’¹⁸ Because of the high abundance of atmospheric O_2 , it often enters the vacant positions in formation of subproducts, thus drastically changing the cycling of oxygen in the reaction chains. Within the scope of the current work, the regarded important oxygen interchanges are those related to O_3 . Ozone production in the atmosphere is escorted with an isotope effect leading to its eminent anomalous (mass-independently fractionated, MIF) enrichment (see below, Sect. 3.4.3). The latter propagates into the composition of the species from HO_x and NO_x groups, as well as other tracers interacting with them. Many studies employ this MIF phenomenon to investigate chemical interchanges in the atmosphere (see, for example, Lyons^[2001], Brenninkmeijer *et al.*^[2003], Savarino *et al.*^[2008]). Importantly, in many reactions substitution of the mass-dependently fractionated oxygen from O_2 erases the ozone MIF signal from the composition of the product.¹⁹ At last, oxygen isotope exchange with atmospheric water is of considerable importance, due to the large abundance and depleted composition of the latter with respect to O_2 and other atmospheric tracers. The typical result of oxygen interchanges on the compositions of selected atmospheric tracers is sketched in Figure 3.1. The following sections examine individual parts of the chemical mechanism in view of the oxygen transfer particularities. On top of the exchanges in the regular reactions, oxygen isotopes are found to participate in the isotope exchange reactions. These are described in Sect. 3.3.3 (p. 37).

¹⁷ Denoted in the mechanism with the label G4216.

¹⁸ Quoted is the one of many splendid similes by Carl Brenninkmeijer linking common life examples with isotope peculiarities.

¹⁹ Note: Composition of O_2 may be strictly considered mass-dependent in the troposphere only. Reactions of ozone formation and decomposition or $CO_2 \rightleftharpoons O(^1D)$ isotope exchange lead to small but not non-negligible deficiency in $\Delta^{17}O$ of the stratospheric O_2 .

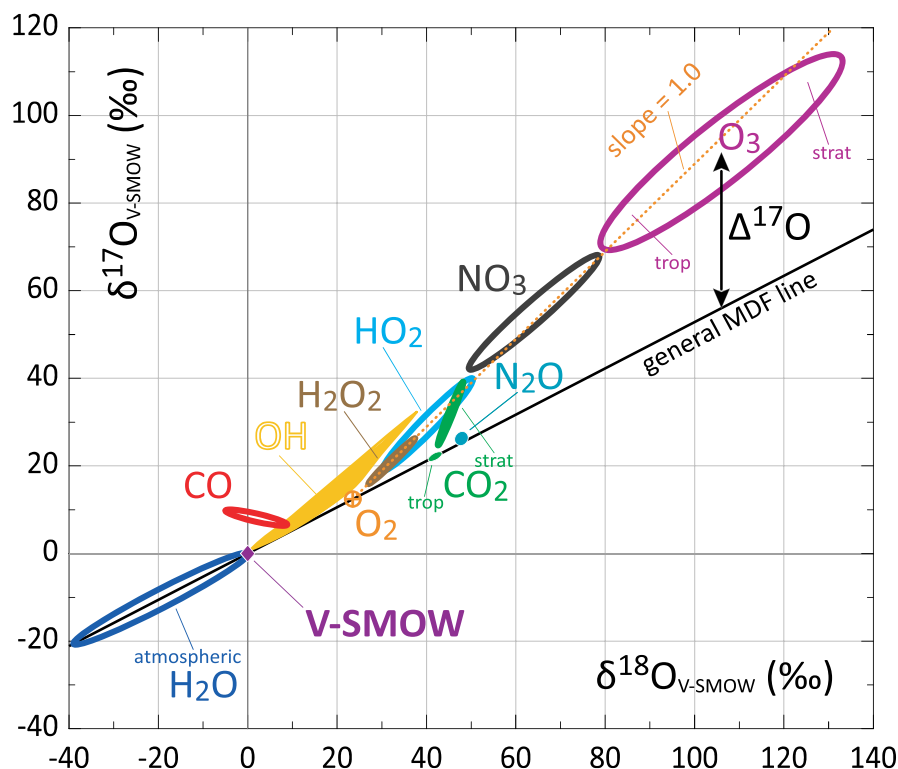


Figure 3.1 The illustrative three-isotope plot of the atmospheric oxygen isotope compositions (from Brenninkmeijer^[2009]). Values along abscissa and ordinate denote the enrichments in ^{18}O and ^{17}O , respectively. The non-anomalous enrichments are expected to lay on the mass-dependent fractionation (MDF) line. Ozone is pushed far off this line, being almost equally enriched in both rare isotopes. Subsequently, O_3 exchanges with NO_x and HO_x species sharing its anomalous composition. In the meanwhile, atmospheric water and O_2 counteract with the MDF oxygen contributions. Eventually, species are found anomalously enriched proportionally to the input of these three important oxygen reservoirs. Remark: For a correct view, enrichments are to be plotted in $\ln(1+\delta)$ values to comply the logarithm-based definition of $\Delta^{17}\text{O}$ given by Eq. (3.5).

3.3.2.1 HO_x chemistry

HO_x species are largely involved in exchanges with ozone.²⁰ In particular, O_3 contributes to the hydroxyl radical (OH) and perhydroxy radical (HO_2) production, and indirectly to the hydrogen peroxide (H_2O_2) produced by self-reaction of HO_2 . Generally, in MECCA the isotope transfer in HO_x reactions follows the reaction stoichiometry. As a rule, when a reaction with OH follows the H-abstraction mechanism, OH oxygen is converted into H_2O . In the troposphere, any anomalous signal in OH vanishes in the highly abundant water, whilst in the stratosphere this is reckoned to be the main cause for the anomalous enrichment of H_2O (Dubey *et al.*^[1997], Lyons^[2001]). This transfer scheme is prevailing in the majority of reactions, *e.g.* NO_x chemistry and oxidation of VOCs. The H-abstraction mechanism also determines the conversion of the HO_2 oxygen to O_2 (when HO_2 loses its hydrogen). A converse transfer of O_2 composition into HO_2 occurs in most of the NMHC and VOC oxidation reactions (see below Sect. 3.3.2.4). The latter, in addition to the reactions of HO_2 with $\text{O}(^3\text{P})$ and $\text{OH}+\text{O}_3$ contribute to the cycling of oxygen between the HO_2 and OH reservoirs.

3.3.2.2 NO_x chemistry

The OH oxidation of the hydrogenated/oxygenated nitrogen proceeds with a direct transfer of the oxygen to the subsequent nitrogenated products.²¹ The influence of O_3 on nitrogen oxides is substantial. NO and NO_2 species interact directly with O_3 in the oxidation reaction



where n stands for the oxidation degree of the product ($n = 2$ or 3). In the simplest case assumed here, O_3 shares one of its oxygen atoms, thus constituting the oxygen composition fraction of $1/n$. That is, when NO is oxi-

²⁰ HO_x chemistry reactions are denoted as G2100–G2112, J2100–J2101 in the mechanism.

²¹ NO_x chemistry is represented by the reactions labelled G3100–G3208, J3100–J3202 in the mechanism.

dised, the product NO_2 acquires at least a half of the O_3 anomalous enrichment, as the rest of the oxygen is received from the educt NO_x species.²² Principally, the oxygen transfer in reactions of NO_x with HO_2 follows that in the HO_x group. For the rest of nitrogen gas-phase and photolysis chemistry, the transfer unambiguously follows the reactions stoichiometry.

3.3.2.3 Methane chemistry

The oxygen composition interchanges in methane chemistry²³ are based upon the study by Weston^[2001] and characterised by a few important steps. First, the oxidation of CH_4 by OH and $\text{O}(^1\text{D})$ implies that the methyl peroxy radical (CH_3O_2) composition is determined by the molecular oxygen in the termolecular reaction with the methyl radical (CH_3). Weston^[2001] attributes this step and the fractionation escorting it to be determinative for the oxygen composition of the subsequently produced species, including CO (see Figure 3.2). Conformably, the successive oxygen transfer from CH_3O_2 to CO via methyl hydroperoxide (CH_3OOH), methanol (CH_3OH) and formaldehyde is assigned in the mechanism. Interestingly, methanol is, besides CH_3O_2 , the only alternative source of oxygen in the methane chain. To note, CH_3OH is moderately emitted by vegetation (see Sect. 5.2.4) and is produced during the higher hydrocarbon oxidation. The methyl peroxy radical contributes to the oxygen composition of the NO_2 produced in the reactions with NO and NO_3 . That is expected to suppress the anomalous enrichment of the nitrogen dioxide. The photolysis of HCHO and CH_3OOH proceeds with a substitution of molecular oxygen in the side-produced HO_2 .

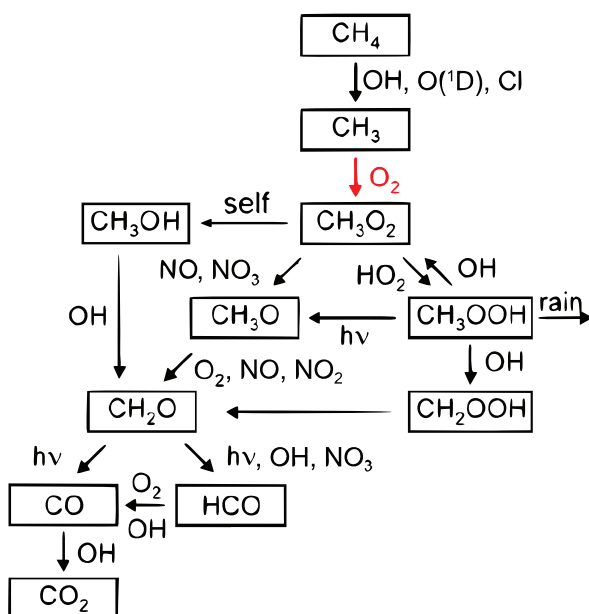


Figure 3.2 Diagram of the methane oxidation chain (after Weston^[2001]). Note that being principally identical, the chemical mechanism of MECCA represents this chain in different detail (*e.g.*, fast reaction steps involving CH_3 and HCO radicals are approximated with one superposed reaction, *etc.*, cf. Figure 2.2, p. 25).

²² Such simple parameterisation of the oxygen composition transfer ensues from the limitations of the isotope tagging approach implemented in this study (see Sect. 2.3.1, p. 14). In actuality, oxygen transfer in (3.10) is a complicated matter, because the MIF in O_3 is shown to be position-dependent, that is the terminal and central atoms in an ozone molecule carry different composition than that of the bulk oxygen in O_3 (see details in Sect. 3.4.3, p. 45). Bhattacharya *et al.*^[2008] show that the $\Delta^{17}\text{O}$ of the symmetric (*i.e.* having the “interior” oxygen atom substituted by the heavier isotope) and asymmetric (with an exterior substitution) isotopomers differ significantly from that of the bulk O_3 . For instance, they estimate that for typical tropospheric compositions (bulk $\delta^{18}\text{O} \approx +80\text{‰}$), the composition of symmetric species deviates from the bulk $\Delta^{17}\text{O}(\text{O}_3)$ of $\sim +31\text{‰}$ by as much as -18‰ ($+26\text{‰}$ for asymmetric, respectively). Furthermore, atom transfer in reactions of NO_x with ozone is expected to favour the abstraction of the terminal O_3 atom over the apex one. In the reaction with NO , however, Savarino *et al.*^[2008] discovered that produced NO_2 is not entirely augmented with O originating from terminal positions, estimating $(8 \pm 5)\text{‰}$ of the cases to proceed via the central atom abstraction mechanism. This eventually leads to the production of NO_2 whose $\Delta^{17}\text{O}$ is higher than that of the bulk O_3 composition. Empirically these may be related using $\Delta^{17}\text{O}(\text{NO}_2) = 1.17 \cdot \Delta^{17}\text{O}(\text{O}_3) + 6.7$ (Savarino^[1], values are in permil units). Savarino *et al.*^[2008] note that in presence of additional oxidation processes that convert NO to NO_2 the abovementioned relation may be deviated, because NO_2 would be no longer in the sole isotopic equilibrium with ozone.

²³ Reactions G4100–G4111 and J4100–J4103 in the mechanism.

3.3.2.4 NMHC chemistry

Oxygen isotope exchange is rather equivocal in the non-methane hydrocarbon chemistry.²⁴ MIM describes consecutive hydrocarbon and VOC degradation mediated by various oxidants, whose oxygen composition contributes to the various products. Functionally, the transfer particularities can be summarised with respect to the individual oxidant, namely OH, RO₂, HO₂, NO_x, NO₃ and O₃.

The transfer during the oxidation by RO₂ resembles that for the carbon isotopes (see Eq. (3.9)), *i.e.* oxygen from the reactive peroxy radical is passed on to the lower VOC, in this case exclusively formaldehyde or methanol. If RO₂ is recycled, its composition is reset by molecular oxygen. The latter also ultimately determines the composition of every HO₂ produced in MIM. Any oxidation by hydrogen peroxide, in turn, recycles its O atoms back to O₂ with an exception for the reaction with PA (peroxy acetyl radical, see above¹⁷, Sect. 3.3.1). Here, together with HO₂ it participates in ozone formation, sharing the contributions as 2:1, respectively. In any of the HO₂-initiated reactions the composition of the oxidised reactant is transferred directly to the subsequently produced VOCs. The oxidation of hydrocarbons by OH usually leads to the production of water (receives O from OH) and either subsequent lower VOC or RO₂, both incorporating O₂. The OH oxidation of the sequent VOCs proceeds without RO₂ production and with the plain transfer of the educt VOC composition to the products. Often multiply oxygenated peroxy radicals like PA or those from higher ketones are supplemented with additional oxygen atoms from O₂.

Exchanges in reactions with NO resemble those in oxidation by OH and lead to the NO₂ production with one oxygen atom arriving from the reacting VOC. In this step, the anomalous enrichment of NO₂ can be affected. Conversely, reactions with NO₂ and NO₃ may introduce their MIF composition into the VOC chain through the organic nitrate species formed in reactions with hydrocarbons. The number of oxygen atoms acquired from the nitrogen dioxide and trioxide in various reactions is different and not systematic. In reactions with the other VOCs, commonly NO₃ participates only in the subsequent NO₂ production.

The alternative pathway of introducing a MIF signal into the VOC oxidation chain is the reactions of alkenes with O₃. MIM comprises ozonolysis of ethene (C₂H₄), propene (C₃H₆), methyl vinyl ketone (MVK) and isoprene, omitting methyl ethyl ketone (MEK). The initial step of the reaction is the breaking of the alkene double bond permitting the formation of the excited primary ozonide. The latter either quenches termolecularly or decomposes further to yield the chemically activated carbonyl oxide (so-called Criegee biradical) and an aldehyde or ketone. The formaldehyde, formic acid, MVK and its oxidants produced in this step acquire one oxygen atom from O₃. The Criegee biradical further decomposes to the set of products, including CO that carries exclusively the ozone composition (Röckmann *et al.*^[1998a]). The other products are usually augmented with oxygen from O₂ or water in addition to the single atom derived from O₃. Unfortunately, due to the reduced formulation of the reactions in MIM, it is generally difficult to achieve a more detailed description of the oxygen composition transfer, especially in ozonolysis reactions. Nevertheless, care is taken to account properly for the overall isotope mass balance of the oxygen arriving from O₃ and passing to the VOCs, as well as for the important CO production step. The latter is of particular interest in view of introducing the ozone MIF signal in carbon monoxide.

Apart from oxidation, VOCs undergo transformations in photolysis reactions. The composition of the produced RO₂ radicals including HO₂ is usually reset by O₂ entering after the photolytic breakdown of the source VOC. In a few cases²⁵ only, a single O atom of the educt is passed to the higher VOC product, assuming equal sharing of the composition with the jointly produced aldehydes and OH. Otherwise, the composition of subsequently produced VOCs is always derived from the source VOC, as well as the oxygen in aldehydes and CO.

3.3.2.5 Oxygen transfer in other reactions

The interchanges in the remaining parts of the mechanism, namely halogen (Cl, Br, I) and sulphur chemistry can briefly be summarised as follows. The creation of the radicals, mainly CH₃O₂ and HO₂, is always characterised by addition of molecular oxygen. In the halogen chemistry, the reactions with RO₂ favour the transfer of the isotopic oxygen of the latter to the aldehyde products. In these reactions, oxygenated halogens

²⁴ MIM comprises reactions labelled G4200–G4508 and J4200–J4501 in the mechanism, respectively.

²⁵ Reactions J4302–J4304 and J4402–J4405.

recycle their oxygen back to the O_2 pool. In contrast to the aldehydes, the reactions of halogen oxides are of significant importance for the nitrogen oxides. This is owing to the interactions with ozone, particularly in the marine boundary layer (MBL) chemistry (Sander and Crutzen^[1996]). For example, bromine oxide acquires its oxygen composition from O_3 reacting with atomic bromine. Later on, BrO passes it in a series of transformations to NO_x and NO_3 . That is considered to explain the significant MIF enrichments in nitrate in the spring arctic atmosphere during the so-called bromine explosion events (Morin *et al.*^[2008]). The transfer of the MIF also takes place for chlorine and iodine oxides in similar reactions with O_3 . In the majority of the halogen reactions in the mechanism, the oxygen transfer follows unequivocally the isotope balance of the reactions. The photolysis of methylated halogens proceeds with the production of the methyl peroxy radical or CO, which receive the oxygen composition from the molecular O_2 .

The sulphur chemistry exchanges follow the general oxygen transfer characteristics outlined above. Exceptionally, the dimethyl sulphide (DMS) oxidation via the OH-addition channel²⁶ (Seinfeld and Pandis^[2006], p. 269) proceeds with incorporation of the OH oxygen into the product dimethyl sulphoxide (DMSO). In the H-abstraction channel, the formaldehyde and CH_3SO_2 radical are produced by addition of air O_2 . The subsequent oxidation²⁶ of DMSO follows analogously with addition of OH oxygen into the product SO_2 .

3.3.3 Isotope exchange reactions

The isotope exchange reactions are the particularity of isotope kinetic chemistry. Isotope exchange alters the isotopic ratios of reacting species, but not their concentrations (see the formulation in Sect. 2.3.4, p. 18). From the point of view of the regular chemistry, isotope exchange reactions are the additional “shortcuts” for the isotope atoms transfer between the species. Importantly, isotope exchange is an equilibration process also accompanied by kinetic isotope effects. If it is rapid, isotope exchange becomes the dominant factor determining the composition of the species, ruling out the regular chemistry-induced exchanges. As a whole, carbon isotope exchange reactions are not relevant to atmospheric gas-phase chemistry. On the contrary, isotope exchange is of importance for the oxygen isotopes. Amongst the atmospheric tracers, OH, $O(^1P)$, $O(^3P)$, H_2O , NO, NO_2 and CO_2 are subject to moderate or intensive equilibration. Within the current study the oxygen isotope exchange reaction mechanism following the studies of Lyons^[2001] and Zahn *et al.*^[2006] is implemented. A summary of the oxygen isotope exchange reactions is presented in Table 3.1.

The most important equilibrations are those related to atmospheric H_2O and O_2 , because of their large atmospheric abundance. In the troposphere, exchange forces the composition of the hydroxyl radical to be largely determined by water vapour, while under stratospheric conditions the production of H_2O from OH becomes competitive to their mutual isotope exchange. In addition, OH equilibrates with HO_2 , NO and NO_2 thus serving as the intermediate oxygen pool for these species. The production of atomic oxygen is governed by the photolysis of ozone, thus both $O(^3P)$ and $O(^1D)$ are produced with the characteristic MIF composition. However, the very rapid exchange of O_2 with $O(^3P)$ (in the ozone formation mechanism, see Sect. 3.4.3, p. 45) efficiently washes out the MIF composition from the latter.

From the above, the isotope exchange is apparently influential in $HO_2 \rightleftharpoons O_2$ and $NO_2 \rightleftharpoons H_2O$ reactions, but these are badly quantified from experimental data. Both reactions, at the given upper limit of the reaction rate coefficient, lead from significant to complete reduction of MIF in HO_x and NO_x groups’ species. According to Zahn *et al.*^[2006], this is unlikely in view of the observed MIF in stratospheric H_2O ensuing from MIF in OH, as their modelling results suggest. Therefore, in the current setup these reactions are excluded. Furthermore, for the majority of the isotope exchange reactions the kinetic isotope effects are not quantified. In this respect, the largest uncertainties are associated with the exchanges with O_2 and H_2O , since these may be considered as infinite oxygen reservoirs. A tracer equilibrating with such a reservoir ultimately receives its composition enriched (or depleted) due to the fractionation in the isotope exchange, whilst losing own composition irreversibly. In other words, isotope exchange with O_2 and atmospheric water is a source effect with the uncertainty of the magnitude of the unknown isotope exchange KIEs. Exceptionally, the unknown KIEs may be not of importance in the isotope exchange between compartments whose compositions differ substantially compared to the (anticipated) KIE magnitude, because this way the function of the isotope exchange is merely the equilibration of the compartments’ composition.

²⁶ Reactions G9400b, G9402.

The kinetic effects in the oxygen isotope exchange reactions regarded here are not quantified to date. Two studies on the $\text{O}(^3\text{P}) \rightleftharpoons \text{O}_2$ reaction (Anderson *et al.*^[1985], Fleurat-Lessard *et al.*^[2003]) measured the exchange reaction rates for the $^{18}\text{O}(^3\text{P})+^{16}\text{O}_2$ and $^{16}\text{O}(^3\text{P})+^{18}\text{O}_2$ isotopologue pairs, though no measurements for the $^{16}\text{O}(^3\text{P})+^{18}\text{O}^{16}\text{O}$ pair are available. For the modelling approach applied here (neglecting the doubly substituted $^{18}\text{O}_2$) these data are not of use. For the same reason, the KIE for this exchange reaction calculated by Janssen^[2005] cannot be used, as this author used an extended mechanism for atomic O, O_2 and O_3 exchanges that includes double and triple substituted isotopomers. The single-substituted isotopologue KIE for this reaction was calculated by Johnston *et al.*^[2000] and applied here (assumed to be mass-dependent, see Sect. 3.4.2).

Table 3.1 Oxygen isotope exchange reactions

Reaction ^a			Rate coefficient ^{b, c}		$\frac{\lambda_{\text{Q} \rightarrow \text{O}}}{\lambda_{\text{O} \rightarrow \text{Q}}}$ ^d	Reference
			A	E/R		
IEXO01	$\text{QH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{Q} + \text{OH}$		$2.3 \cdot 10^{-13}$	2100	1	Dubey <i>et al.</i> ^[1997]
IEXO02	$\text{QH} + \text{HO}_2 \rightleftharpoons \text{HOQ} + \text{OH}$		$1.7 \cdot 10^{-11}$	-400	2	Dransfeld and Wagner ^[1987]
IEXO03	$\text{QH} + \text{NO} \rightleftharpoons \text{NQ} + \text{OH}$		$1.8 \cdot 10^{-11}$		1	Greenblatt and Howard ^[1989]
IEXO04	$\text{QH} + \text{NO}_2 \rightleftharpoons \text{NOQ} + \text{OH}$		$1.0 \cdot 10^{-11}$		2	Greenblatt and Howard ^[1989]
IEXO05 ^e	$\text{Q}(^3\text{P}) + \text{O}_2 \rightleftharpoons \text{OQ} + \text{O}(^3\text{P})$		$1.4 \cdot 10^{-12}$	-262	2	Fleurat-Lessard <i>et al.</i> ^[2003]
IEXO06	$\text{Q}(^3\text{P}) + \text{NO} \rightleftharpoons \text{NQ} + \text{O}(^3\text{P})$		$3.7 \cdot 10^{-11}$		1	Anderson <i>et al.</i> ^[1985]
IEXO07	$\text{NQ} + \text{NO}_2 \rightleftharpoons \text{NOQ} + \text{NO}$		$3.6 \cdot 10^{-14}$		2	Klein <i>et al.</i> ^[1963]
- ^f	$\text{HOQ} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{OQ}$		$3.0 \cdot 10^{-17}$		1	Sinha <i>et al.</i> ^[1987]
- ^f	$\text{NOQ} + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2 + \text{H}_2\text{Q}$		$2.3 \cdot 10^{-13}$	2100	1/2	Jaffe and Klein ^[1966]
IEXOCO2 {	$\text{Q}(^1\text{D}) + \text{CO}_2 \rightarrow \text{COQ} + \text{O}(^3\text{P})$		$6.9 \cdot 10^{-11}$	-117	1	Yung <i>et al.</i> ^[1997]
	$\text{O}(^1\text{D}) + \text{COQ} \rightarrow \text{CO}_2 + \text{Q}(^3\text{P})$				2	

^a) The rare and abundant oxygen isotopes are denoted as Q and O, respectively; equations are listed with the MECCA reaction number.

^b) Given as $k(T) = A \cdot \exp(-E/R/T)$ where A is the Arrhenius factor, E/R is the temperature dependence factor, T is the temperature.

^c) The rate coefficient is given for the forward (left-to-right) reaction.

^d) The ratio of the forward to the backward reaction rate (see rare isotope transfer in Sect. 2.3.4).

^e) The original fit of the rate coefficient ($k_{8+66} = 3.4 \cdot 10^{-12} \times (300\text{K}/T)^{1.1}$) is reduced to the form given in the note^b).

^f) Excluded from the reference setup (see text).

Although not being by definition an isotope exchange reaction, the oxygen isotope transfer between the $\text{O}(^1\text{D})$ and CO_2 can be regarded in terms of isotope exchange. Proposed by Yung *et al.*^[1991], the quenching reaction of $\text{O}(^1\text{D})$ with CO_2 proceeds via the intermediate $(\text{CO}_3)^\ddagger$ complex, with subsequent decomposition to CO_2 and $\text{O}(^3\text{P})$. The exchange with CO_2 does, however, not take place with the ejection from $(\text{CO}_3)^\ddagger$ of the rare isotope of $\text{O}(^3\text{P})$ arriving from $\text{O}(^1\text{D})$, which is statistically expected in $1/3$ of the cases. Analogously, statistically in one third of the reactions of the abundant $\text{O}(^1\text{D})$ and substituted CO_2 , $\text{O}(^3\text{P})$ carries away the rare isotope from the intermediate. The equilibration of CO_2 , however, proceeds with respect to $\text{O}(^1\text{D})$; since the latter is expected to be mass-independently enriched stemming dominantly from O_3 (Slanger^[1994]), this process is believed to be the main MIF transfer pathway into CO_2 in the stratosphere (Yeung *et al.*^[2009]). For the present setup, the kinetics of this exchange are taken from the study of Yung *et al.*^[1997].

3.4 Kinetic isotope effects

3.4.1 Carbon KIEs

The kinetic effects related to the stable carbon isotope chemistry in MECCA are summarised in Tables 3.2 and 3.3. Unless stated otherwise, the magnitudes of the KIEs are measured at standard atmospheric conditions (298K and 10^5 Pa pressure) and show either negligible or no dependence on temperature or pressure. The majority of the reactions are escorted by the normal (*i.e.* characterised with $^{13}\text{C}\alpha < 1$ or $^{13}\text{C}\eta > 1$) kinetic effects that enrich the composition of the remaining reacting species. The reactions of formaldehyde with OH and NO_3 radicals are reported to have inverse KIEs; these are discussed in Sect. 3.4.1.2. Uniquely, the ^{13}C KIE of the reaction of the carbon monoxide with OH traverses from normal to inverse, due to its pressure dependence. This KIE is scrutinised in Sect. 3.4.4.

3.4.1.1 Methane chemistry

All methane oxidation reactions are escorted by normal KIEs, *i.e.* lighter isotopologues react more rapidly, thus enriching CH₄ in ¹³C and depleting the composition of the products entering the subsequent oxidation chain. The main removal pathway of CH₄ in the atmosphere is the reaction with OH with production of CH₃ radicals and H₂O. The consecutive combination of methyl radicals with air O₂ leads to the production of CH₃O₂. In MECCA, this sequence is parameterised in one reaction, assuming the reaction with OH to be the rate limiting step. The above said is valid for the reaction of CH₄+O(¹D) that proceeds to methyl radical and OH. The KIE of the CH₄+OH attack step is a subject of several experimental studies not reconciled to date yet (see Brenninkmeijer *et al.*^[2003] for a concise review). The most credible value is provided by Saueressig *et al.*^[2001] who measured the ¹³C KIE at an equivalent CH₄ enrichment of ¹³C $\eta_{\text{CH}_4+\text{OH}}$ = +3.9‰. Another estimate of +5.4‰ conferred by Cantrell *et al.*^[1990] is to date employed in the model sensitivity studies, but is likely less reliable due to possible interference from the CH₄+O(¹D) reaction that was loosely constrained in the laboratory (McCarthy *et al.*^[2003]). The KIE in the reaction with O(¹D) is larger than that with OH, being +13‰ (Saueressig *et al.*^[2001]).

The kinetic isotope effects in the reaction of CH₄ with atomic chlorine is found to be temperature-dependent, based on experimental data (Saueressig *et al.*^[1995]):

$$^{13}\text{C}\alpha_{\text{CH}_4+\text{Cl}} = \left(1.043 \cdot e^{\frac{6.455}{T}} \right)^{-1}$$

exhibiting the decrease in the equivalent KIE enrichment ¹³C $\eta_{\text{CH}_4+\text{Cl}}$ from +74‰ to +66‰ in the 220–300K temperature range. Another determination of the CH₄+Cl KIE was done subsequently by Tyler *et al.*^[2000]; their results suggest a slightly stronger temperature dependence and generally lower ¹³C $\eta_{\text{CH}_4+\text{Cl}}$ spanning within +71‰ to +61‰ in the same temperature range. Because Crowley *et al.*^[1999] firmly corroborated the former results of Saueressig *et al.*^[1995] at 298K in an alternative laboratory study, these are adopted here. The reaction with atomic chlorine and O(¹D) become significant in the middle and upper stratosphere, where they may account for more than 50% loss of CH₄ (Bergamaschi *et al.*^[1996]). In the troposphere, the presence of atomic Cl in the marine boundary layer is suspected to have an effect on CH₄ composition resulting in the larger observed variability in $\delta^{13}\text{C}(\text{CH}_4)$ compared to that expected from the dominant removal by OH oxidation (Allan *et al.*^[2005]).²⁷ The variation of ¹³C $\eta_{\text{CH}_4+\text{Cl}}$ with height resulting from the standard atmosphere temperature profile is presented in Figure 3.7 (p. 54).

Table 3.2 Methane chain chemistry ¹³C kinetic isotope effects

Reactions ^a	KIE		Reference
	¹³ C α	¹³ C η (‰) ^b	
G4100 CH ₄ + O(¹ D) → 0.75 CH ₃ O ₂ + 0.25 HCHO	0.9872±0.0006	+13.0±0.6	Saueressig <i>et al.</i> ^[2001]
G4101 CH ₄ + OH → CH ₃ O ₂	0.9961±0.0004	+3.9±0.4	
G6400 ^c CH ₄ + Cl → CH ₃ O ₂	0.938±0.002	+65.8±2.3	Saueressig <i>et al.</i> ^[1995]
G4102 CH ₃ OH + OH → HCHO	0.9699±0.02	+31.0±21.3	Feilberg <i>et al.</i> ^[2008] ^d
G4108 HCHO + OH → CO	1.0504±0.005	-48.0±4.5	Feilberg <i>et al.</i> ^[2004] ^d
G4109 HCHO + NO ₃ → CO	1.0526±0.01	-50.0±9.0	
G6401 HCHO + Cl → CO	0.9452±0.007	+58.0±7.8	
G7400 HCHO + Br → CO	0.885±0.01	+130.0±12.8	
J4101a,b HCHO + <i>h</i> ν → CO	0.894±0.0075	+118.6±9.4	Feilberg <i>et al.</i> ^[2005a] ^d
G4110 ^e CO + OH → CO ₂	0.9935±0.0001	+6.7±2.1	Röckmann <i>et al.</i> ^[1998b] , Stevens <i>et al.</i> ^[1980]

^a) MECCA reaction number, reactants and only the carbonaceous products are listed.

^b) Denotes the equivalent enrichment in ¹³C the reacting species acquires due to the KIE (see Sect. 3.2).

^c) Temperature-dependent KIE, given are the approximate values for 298K.

^d) Values from this study appear to be unreliably quantified; excluded from the reference setup (see text).

^e) Value and uncertainty are from the conventional, pressure-dependent fit for 10⁵ Pa (see Sect. 3.4.4).

²⁷ This hypothesis, however, is not supported by the observational data on CO (see details in Sect. 6.1.1.2, p. 144).

3.4.1.2 Formaldehyde and methanol KIEs

The kinetic isotope effects in reactions of formaldehyde and methanol (Feilberg *et al.*^[2008], Feilberg *et al.*^[2004], Feilberg *et al.*^[2005a]) are listed in Table 3.2 for comparison but not included in the reference setup due to the suspected unreliability of these laboratory results. There are a few other studies of these authors that do not agree with alternative laboratory results, which was attributed to the complications in the experimental setup (see, for instance, Chen and Marcus^[2005]). Regarding the photolysis of HCHO, it is estimated to be of a rather large value of $^{13}\text{C}\eta_{\text{HCHO}+bv} = +118\text{‰}$ (Feilberg *et al.*^[2005a]). From the competitiveness of the primary formaldehyde sink pathways (photolysis is estimated to be about 5 times faster than reaction with OH at the concentration of 10^6 molec/cm³ and at the solar zenith angle of 40°, Weston^[2001]), one expects a significantly enriched composition of formaldehyde to be observed in the background air at low latitudes. For instance, assuming a 5:1 partitioning between the photolysis and the OH sink channels, the effective enrichments of $\delta^{13}\text{C}(\text{HCHO})$ due to the reported KIEs in these reactions yield +53‰ and -8‰, respectively (see the example of the effective enrichment calculation in Sect. 5.1.5). Given the average signature of the formaldehyde sources of -40‰ (expected from a large fraction of the light atmospheric methane source of ~0.6 and the remaining relatively enriched surface/in-situ sources, Stavrou *et al.*^[2009]), one should observe a quite enriched average HCHO composition of around +4‰. The few available measurements of the background $\delta^{13}\text{C}(\text{HCHO})$ do not support this conclusion, ranging from -31‰ to -17‰ (Johnson and Dawson^[1990], 23.4°N/41.1°S and Rice and Quay^[2009], 38.6°N), *i.e.* within the spread of emission $\delta^{13}\text{C}$ signatures estimated for formaldehyde (see Shen^[2008], also Sect. 5.2.5, p. 131). The uncertain HCHO KIEs were further tested in the sensitivity simulations complementary to the box-model evaluation of the isotope kinetic chemistry (presented in Sect. 3.5). There, the results also attest rather large ^{13}C fractionations leading to unrealistic (positive) values of the simulated $\delta^{13}\text{C}(\text{HCHO})$ in the tropospheric conditions. Finally, an earlier alternative measurement of the HCHO photolysis KIE (Stone^[1989]) yielded a comparatively “moderate” value of $^{13}\text{C}\eta_{\text{HCHO}+bv} = (25.0 \pm 5.3)\text{‰}$; unfortunately, this preliminary work was not finished. Regarding the uncertain methanol oxidation KIE, it is further tested in a sensitivity simulation with the 3D model in this study (see Sect. [394], p. 197).

3.4.1.3 Non-methane chemistry KIEs

The carbon kinetic isotope effects in NMHC chemistry are summarised in Table 3.3. To date, only the effects in the dominating VOC removal reactions with OH and O₃ have been measured. The KIE values for the C₂–C₄ alkanes and alkenes oxidation by OH are taken from the studies by Rudolph and Czuba^[2000] and Anderson *et al.*^[2004]. Both studies derive an empirical dependency of the effect on the inverse molecular mass of the reacting species (see Figure 3.3). Rudolph *et al.*^[2000] note that the alkanes OH oxidation KIE is likely to be attributed to collision frequency changes upon the isotopologues substitution. The KIEs in reactions of alkenes with OH, however, are found to be larger than those for alkanes, explained to have an extra fractionation due to the addition of OH to the double bond. The magnitudes of KIEs in the reactions of isoprene and MVK with OH are taken from the study by Iannone *et al.*^[2009], who have improved the results of Rudolph *et al.*^[2000].

The measured kinetic isotope effects in the gas-phase reactions of unsaturated VOCs with O₃ were also found to be dependent on the inverse molecular mass of the reacting species (Iannone *et al.*^[2003]). The magnitudes are somewhat similar to those for the OH oxidation of alkenes (see Figure 3.3). Similar to the case of the OH reactions, it is proposed that such a dependence of the KIE is dominantly related to the substitution of a carbon isotope positioned in the alkene double bond. Recent more precise measurements of (Iannone *et al.*^[2008]) attest slightly larger fractionations (in the OH reactions) for the heavier molecules of isoprene, MVK and methacrolein (MACR). The latter species is lumped into MVK in MIM; that, however, is not expected to maltreat the KIEs associated with the alkene ozonolysis, since for these two compounds the effects have similar magnitudes of $(8.38 \pm 0.42)\text{‰}$ and $(8.01 \pm 0.07)\text{‰}$ for MACR and MVK, respectively.

Similar to the methane chemistry carbon isotope effects, the oxidation of NMHCs and VOCs by OH and O₃ in the atmosphere is expected to enrich these species in ^{13}C . The OH oxidation chemistry generally dominates at daytime. However, the effect of the ozonolysis reactions on the isotopic composition of VOCs is not negligible, especially during nighttime. For instance, Iannone *et al.*^[2003] estimate the contribution of reactions with ozone to the overall change in the ^{13}C ratio for various NMHCs to be up to 50%, with 20% for isoprene. Overall, the KIEs in VOCs removal are expected to have a small effect on the composition of the oxidation end-products (primarily HCHO and subsequent CO). In other words, the isotope composition of the CO

produced in the isoprene oxidation chain will be nearly that of the *emitted* isoprene, whilst the composition of the latter, being measured in the atmosphere, will be found enriched. That is owing to the relatively short lifetimes of VOCs against the chemical removal that dominates over the fractionation induced by the atmospheric transport. However, if an enriched airborne species is subject to other removal processes (*e.g.*, dry deposition or wet scavenging), this effects in depletion of its chemical products, since preferential removal of the heavier isotopologues occurs. Additionally, the removal processes itself may be escorted by kinetic effects, which generally introduce a positive fractionation (*i.e.* preferentially remove ^{12}C) and are expected to compensate the chemical KIEs for VOCs. The isotope carbon fractionation in the deposition processes and its effect on the species composition are discussed in Sects. 5.1.5 (p. 114) and 6.2.4.2 (p. 182).

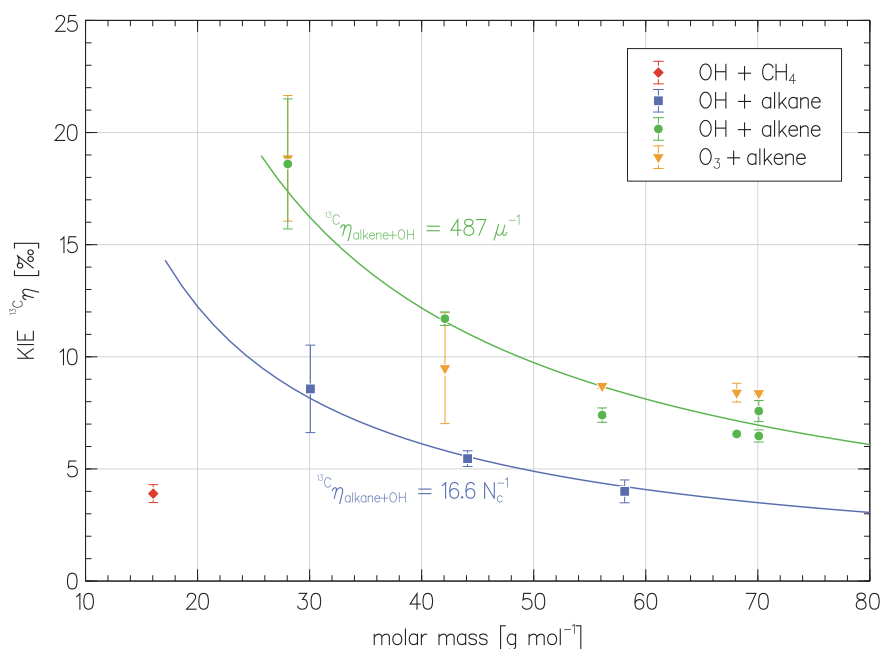


Figure 3.3 Kinetic isotope effects in the reactions of alkanes and alkenes with OH and ozone (symbols, data is from refs. in Table 3.3). Lines denote the empirical approximation through the experimental values; μ and N_c denote the molecular mass and the number of carbons in the reactant's molecule, respectively. The ^{13}C KIE of the $\text{CH}_4 + \text{OH}$ reaction is plotted for comparison.

Table 3.3 NMHC chemistry ^{13}C kinetic isotope effects

Reaction ^a		KIE		Reference
		¹³ C α	¹³ C η (‰) ^b	
OH-oxidation of NMHCs				
G4200	C ₂ H ₆ + OH → EtO ₂	0.9915±0.002	+8.6±2.0	Anderson <i>et al.</i> ^[2004]
G4202	C ₂ H ₄ + OH → 2/3 C ₃ H ₆ O ₂	0.9817±0.003	+18.6±3.1	
G4300	C ₃ H ₈ + OH → 0.85 PrO ₂ + 0.18 EtO ₂	0.9946±0.0004	+5.5±0.4	
G4410	C ₄ H ₁₀ + OH → C ₄ H ₉ O ₂	0.996±0.0005	+4.0±0.5	
G4302	C ₃ H ₆ + OH → C ₃ H ₆ O ₂	0.9884±0.0003	+11.7±0.3	Rudolph and Czuba ^[2000]
G4406	MVK + OH → MVKO ₂	0.9925±0.0005	+7.6±0.5	Iannone <i>et al.</i> ^[2009]
G4501	C ₅ H ₈ + OH → ISO ₂	0.9935±0.0001	+6.6±0.1	
Alkene ozonolysis				
G4201	C ₂ H ₄ + O ₃ → HCHO + 0.23 CO + 0.54 HCOOH	0.9815±0.0029	+18.9±3.0	Iannone <i>et al.</i> ^[2003]
G4301	C ₃ H ₆ + O ₃ → 0.57 HCHO + 0.47 CH ₃ CHO + 0.07 CH ₃ O ₂ + 0.06 EtO ₂ + 0.23 PA + 0.04 CH ₃ COCHO + 0.06 CH ₄ + 0.31 CO + 0.22 HCOOH + 0.03 CH ₃ OH	0.9906±0.0025	+9.5±2.6	
G4405	MVK + O ₃ → 0.45 HCOOH + 0.9 CH ₃ COCHO + 0.1 PA + 0.22 CO	0.9921±0.0001	+8.0±0.1	Iannone <i>et al.</i> ^[2008]
G4500	C ₅ H ₈ + O ₃ → 0.28 HCOOH + 0.65 MVK + 0.1 MVKO ₂ + 0.1 PA + 0.14 CO + 0.58 HCHO + 0.08 CH ₃ O ₂	0.9917±0.0001	+8.4±0.1	

^a) MECCA reaction number, reactants and only the carbonaceous products are listed.

^b) Denotes the equivalent enrichment in ^{13}C the reacting species acquires due to the KIE (see Sect. 3.2).

3.4.2 Oxygen KIEs

The oxygen kinetic isotope effects included in this study are summarised in Table 3.1. Compared to the stable carbon KIEs, current information on oxygen effects is scarcer with respect to the chemistry relevant to CO. In particular, no measurements are reported to date for the oxygen isotope effects or atmospheric compositions of the oxygenated VOCs, a considerable in-situ source of formaldehyde and carbon monoxide in the atmosphere. Generally, the oxygen of these sources originates from the atmospheric O₂ during the oxidation of methane and VOCs, with the exception of ozonolysis reactions, when oxygen from O₃ enters the oxidation (see Sect. 3.3.2.4). Similar to what is pointed out for oxygen isotope exchange reactions (Sect. 3.3.3), the signatures of the oxygenated VOCs are determined by the air O₂ reservoir composition, plus unknown KIEs escorting the incorporation of O₂ into source NMHCs. Further possible KIEs in the oxidation chain, if present, should play a minor role in the composition of the end-products like CO, assuming that the chemical sink is the dominant removal process for VOCs (see discussion in the previous section).

Likewise, air oxygen enters the methane chain via the methyl peroxy radical in reactions of CH₄ oxidation by OH and O(¹D). By using an estimate of δ¹⁸O(CO) originating from the methane source as a proxy, an approximation of the unknown KIEs escorting these reactions can be made. Brenninkmeijer^[1993] and Brenninkmeijer and Röckmann^[1997] (“BR97”) derive largely depleted values of δ¹⁸O(CO) in the SH from the CH₄+OH source, indicating that the ¹⁸O KIE for CH₃+O₂ should be inverse and large. Furthermore, Weston^[2001] infers the depletions ¹⁸Oε (and accordingly the KIEs ¹⁸Oη) escorting the CH₃O₂ production within the range from -20.5‰ to -35.1‰. Another estimate from the inverse model study of Bergamaschi *et al.*^[2000] suggests depletions of -11.2‰ to -15.2‰, respectively (scenarios S1–S5). Recent results obtained with the simplified source-tagged CO simulations of C¹⁸O isotopes with the MOZART4 model (Emmons *et al.*^[2010]) attest the depletions of at least -24‰ to be plausible, comparing simulated δ¹⁸O(CO) to the observational data (K. H. Park, Stony Brook Univ., 2010 unpublished results). Summarising the above, the KIE magnitudes for the CH₃+O₂ reaction yielding ~0‰ or lower compositions appear to be a credible approximation. For the current study, the KIEs actuated in the modelling study by Zahn *et al.*^[2006] corresponding to depletions of approx. -28‰ are adopted in MECCA for the OH and O(¹D) reactions with methane.

The estimates of the oxygen isotope composition of CO arriving from NMHC oxidation are dependent on those from the CH₄ oxidation, because these two major in-situ sources of atmospheric CO are the most uncertain ones. Indeed, the high δ¹⁸O(CO) value of +9‰ from the methane oxidation source inferred by Bergamaschi *et al.*^[2000] is counterbalanced with rather depleted VOCs-derived CO of -15.3‰ (scenario S2, flux-weighted mean of the sum of the isoprene and terpenes sources is taken). Earlier, BR97 derive both, CH₄ and NMHC, sources close to ~0‰. Further distinguishing of these two sources’ signatures by surveying the composition of the end-product CO is difficult, because it stems from the common CH₃O₂ and HCHO intermediates. It is likely that the KIE of CH₃O₂ production from VOC/CH₃ oxidation should be close to that from the oxidation of methane; however, the KIEs escorting the O₂ incorporation into HCHO and higher oxygenated VOCs are not known. Recurring to the estimates of BR97, to conform our chosen methane KIEs the average non-methane KIEs should yield ~0‰ in the NMHCs oxidation products. In application to the MECCA mechanism, it is practicable to assign a uniform KIE to the reactions of initial NMHC oxidation. Therefore, the KIEs in reactions of alkanes, alkenes, MVK and isoprene with OH are set to the value of ¹⁸Oη ≈ 24‰, so that the oxygenated VOCs acquire the composition close to 0‰ in δ¹⁸O.

Analogously to the stable carbon KIE values for formaldehyde and methanol, the listed values for stable oxygen KIEs in reactions of these species from Feilberg *et al.*^[2005a], Feilberg *et al.*^[2008] and Feilberg *et al.*^[2004] are not included in the reference setup, but tabled for comparison. As described above (see Sect. 3.4.1.2), the sensitivity simulations including uncertain ¹³C KIEs with the tropospheric box-model predict rather unrealistic ¹³C enrichments in HCHO. Similarly, corresponding formaldehyde ¹⁸O KIEs were tested in the box-model setup. The simulated δ¹⁸O(HCHO) values show a large variation within a ~40‰ range, reflecting a strong sensitivity to the change of the chemical regimes, particularly the switching between the dominant removal pathways escorted with KIEs of the opposite directions (*cf.* OH and photolysis KIEs from Table 3.4). Overall, inclusion of all formaldehyde KIEs results in a stark enrichment of HCHO in ¹⁸O that, in turn, leads to depletions larger than 10‰ in subsequently produced CO even at a moderate HCHO deposition from the box (the deposition velocity was set to *v_d* = 0.5 cm⁻¹ at a scale height *z_b* of 1000 m, see details in Sect. 3.5.1, p. 55). Unfortunately, no estimates or observations of atmospheric δ¹⁸O(HCHO) are available for a comparison with this result to conclude unambiguously if these effects should be incorporated in the mechanism. Inclusion of the

CH₃OH+OH KIE results in similar but moderate $\delta^{18}\text{O}(\text{CO})$ depletions of 1–2‰. Additional measurements of these KIEs (preferably with an alternative experimental setup or technique) could reduce the uncertainty about these important kinetic isotope effects.

In the remaining KIE data, the ozone formation and CO oxidation kinetic isotope effects are of great importance, presenting a clear a mass-independent behaviour producing positive $\Delta^{17}\text{O}$ values in O₃ and CO. Except for these two KIEs, the rest of the effects in the setup are of mass-dependent origin, so that $\Delta^{17}\text{O}\eta \approx 0$. A small deviation from the strict zero value for different reactions arises from the slight differences in the slopes of the mass-dependent lines for different species and reactions, while the value of $\Delta^{17}\text{O}\eta$ is calculated using the universal β of 0.528 (Sect. 3.2). The kinetic isotope effect in the isotope exchange between O₂ and O(³P) is adopted from the study of Johnston *et al.*^[2000], leading to a depletion of the O(¹D) in heavy isotopologues.

A moderate KIE for the ozone photolysis reactions was added to the box-model setup to bring the simulated O₃ isotopic composition to the desired tropospheric $\delta^{18}\text{O}(\text{O}_3)$ and $\delta^{17}\text{O}(\text{O}_3)$ values ($\Delta^{17}\text{O}(\text{O}_3)$ is not affected). It is important to note, however, that the isotope effects in O₃ photolytic decomposition are not well quantified yet. Morton *et al.*^[1990] report no significant (within $\pm 6\%$) fractionation in their experiments with visible light (absorption in Chappuis bands). The UV photolysis of O₃ is found to induce positive ¹⁸O fractionations on the order of $\sim +20\%$ (Bhattacharya and Thiemens^[1988], Wen and Thiemens^[1991], Tuzson^[2005]), although the attained experimental results are difficult to interpret in view of the unknown role of the secondary kinetics of the reaction products in various experimental setups (see more in Brenninkmeijer *et al.*^[2003], Cole and Boering^[2006]). The investigation employing two alternative laboratory techniques by Tuzson^[2005] as well puts an upper limit of $+20\%$ on the ¹⁸O fractionation magnitude in ozone decomposition in experiments of photolytic dissociation in Chappuis bands. The KIEs for the photolysis reactions included in MECCA are to a certain extent in accordance with the abovementioned experimental data, producing O₃ enrichments of $+22\%$ in ¹⁸O. Notwithstanding, the O₃ photolysis KIE is believed to play the minor role in determining the isotopic composition of ozone compared to its formation reaction; the latter is escorted with fractionations of much larger magnitudes.

Table 3.4 Oxygen kinetic isotope effects

Reactions ^a		KIE ^b					Reference
		¹⁸ O α	¹⁸ O η (‰)	¹⁷ O α	¹⁷ O η (‰)	Δ^{17} O η (‰)	
G4100 ^{c, d}	CH ₄ + O(¹ D) $\rightarrow$ 0.75 CH ₃ O ₂ + 0.75 OH + 0.25 HCHO	0.972	+28.8	0.985	+15.2	+0.12	Zahn <i>et al.</i> ^[2006] , Weston ^[2001] , Brenninkmeijer and Röckmann ^[1997]
G4101 ^{c, d}	CH ₄ + OH $\rightarrow$ CH ₃ O ₂ + H ₂ O	0.973	+27.7	0.986	+14.2	−0.36	
– ^{c, d, e}	NMHC + OH $\rightarrow$ OVOCs + H ₂ O	0.9765	+24.1	0.9876	+12.6	−0.07	
G4102	CH ₃ OH + OH $\rightarrow$ HCHO	0.9833±0.012	+17.0±12.4	0.9911±0.0063	+9.0±6.4	+0.02±9.05	Feilberg <i>et al.</i> ^[2008] ^{f, g}
G4108	HCHO + OH $\rightarrow$ CO + H ₂ O + HO ₂	1.0246±0.006	−24.0±5.7	1.0129±0.0032	−12.8±3.1	−0.03±4.43	Feilberg <i>et al.</i> ^[2004] ^{f, g}
G4109	HCHO + NO ₃ $\rightarrow$ HNO ₃ + CO + HO ₂	1.0204±0.010	−20.0±9.6	1.0108±0.0053	−10.6±5.2	−0.03±7.4	
G6401	HCHO + Cl $\rightarrow$ CO + HO ₂	0.9259±0.010	+80.0±11.7	0.9601±0.0051	+41.6±5.5	+0.1±7.8	
G7400	HCHO + Br $\rightarrow$ CO + HO ₂	0.7843±0.008	+275.0±13.0	0.8793±0.0038	+137.3±4.9	+0.32±6.89	
J4101a,b	HCHO + <i>h</i> ν $\rightarrow$ CO + HO ₂	0.9110±0.0133	+97.7±16.0	0.9519±0.0067	+50.6±7.4	+0.12±10.43	Feilberg <i>et al.</i> ^[2005a] ^{f, g}
G4110 ^{h, i}	CO + OH $\rightarrow$ CO ₂		−9.29±1.52		−0.21±1.30	+4.59±1.54	Röckmann <i>et al.</i> ^[1998b] Stevens <i>et al.</i> ^[1980]
G1001 ^{i, j}	O ₂ + O(³ P) $\rightarrow$ O ₃	1.0775±0.0043	−72.0±3.7	1.0938±0.0029	−85.8±2.4	−49.0±3.6	Morton <i>et al.</i> ^[1990] , Guenther <i>et al.</i> ^[1999] , Janssen <i>et al.</i> ^[2003] , Brenninkmeijer et al. ^[2003]
J1001a,b ^{d, k}	O ₃ + <i>h</i> ν $\rightarrow$ O(¹ D) and O(³ P)	0.978	+22.5	0.986	+14.2	+2.35	– ^{d, k}
IEXO05 ^d	O(³ P) $\rightleftharpoons$ O ₂	0.9235	+82.8	0.9611	+40.5	−2.35	Johnston <i>et al.</i> ^[2000]

^{a)} MECCA reaction number, reactants and only the oxygen-bearing products are listed.

^{b)} α and η denote the fractionation factor and enrichment (depletion) in ¹⁸O, ¹⁷O and Δ^{17} O the reacting species acquires due to the KIE (see Sect. 3.2).

^{c)} O₂ is omitted among the reactants; produced RO₂ radicals acquire the composition of the air O₂ altered by the KIE, yielding δ^{18} O ≈ 0‰ and δ^{17} O ≈ 0‰ or less.

^{d)} Calculated or assumed value (no measurements/uncertainties are available).

^{e)} KIE applied to the NMHC oxidation initiating reactions with OH: G4200, G4202, G4222, G4300, G4302, G4400, G4406, G4413, G4501.

^{f)} Values from this study appear to be unreliably quantified; excluded from the reference setup (see text).

^{g)} Assumed mass-dependent KIE for ¹⁷O (no measurements available, MDF-composition β = 0.5294, see Sect. 3.2).

^{h)} Values from the conventional, pressure-dependent approximation at 10⁵ Pa (see Sect. 3.4.4).

ⁱ⁾ Pressure- and/or temperature-dependent KIE, given are the approximate values at 298K, 10⁵ Pa.

^{j)} The uncertainties are given for the temperature and pressure fit (see Sect. 3.4.3).

^{k)} Included in the tropospheric box-model setup; together with G1001 and IEXO05, the kinetic isotope effects yield δ^{18} O(O₃) ≈ +90.0‰ and δ^{17} O(O₃) ≈ +78.0‰, respectively.

3.4.3 Ozone formation

The uncommon isotope composition of ozone is the most extensively studied phenomenon in oxygen isotope studies of the atmosphere. The processes that ozone's isotopic composition are its formation, photolytic destruction and catalytic cycling of the related oxygen species. The formation reaction is a three-body recombination reaction proceeding with the energy-transfer mechanism of the following steps:



where $(\text{O}_3)^\dagger$ denotes a vibrationally excited intermediate that forms stable ozone if quenched by an inert molecule M, or dissociates back to the educts. Under atmospheric conditions, when the pressure is relatively low, the first association/dissociation step of (3.11) in essence constitutes the isotope exchange mechanism between O_2 and $\text{O}(^3\text{P})$ described above²⁸. The photolysis of produced O_3 , in turn, leads ultimately to the formation of $\text{O}(^3\text{P})$ atoms, as $\text{O}(^1\text{D})$ produced in the alternative photolysis channel is expected to be quenched rapidly by O_2/N_2 to the same ground-state $\text{O}(^3\text{P})$. The latter may *de novo* participate in ozone formation, thus becoming a catalyst. A fast cycling this way leads to equilibration of the compositions of O_3 and $\text{O}(^3\text{P})$ up to the magnitude of the photolysis KIE. On the other hand, this kinetic effect is largely damped by the rapid oxygen exchange of $\text{O}(^3\text{P})$ with the virtually infinite O_2 reservoir. Thus, the KIEs in the formation reaction (3.11) become the dominant effects determining the O_3 isotopic composition. The other ozone-related reactions, namely oxygen cycling in the HO_x and NO_x groups and the sink reaction with atomic oxygen, can be singled out as well, as they proceed with at least 1–2 orders of magnitude slower rates (Brenninkmeijer *et al.*^[2003]).

The kinetic effects in the O_3 formation reaction have been extensively studied; however, no fully concordant model accounting for the unconventional fractionations (see below) in (3.11) exists to date. The outlines of the experimental discoveries on kinetic isotope effects in O_3 formation are:

- The bulk composition of produced ozone is nearly equally enriched in both, ^{17}O and ^{18}O with respect to the educts' composition, thus not following the mass-dependent enrichment ratio of ~1:2. The magnitude of isotope fractionation (including the mass-independent $\Delta^{17}\text{O}$ signal, or MIF) decreases with lowering temperature and increasing pressure of the bath gas (Heidenreich III and Thiemens^[1983], Heidenreich III and Thiemens^[1986], Morton *et al.*^[1990], Thiemens and Jackson^[1990]).
- For selected isotopic substitutions of the reactants, a very large difference in rate coefficients is observed (within 0.90 to 1.53 times relative to the major isotopologues channel), selectively exhibiting temperature or pressure dependence (Anderson *et al.*^[1997], Mauersberger *et al.*^[1999], Guenther *et al.*^[1999], Janssen *et al.*^[2003]).²⁹
- Consequently, different formation rates result in the specific intra-molecular distribution of the isotopomers in ozone (Janssen^[2005], Bhattacharya *et al.*^[2008], Savarino *et al.*^[2008]). In particular, asymmetric isotopomers become more abundant than symmetric ones in heavy O_3 , which also affects the isotopic ratio of the terminal ozone oxygen atoms.^{22,30}

Continuous attempts to qualitatively explain these effects lead to new experiments posing new questions and sieving out some of the proposed theories. For brevity, the reader is referred to the literature (Weston^[1999], Brenninkmeijer *et al.*^[2003], Thiemens^[2006], Schinke *et al.*^[2006]) for a consistent review of these. Generally, current findings are in line with those given earlier by Janssen *et al.*^[2001]. They link, in particular, the relative change in the overall ozone formation rate with the difference in zero-point energies of the O_2 isotopologues dissociating via two possible channels in the backward isotope exchange step. For instance, the dissociation rate of $(\text{QOO})^\dagger$ differs for the heteronuclear (QO) and homonuclear (OO or QQ) isotopologues³¹ pro-

²⁸ Reaction IEXO05, see Table 3.1 (p. 38).

²⁹ For instance, in the channels leading to non-symmetric (*i.e.* OOQ)³¹ products, slower rates of $\text{Q}+\text{OO}$ pairs reactions exhibit a pronounced temperature dependence, although no significant variation with pressure changes is observed. Concomitantly, the faster rates of reacting $\text{O}+\text{QO}$ pairs are pressure-dependent, but do not vary significantly with temperature. Similarly, the rates of reactions $\text{Q}+\text{QO} \rightarrow \text{QQO}$ are pressure dependent. No variation with temperature or pressure changes is expected in the channels leading to the production of symmetric O_3 isotopologues, however (Shaheen^[2005]).

³⁰ The measured (a)symmetric isotopomer abundance ratios ($r^\mu = [\text{QOO}]/[\text{OOQ}]$) increase from 1.92 to 2.15 as the enrichment of the bulk composition of the formed O_3 increases. Such a deviation from $r^\mu = 2$, which one would expect assuming the statistical isotope distribution in ozone, is reciprocal to the measured enrichment/depletion in the asymmetric/symmetric species with respect to the bulk composition.

³¹ Q denotes the heavy oxygen isotope substitution, *i.e.* ^{17}O or ^{18}O .

duced, changing the lifetime of the $(\text{O}_3)^\ddagger$ intermediate and hence its probability to become stabilised. In addition, symmetry-selective processes are present; for example, the dissociation channels corresponding to the ejection of the central positioned oxygen atom (*i.e.* $(\text{OQO})^\ddagger \rightarrow \text{OO} + \text{Q}$) appear to be inhibited. Overall, the superposition of these kinetic processes already adds the fractionations independent of the mass of the produced O_3 molecule, favouring the production of the anomalously enriched O_3 . Notwithstanding, the theoretical analysis of the complete recombination mechanism still leaves several essential questions to be solved in detail (see Schinke *et al.*^[2006] for a review).

The implementation of the abovementioned kinetics cannot be easily realised in MECCA, first of all because the approximations introduced for the isotope tagging approach restrict multiply substituted isotopologues and isotopomeric differences of the simulated species. In fact, for an accurate parameterisation of the kinetics in (3.11), the regular oxygen kinetic scheme of MECCA has to be sufficiently detailed. An alternative approximation of the O_3 formation KIE effects is possible, however, regarding exclusively the most abundant species of the heavy ozone (in a standard way in the current isotopic tagging). These are the singly ^{17}O - and ^{18}O -substituted isotopologues of masses 49 and 50, respectively, representing the aggregates of symmetric and asymmetric isotopomers of $^{49}\text{O}_3$ and $^{50}\text{O}_3$. The bulk compositions of the latter can be used to derive the compositions of (a)symmetric species, as well as the terminal oxygen atoms (see Bhattacharya *et al.*^[2008]). For typical enrichments of 120‰ in ozone, neglecting the multiply substituted isotopologues introduces offsets less than 5‰ and 1‰ in simulated $\delta^{18}\text{O}(\text{O}_3)$ and $\delta^{17}\text{O}(\text{O}_3)$, respectively³².

The formation reaction KIE enrichments for $^{49}\text{O}_3$ and $^{50}\text{O}_3$ isotopologues can be derived from the semi-empiric model approximations of the obtained data on pressure and temperature dependence of selected O_3 isotopologue enrichments. The final product enrichment for the i^{th} ozone isotopologue is formulated as

$$i\eta(p, T) = \left(1 + \frac{p}{i p_{1/2}}\right)^{-1} i\eta_0 \left(i b + i s_1 (T - T_0) + i s_2 \left(\frac{T_0}{T} - 1 \right) \right) . \quad (3.12)$$

The first term in Eq. (3.12) describes the drop in the fractionation magnitude (contribution from $\text{O} + \text{OO} \rightarrow \text{OOO}$ channels) throughout the transition from the low-pressure to the high-pressure regime. The value of $p_{1/2}$ corresponds to the pressure at which the overall enrichment drops by the half of its low-pressure limit η_0 . The second term defines the temperature dependence of the latter, respectively, referenced at the given temperature T_0 . The sub-terms next to s_1 and s_2 represent contributions of the $\text{Q} + \text{OO} \rightarrow$ channels (*cf.* model rates from Janssen^[2005]). Parameter values (b, s_1, s_2) derived for $^{49}\text{O}_3$ and $^{50}\text{O}_3$ enrichment fits are listed in Table 3.5. For $^{49}\text{O}_3$, missing literature values are obtained by fitting (3.12) to the laboratory data. The reaction rates for $^{49}\text{O}_3$ and $^{50}\text{O}_3$ are derived from the calculated enrichments.

Table 3.5 Ozone formation KIE parameters

Isotopologue	Parameter values ^{a,b}					Reference
	$p_{1/2}$ (10^5 Pa)	η_0 (‰)	b	s_1	s_2	
$^{50}\text{O}_3$	2.02 ± 0.29	113.7 ± 6.0	0.9176	$3.7 \cdot 10^{-3}$	-0.105	Guenther <i>et al.</i> ^[1999] , Janssen ^[2005]
$^{49}\text{O}_3$	2.60 ± 0.32	98.6 ± 6.0	0.9244	$2.8 \cdot 10^{-3}$	-0.118	

^{a)} The original (referenced) values are adapted to bulk enrichments of the $^{50}\text{O}_3$ and $^{49}\text{O}_3$ isotopologues.

^{b)} Parameters s_1 and s_2 refer to $T_0 = 300\text{K}$.

³² Thus, simulated $\delta^{18}\text{O}(\text{O}_3)$ and $\delta^{17}\text{O}(\text{O}_3)$ appear to be slightly depleted (jointly with $\Delta^{17}\text{O}(\text{O}_3)$ enriched) with respect to the “true” bulk compositions accounting for multiply substituted isotopologues. The given offsets are calculated from the enrichments and standard isotope ratios (Sect. 3.2), assuming a statistical distribution of the isotopomers in O_3 .

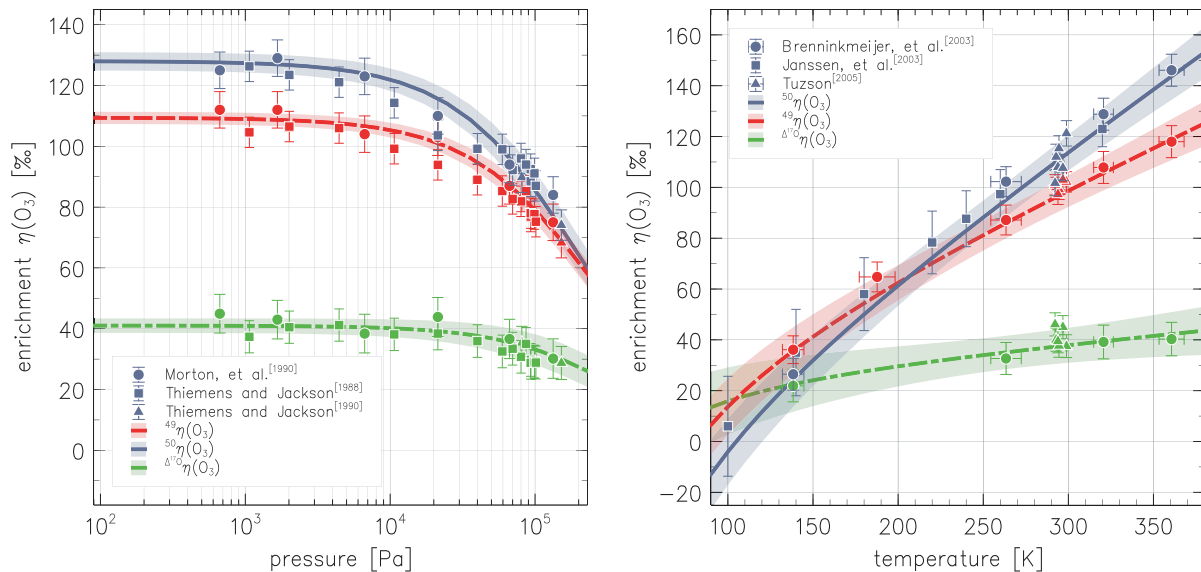
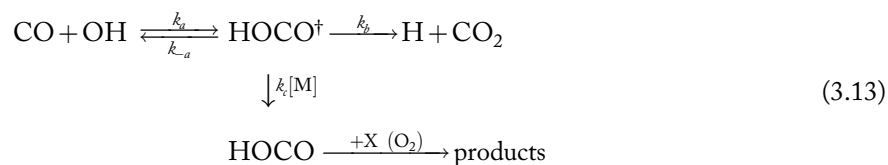


Figure 3.4 Pressure (left) and temperature (right) dependence of the ozone formation KIE at 321K temperature and 50 Torr (approx. 6600 Pa) pressure, respectively. Solid, dashed and dash-dotted lines denote the fits calculated within this study (see text), shaded areas signify the regression uncertainties. Symbols denote the laboratory data.

The resulting fractionation values are depicted in Figure 3.4. As it is seen, the enrichments are pressure-insensitive below values of 10^3 Pa, becoming dominantly determined by temperature. At the surface pressure (10^5 Pa), fractionations reduce to $\sim 60\%$ of the low-pressure limit. The equivalent anomalous enrichment $\Delta^{17}\text{O}\eta(\text{O}_3)$ shows a much smaller variation of 33‰ to 41‰ within the atmospheric pressure range, with a virtually constant value below 10^4 Pa. Much larger changes in the enrichments of produced O_3 are expected, owing to the strong temperature dependence, which increases below 200K. Above this value, enrichments increase nearly linearly with approx. 5‰ and 4‰ per each 10K for $^{50}\eta(\text{O}_3)$ and $^{49}\eta(\text{O}_3)$, respectively. For $\Delta^{17}\text{O}\eta(\text{O}_3)$, the variation within the 200–300K range is $\sim 10\text{‰}$, similar to that for the atmospheric pressure range. The expected $\Delta^{17}\text{O}(\text{O}_3)$ values of the ozone produced in the atmosphere are thus within mere 29–36‰, when calculated for the temperatures of the Standard Atmosphere profile (see Figure 3.7, p. 54). The actual variation of the isotopic composition of O_3 in the atmosphere with height is expected to be larger due to the temperature variations. Noteworthy, the uncertainties indicated in Figure 3.4 refer solely to the respective pressure or temperature terms in Eq. (3.12) for comparison; the overall uncertainties are listed in Table 3.4.

3.4.4 CO oxidation

Kinetic isotope effects escorting the OH oxidation of carbon monoxide play the main role in determining its isotopic composition, as this reaction constitutes the principal sink for CO in the atmosphere. Owing to its complex kinetics, it has been subject to extensive laboratory (*e.g.* Smith and Zellner^[1973], Ravishankara *et al.*^[1983], Paraskevopoulos and Irwin^[1984], Weston^[1988], McCabe *et al.*^[2001]) and theoretical studies (*e.g.* Mozurkewich *et al.*^[1984], Fulle *et al.*^[1996], Zhu *et al.*^[2001], Joshi and Wang^[2006], Chen and Marcus^[2006]). Specifically, the observed pressure dependence and non-Arrhenius behaviour (exhibiting a non-standard temperature dependence) of the overall rate coefficient, attribute this reaction to the collision complex-forming bimolecular kind (Troe^[1994]). The established kinetic mechanism is characterised by the formation of the excited intermediate $\text{HOCO}^\dagger$ complex (step *a*) with its subsequent dissociation to H and CO_2 (step *b*) or quenching (step *c*) by collision with a third body (Smith and Zellner^[1973], Smith^[1977]):



Produced in step *c*, stabilised HOCO reacts to further products. The $\text{HOCO}^\dagger$ intermediate may dissociate back to the educts (step *-a*), if the rate of its collisional stabilisation is low, *i.e.* at low pressures. In the presence of molecular oxygen, both channels lead to the production of HO_2 , thus $\text{CO} + \text{OH}$ establishes an important process

of OH to HO₂ conversion in the atmosphere (McCabe *et al.*^[2001]). The overall reaction rate of (3.13) exhibits a distinct dependence on pressure and bath gas composition, resulting from the competition of the pressure-dependent (via step *c*) and pressure-independent (via step *b*) exit channels. Their rate coefficients become comparable at around 1200 hPa in air (see Figure 3.6, left on p. 53), which is of particular interest considering the atmospheric pressure ranges. Notwithstanding, below 500 K the reaction rate is weakly sensitive to the temperature changes at pressures below 100 hPa, showing even a slight inverse *T*-dependence above this value.

In addition to the peculiar temperature and pressure dependence of the rate constant, the kinetic isotope effects escorting CO oxidation by OH are unconventional. Laboratory measurements of the ¹³C/¹⁸O KIE were performed at early stage by Stevens *et al.*^[1980] within the range of pressures from 100 to 1100 hPa. Both, carbon and oxygen KIE magnitudes, display a clear dependence on the bath gas composition and pressure. A generally inverse KIE for C¹⁸O exhibits a weak dependence on pressure, in contrast to the ¹³C effect. The latter is found to change from negative to positive values with a turning point at around 300 hPa in N₂ (see Figure 3.5, left on p. 53), clearly suggesting the superposition of at least two, inverse and normal, partial KIEs. Subsequently, Smit *et al.*^[1982] obtained similar results in their study of the ¹³C KIE in CO+OH.

Extending the information on the kinetic effect for the C¹⁷O isotopologue, Röckmann *et al.*^[1998b] discovered the oxygen mass-independent fractionation in CO+OH. Yet denoted as MIF, the effect for C¹⁷O has a different character from that for ozone³³: if the latter becomes almost equally enriched in both heavy isotopologues, CO+OH exclusively favours C¹⁸O reactivity, leaving C¹⁶O and C¹⁷O to react with nearly equal rates at atmospheric pressure. Unlike for ¹⁸O and similar to the ¹³C KIE, the effect for ¹⁷O changes its direction from inverse to normal as the pressure increases, with the turning point at around 1000 hPa (extrapolating measurement data in N₂). The magnitude of the anomalous deviation (*i.e.* Δ¹⁷O(CO)) raises with pressure too, thus denoting that MIF appears in both exit channels. Importantly, Röckmann^[1998] remarks that the oxygen isotopes enrichment retains its mass-independent fashion even in the low-pressure range, although suppressed. The elementary steady-state rate constant analysis identifies at least step *c* being unequivocally responsible for the mass-independent enrichment. At present, the underlying reasons for the MIF in CO+OH remain unknown, owing to the complexity of the reaction mechanism. Perhaps, analogous to the case of the O₃ formation KIE, peculiar symmetry or spin selection rules or zero-point energy differences inhibit the reactivity of a particular isotopologue along the specific channel.³⁴ To date, no further examination of the oxygen isotopes MIF in CO+OH after Röckmann^[1998] is accomplished, thus prospecting for its causes is calling for further studies.

The results of Röckmann *et al.*^[1998b] for the ¹³C and ¹⁸O KIEs confirm earlier findings of Stevens *et al.*^[1980]; however, an alternative FTIR-technique determination of the CO+OH KIEs at atmospheric pressure by Feilberg *et al.*^[2005b] (a re-analysis of the earlier results from Feilberg *et al.*^[2002]) is not consistent with both earlier studies. While the derived fractionation for C¹⁷O is of similar magnitude (~0‰), the KIEs for the other rare isotopologues were found to be larger (11‰ vs. ~7‰ for ¹³C and -15‰ vs. -9‰ for ¹⁸O, respectively). The discrepancies may be attributed to the imperfections in the experimental setup. For instance, ozone was used as the precursor of OH radicals, which complicates the overall chemical scheme of the experiment compared to that of Stevens *et al.*^[1980] and Röckmann *et al.*^[1998b]. The faulty equipment also restricted the authors to use rare isotopologue data only (¹²C¹⁶O measurements were discarded), thus the final fractionation factors (with respect to the abundant isotopologue) were deduced using the KIE data from Röckmann *et al.*^[1998b], yet obtained with a different technique.

Despite the large number of theoretical studies on CO+OH kinetics, only few of them consider isotope effects, regarding the primary effect³⁵ of D/H isotope substitutions in OH. Only Chen and Marcus^[2005] appear to have studied the ¹³CO KIE in a framework of the Rice-Ramsperger-Kassel-Marcus (RRKM) unimolecular theory and several *ab initio* methods. Their calculations included tunnelling effects and non-statistical modification of the theory. The latter impacts the rate of the energy redistribution between the intramolecular states of the HOCO⁺ intermediate, lowering it with respect to that derived conventionally assuming statistical microcan-

³³ See previous section (p. 45).

³⁴ For example, theoretical studies consider the HOCO⁺ intermediate to have two, *cis*- and *trans*-HOCO, isomers that have various dissociation channels open to one isomer but not the other (Yu *et al.*^[2001], McLean and Ellinger^[1985]). In case the isomers are subject to the interconversion (as, for instance, assumed by Joshi and Wang^[2006]), the presence of complementary equilibrium and kinetic isotope effects should be expected.

³⁵ Primary and secondary kinetic isotope effects are attributed to the isotope substitution of an atom adjacent and remote to the bond being formed or cleaved in the reaction, correspondingly (McNaught and Wilkinson^[1997]).

onical behaviour of the system. The non-statistical model was shown to improve the rate constant in the low-pressure region, due to the sensitivity of the forward and backward $\text{HOCO}^\ddagger$ dissociation rates (steps b and $-a$, respectively) to the modification. The specific competition of these rates (step b is distinctively accompanied by tunnelling effects) is attributed to the anomalous negative T -dependence of the overall $\text{CO}+\text{OH}$ reaction rate. The reproduction of the kinetic isotope effects also improves in the non-statistical approach, particularly for D/H substitution. The authors remark the relatively large negative temperature dependence of the D/H KIE in the low pressure and temperature regimes. Regrettably, the sensitivity of the ^{13}C effect to the temperature was not investigated, perhaps assumed being small compared to that for D/H.

Chen and Marcus^[2005] conclude a reasonable agreement of the simulated ^{13}C KIE with the experimental data; models reproduce the pressure dependence and the switch in the KIE direction at ~ 300 hPa. The present theory explains the *inverse* low-pressure kinetic effect as a result of the higher density of the rovibrational states for heavier isotopologues. That is, ^{13}C -substitutes react faster in both steps a and b , owing to changes in zero-point energy (ZPE) of the reacting complexes upon the isotope substitution. The calculated low-pressure KIE value amounted to -4% at 298K. Considering step c , its calculated rate is merely proportional to the collisional frequency of the intermediate stabilisation. The fractionation this way is proportional to $\mu^{-1/2}$, where μ is the reduced mass of $\text{HOCO}^\ddagger$ and the bath gas molecule. In light diluents (*e.g.*, He, N_2 or air), $\text{HO}^{13}\text{CO}^\ddagger$ substitution establishes a *positive* fractionation, denoting that quenching proceeds slower for the ^{12}C intermediate. The simulated stabilisation step in N_2 introduces a ^{13}CO enrichment of around $+7\%$. This value, however, leads to an apparent underestimation of the overall sensitivity to changing pressure: the calculated $^{13}\text{C}\eta$ increase of $\sim 0.6\%$ per 100 hPa accounts only for a half of the observed 1.1% . Statistical and non-statistical modifications can satisfactorily reproduce the fractionation in either low- or intermediate (1 atm.) pressure ranges, respectively, with a difference of 2–4% between these approaches. The results of *ab initio* methods are similar to those obtained with the RRKM theory, showing larger variations but a comparable or lower KIE pressure dependence.

Noteworthy, none of the models were able to reproduce the abrupt KIE response to bath gas changes (from N_2 to He) in the low-pressure range. With a vanishing rate of stabilisation one would expect both, N_2 and He, KIEs to converge asymptotically to the equal low-pressure value, alike the abovementioned theoretical calculations predict. However, according to experimental data, quenching in various bath gases induces various subsidiary fractionations that appear to be p -invariable, *i.e.* adding on top of the common pressure-driven changes. This feature can be tracked down to 200 hPa for any CO isotope substitution (*cf.* data from Röckmann *et al.*^[1998b]³⁶): the KIE variation in N_2/He looks similar with a bias of 3–4% for ^{13}CO or C^{17}O and slightly larger ($\sim 6\%$) for C^{18}O . From the theoretical results on ^{13}C one may suggest that either the fractionation associated with quenching should be larger, or the calculated partitioning between the elementary rates in (3.13) is erroneous, disfavours the rate of step c . With the latter being less likely (a number of theoretical studies to date predict the overall rate pressure dependence well, see references above), the kinetic isotope effect associated with stabilisation of $\text{HOCO}^\ddagger$ appears to be more intricate than interpreted by means of the collisional frequency changes. Similar normal pressure dependencies of the ^{13}CO and C^{17}O KIEs, in contrast to the inverse effect for C^{18}O , point to the partial mass-selective character of this KIE.³⁷ Scrutinising the pressure peculiarities is the one of the primary objectives for future experimental and theoretical studies on $\text{CO}+\text{OH}$ kinetic isotope effects. This concerns also secondary oxygen KIEs³⁵, which appear to be more complex and are not investigated within the theoretical framework yet.

A conventional and a revised parameterisation of the $\text{CO}+\text{OH}$ KIE are considered within the current study. The former comprises a second-order regression of the observed KIE data with respect to the pressure only. The resulting coefficients are listed in Table 3.6 (p. 52) and are similar to those derived for ^{13}C and ^{18}O KIE in other modelling studies on isotopic CO (Bergamaschi *et al.*^[2000], Manning *et al.*^[1997]). Noteworthy, for the regression here, exclusively the data of Röckmann *et al.*^[1998b] are selected. The coefficient η_0 reports the low-pressure limit enrichment, while η_1 and η_2 essentially represent the pressure dependence of the effect, being proportional. The latter term (η_2) corrects for the increasing non-linear dependence outside the 400–800 hPa range, deflecting the linearity defined by η_1 . The largest p -dependence is attributed to the ^{13}CO KIE, whilst for the

³⁶ Quoted here values of $^{17}\text{O}\eta$ in logarithm-based formulation (see Sect. 3.2, Eq. (3.7)) are recalculated from the reported $E^{17}\text{O}$ and $^{18}\text{O}\eta$ enrichments and the definition $E^{17}\text{O} = {}^{17}\text{O}\eta - 0.52 \times {}^{18}\text{O}\eta$.

³⁷ Apart from the mass, the ^{13}C and ^{17}O isotopes have a nuclear magnetic moment, as opposed to ^{12}C , ^{16}O and ^{18}O . Whereas the nuclear spin selectivity is confirmed to cause mass-independent effects in radical reactions (see Buchachenko^[2013] for a review), an inference of the possible magnetic isotope effects in reaction of CO with OH is yet to be sought.

oxygen KIEs this term is a factor of ~ 3 smaller. Notably, the low-pressure enrichment η_0 is negative for all isotopologues and potentially reflects the effect of ZPE changes on the dissociation rate, as theoretical results suggest (see above). The resulting enrichments for all isotopologues (including the anomalous enrichment $^{17}\text{O}\eta$) are depicted in Figure 3.5 (left panel).

The alteration of the CO+OH KIE magnitude with pressure may be principally attributed to two key factors: (1) the overall fractionation depends on the competition between alternative exit channels, and (2) the end-fractionation values of the transition from low- to high-pressure regimes are different for every isotopologue and exceptionally not mass-dependent. The factor (1) is the basis of the revised *composite* KIE parameterisation proposed here. The factor (2) determines the regression parameters. As the estimates of the alternative channel rates become available, one can approximate the overall KIE with the partial KIEs associated with the reaction elementary steps. Not every study, however, provides adequate data on the CO+OH kinetics. For instance, the parameterisation proposed in Sander *et al.*^[2006] is suited for the wide range of pressures, but fails to reproduce the temperature dependence of the channels' rate coefficients. Here, the results achieved by Troe^[1998], a further improvement of the comprehensive study by Fulle *et al.*^[1996], are implemented. Despite that a more recent analogous inquiry was conducted by Joshi and Wang^[2006], the former approach appears to provide more accurate results. The proposed parameterisation uses a large body of experimental data to approximate the rate coefficients over a wide range of pressure and temperature conditions with help of the unimolecular theory analysis and potential energy surface calculations, similar to the study by Chen and Marcus^[2005] described above. In particular, the model allows the calculation of the contribution of each exit channel to the overall reaction rate, and adequately represents the T -, p - and bath gas-dependence of the latter. For the sake of clarity, a brief description of Troe's parameterisation is given next.

The overall CO+OH reaction rate coefficient $k(T, p)$ is constrained by the T -dependent low- and high-pressure limits $k_0(T)$ and $k_\infty(T)$, respectively. Their values are (in $[\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}]$):

$$\begin{aligned} k_0(T) &= 1.661 \times 10^{-11} \exp(-8050\text{K}/T) + 1.494 \times 10^{-12} \exp(-2300\text{K}/T) + \\ &\quad 1.677 \times 10^{-13} \exp(-30\text{K}/T) \\ k_\infty(T) &= 2.042 \times 10^{-9} \exp(-7520\text{K}/T) + 1.827 \times 10^{-11} \exp(-1850\text{K}/T) + \\ &\quad 1.328 \times 10^{-12} \exp(-120\text{K}/T) \end{aligned}$$

Each of the three Arrhenius-terms above describes the evolution of k_0 and k_∞ in high, medium and low-temperature regimes, respectively. The first two terms are only relevant at high temperatures (*e.g.* combustion studies), being negligibly small within the atmospheric temperature ranges (up to 320K), with an exception of the second term in k_∞ , which is approximately 20 times smaller than k_∞ itself and decreases steeply with decreasing temperatures. The pressure-driven transition between k_0 and k_∞ is described in the form of the fall-off expression including the individual rates of the dissociation channel k_{ab} and stabilisation channel k_{ac} :

$$\begin{cases} k(T, p) = k_{\text{ab}}(T) + k_{\text{ac}}(p, T) \\ k_{\text{ab}}(T) = k_0(T) \left(1 - \frac{x}{1+x} F(x) \right) \\ k_{\text{ac}}(p, T) = A(p, T) \cdot k_0(T) \left(\frac{1+x \cdot [A(p, T)]^{-1}}{1+x} \right) F(x) \end{cases} \quad (3.14)$$

$$x = A(p, T) \frac{k_0(T)}{k_\infty(T) - k_0(T)} ,$$

where $A(p, T)$ is the empirically derived factor accounting for the growth of the stabilisation rate with pressure and its drop with increasing temperature (assuming p in [bar]):

$$A(p, T) = A_0 p \exp(-T/T^*) . \quad (3.15)$$

The experimental data is well represented taking $T^* = 161\text{K}$ and $A_0 = 5.9 \text{ bar}^{-1}$ for N_2 . For the weaker quencher He, the estimated A_0 value is 3.7 bar^{-1} , 1.6 times smaller than that for N_2 . The broadening factor $F(x)$ is customarily introduced in complex combination-dissociation reactions for a more accurate representation of the collisional (de)activation processes and association-dissociation step rates (Baulch *et al.*^[2005]). Troe's $F(x)$ definition for CO+OH is

$$\begin{cases} F(x) = (F_c(T))^{[1+(\log x)^2]^{-1}} \\ F_c(T) = 0.49 + 0.51 \exp(-T/300\text{K}) \end{cases} . \quad (3.16)$$

Recapitulating, the *composite* reaction rate coefficient $k(T, p)$ defined by (3.14)–(3.16) accounts for the pressure and temperature dependence and bathing gas conditions. It is represented by the superposition of the individual components k_{ab} and k_{ac} matching the rates of the alternative exit channels. An example of the calculated composite rate (including both exit channel rates) is presented in Figure 3.6, conjointly with the regular rate calculated by MECCA within this study. To note, the latter is assumed to be exclusively pressure-dependent, as it is conventionally adopted in global atmospheric chemistry models.

Recalling the reaction scheme (3.13), one straightforwardly derives the expression for the substituted isotopologue rate k' as a linear combination

$$k'(T, p) = \alpha_a [\alpha_b k_{ab}(T) + \alpha_c k_{ac}(p, T)] \quad , \quad (3.17)$$

where α_a , α_b and α_c denote the fractionation factors associated with the corresponding elementary steps. Since step a is the “bottleneck” of the reaction (the forward and backward KIEs associated with it are identical for either exit channel), α_a is superimposed on the overall rate k' in (3.17). By relating the latter to the regular rate from (3.14), one receives the overall fractionation factor (or enrichment) that is the function of α_a , α_b and α_c , whereas the pressure and temperature dependence is intrinsically accounted for by the partitioning between k_{ab} and k_{ac} . The simplified formulation (3.17), however, relies on a few assumptions, *viz.*:

- The changes to the low- and high-pressure limit rates $k_0(T)$ and $k_\infty(T)$, and thus the broadening factor $F(x)$ are discarded upon the isotope substitution. Below 320K temperature, the magnitude of $k_0(T)$ is more than 5 times smaller than that of $k_\infty(T)$, hence the changes in x are virtually proportional to the variations in $k_0(T)$. This way the partitioning between k_{ab} and k_{ac} is altered roughly proportional to the magnitude of the KIE associated with the reaction step a (*i.e.*, at maximum 10‰), which is a minor effect.
- For simplicity, isotope substitution has no effect on A_0 , T^* and hence $A(p, T)$. The results of Chen and Marcus^[2005] on OD/OH substitution indicate that the properties of the stabilisation step depend not only on the bath gas, but also on the HOCO isotopologue. This implies changes to A_0 that for OD/OH were assessed as being small, however. For CO carbon and oxygen substitutions no estimates are available, thus A_0 or T^* are kept unaltered.
- The kinetic isotope effects in the elementary reaction steps are assumed to be invariable, *i.e.* the changes in the overall KIE are driven only by the competition between the separate exit channels. Thus, a possible pressure-related variation of the KIE associated with the stabilisation channel, as well as the T -dependence of the association/dissociation channels KIE are disregarded. The latter, if present, are expected to be small, owing to the small temperate KIE values and a small variation of $k_0(T)$ and $k_\infty(T)$: with a 100K temperature decrease their values drop by 5% and 20%, respectively. Besides, low temperatures in the atmosphere are usually accompanied by low pressures, at which the less variable $k_0(T)$ dominates the overall rate coefficient.

The composite KIE approximation based on Troe’s rate parameterisation is calculated using the same experimental data as for the conventional approach (Röckmann *et al.*^[1998b]). We note that the individual fractionation in the reaction entrance step a can not be unequivocally determined from the current rate model and available experimental data, unlike the superposed fractionations in the channels proceeding via steps a, b and a, c . Thus, for consistency, the regression was performed assuming $\eta_a = 0$ ‰, since the calculation yields virtually the same result, insofar as the pair sums $(\eta_a + \eta_b)$ and $(\eta_a + \eta_c)$ retain their values. This was ascertained by varying η_a within a ± 15 ‰ range, which is above the upper limit of the current estimates. Beyond this extent, the regression procedure commonly does not lead to convergence.

Table 3.6 reports the composite enrichments, which resemble those derived within the conventional approach. In contrast to the latter, the values display an apparent magnitude and direction of the KIEs in each exit channel. The largest value is associated with ^{13}CO quenching, with the enrichment of ~ 24 ‰ at the high-pressure limit. For the oxygen isotope substitutions, the KIEs of the stabilisation step are of comparable magnitude, but anomalously opposite. The dissociation channel fractionations $(\eta_a + \eta_b)$ are essentially equal to those derived using the conventional approach (η_0) within uncertainties.

Table 3.6 CO+OH KIE parameterisation parameters

Isotopologue	Parameter values			η (‰) ^a	References
	Conventional approach ^b ($\eta = \eta_0 + \eta_1 p + \eta_2 p^2$)				Röckmann <i>et al.</i> ^[1998b] , Troe ^[1998]
	η_0 (‰) ^c	η_1 (‰) ^d	η_2 (‰) ^d		
¹³ CO	-6.55	+22.69	-9.47	+6.67±2.09	
C ¹⁸ O	-11.91	+6.03	-3.41	-9.29±1.52	
C ¹⁷ O	-4.72	+8.57	-4.06	-0.21±1.30	
$\Delta^{17}\text{O}\eta^e$	+1.60	+5.34	-2.26	+4.59±1.54	
	Composite approach (see text)				
	$\eta_a + \eta_b$ (‰) ^c	$\eta_a + \eta_c$ (‰) ^d	$\Delta\eta/10\text{K}$ (‰) ^f		
¹³ CO	-7.58	+23.92	-0.487	+6.75±0.97	
C ¹⁸ O	-11.90	-5.74	-0.099	-9.02±0.91	
C ¹⁷ O	-4.95	+6.04	-0.167	+0.03±1.36	
$\Delta^{17}\text{O}\eta^e$	+1.36	+9.10	-0.116	+4.83±1.46	

^a) Resulting value at 1 bar, 298K. Error terms denote fit confidence level 90% (conventional) and 95% (composite).

^b) Coefficients are calculated for p given in [bar].

^c) Association-dissociation channel KIE.

^d) Stabilisation channel KIE.

^e) Values are calculated from the enrichments for C¹⁷O and C¹⁸O, respectively.

^f) Calculated KIE sensitivity to the temperature at 1 bar pressure.

Effectively, the composite approach predicts a slight KIE dependence on temperature, owing to the specific partitioning between the exit channels escorted by dissimilar KIEs. From the kinetic point of view, the rate of the pressure-independent quenching outcompetes the rate of the dissociation channel with decreasing temperature, and vice versa. Hence, at ambient temperatures both, conventional and composite, approaches yield identical results, but at lower temperatures the latter predicts the shift of the KIE value towards that of the stabilisation channel. Unfortunately, it is not possible to quantitatively verify this conclusion due to the lack of empirical data. All experiments investigating the CO+OH KIE were conducted at various pressures but nearly identical ambient conditions (around 298K), sensibly assuming temperature effects to be negligible. Indeed, the variation of the overall rate coefficient is small: with the temperature drop of 20K at 1 bar pressure it increases by mere 2.7%.³⁸ The contribution of the stabilisation channel rate, however, concurrently enhances by as much as 3%. In case of the ¹³C KIE, that is enough to add a considerable 1‰ to the overall enrichment. For the oxygen KIEs, the temperature dependence is much weaker due to the smaller fractionations associated with the stabilisation channel (*cf.* sensitivities $\Delta\eta$ from Table 3.6). In addition, the KIE temperature dependence largely degenerates below 100 hPa pressure, thus the effect should be important only for the tropospheric oxidation of ¹³CO under seasonal temperature variations. For example, the calculated composite ¹³C KIE magnitude departs from +6.5‰ to +9.4‰ within the +30°C down to -30°C range at surface pressure. The calculated T -dependence for all isotopologues is presented in Figure 3.5 (right panel).

³⁸ The estimates are from the composite approach calculations. The uncertainty of the CO+OH reaction rate itself (in MECCA) amounts to 15% (McCabe *et al.*^[2001]).

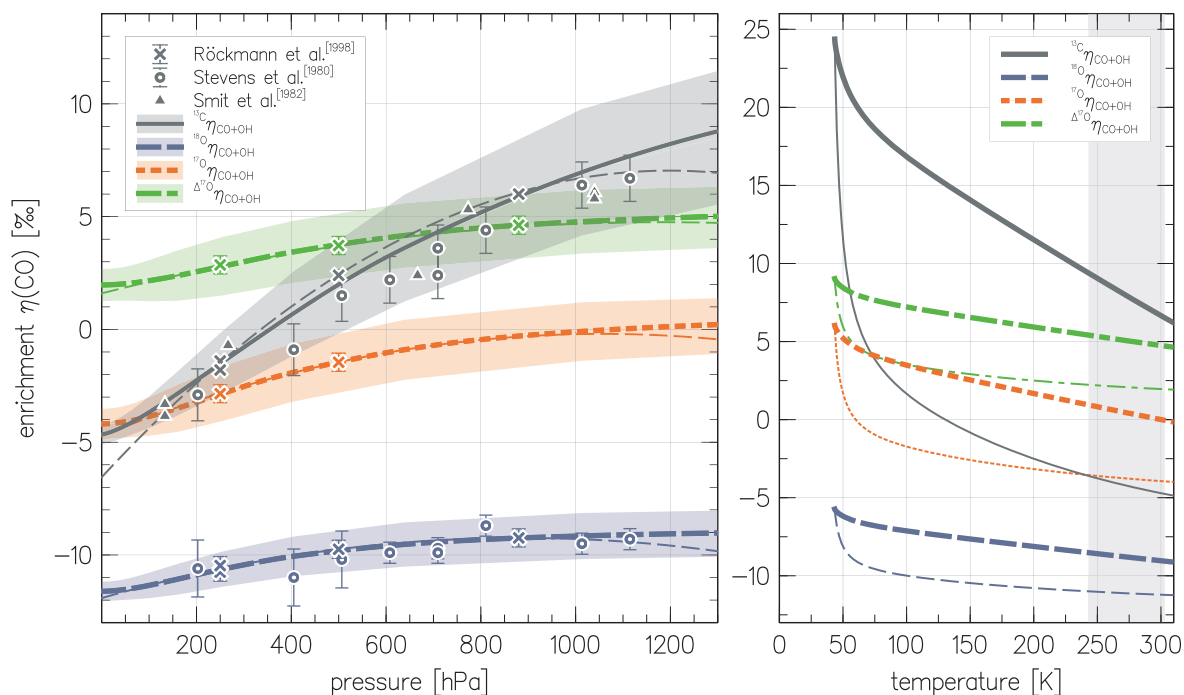


Figure 3.5 Left: Pressure dependence of the KIE in reaction of CO with OH. Symbols denote laboratory measurements at ambient temperature (assumed 298K) with N_2 or N_2/O_2 bath gases. Thin dashed and thick solid lines refer to the conventional and composite approach values, respectively. The shaded areas signify the composite approach errors (see Table 3.6). Right: Temperature dependence of the CO+OH KIE calculated with the composite approach. Thick and thin lines refer to the values calculated at the pressures of 1000 and 100 hPa, respectively. The vertical shaded area spans from -30°C to $+30^\circ\text{C}$ for comparison.

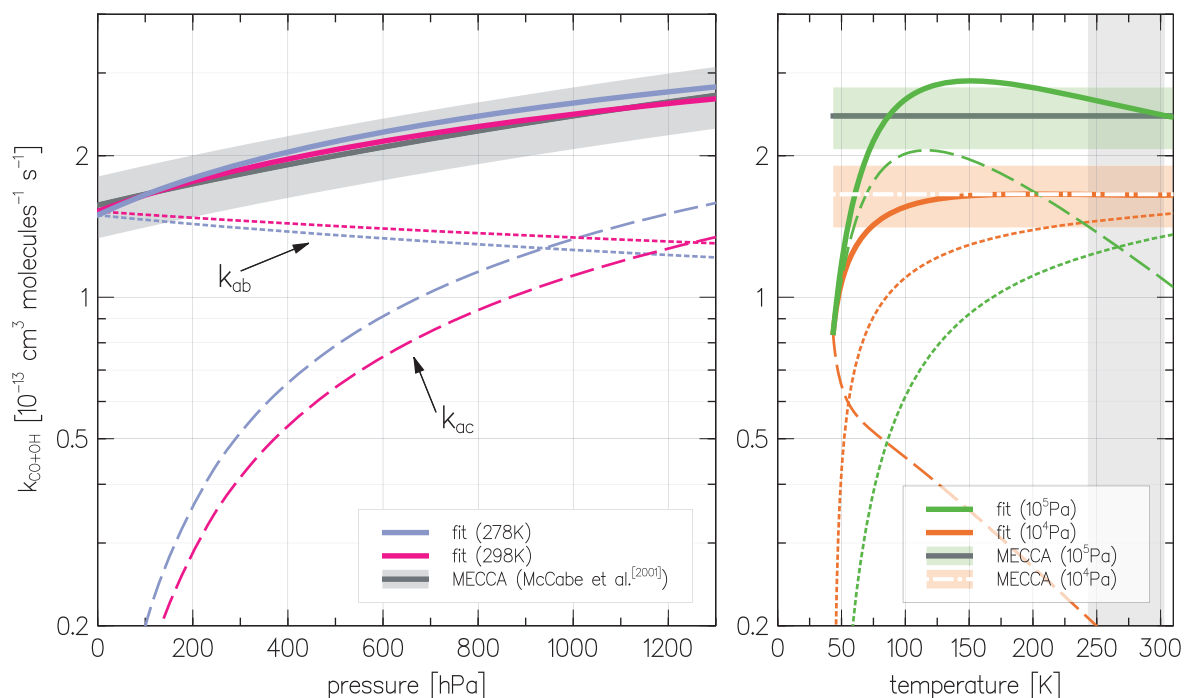


Figure 3.6 CO+OH reaction rate coefficient (in air/ N_2 bath gases) parameterised in MECCA and calculated with the composite approach (see text). Lines refer to the overall rate (thick solid), the quenching channel ($k_{\text{ac}} \rightarrow \text{HOCO}$, thin dashed) and the dissociation channel ($k_{\text{ab}} \rightarrow \text{H} + \text{CO}_2$, thin dotted). Left: Pressure dependence at 278K and 298K. Right: temperature dependence at 1000 and 100 hPa, respectively. Shaded areas denote the uncertainty (15%) of the rate coefficient used in MECCA. The vertical shaded area spans from -30°C to $+30^\circ\text{C}$ for comparison.

The anticipated vertical profile of the CO+OH KIEs in the atmosphere is depicted in Figure 3.7, along with the enrichments for the other pressure- and temperature-sensitive KIEs included in the current carbon and oxygen isotope configurations. The effect for ^{13}C turns inverse at around 350 hPa, according to the conventional parameterisation. The composite approach, however, predicts this point at higher altitudes slightly above 200 hPa, owing to the sensitivity to the atmospheric temperature gradient. Above 100 hPa the composite approach yields slightly lower values than the conventional one. The derived surface values are close for both approaches, however the variation in the composite ^{13}C CO KIE is expected to be large (up to 3%), when the adequate seasonal temperature ranges are considered instead of the Standard Atmosphere profile. The sensitivity of the CO isotopic composition to the conventional and proposed revised CO+OH KIE parameterisations is investigated further in the framework of the 3D model (see Sects. 6.1.4.2 and 6.2.6, pp. 152–196).

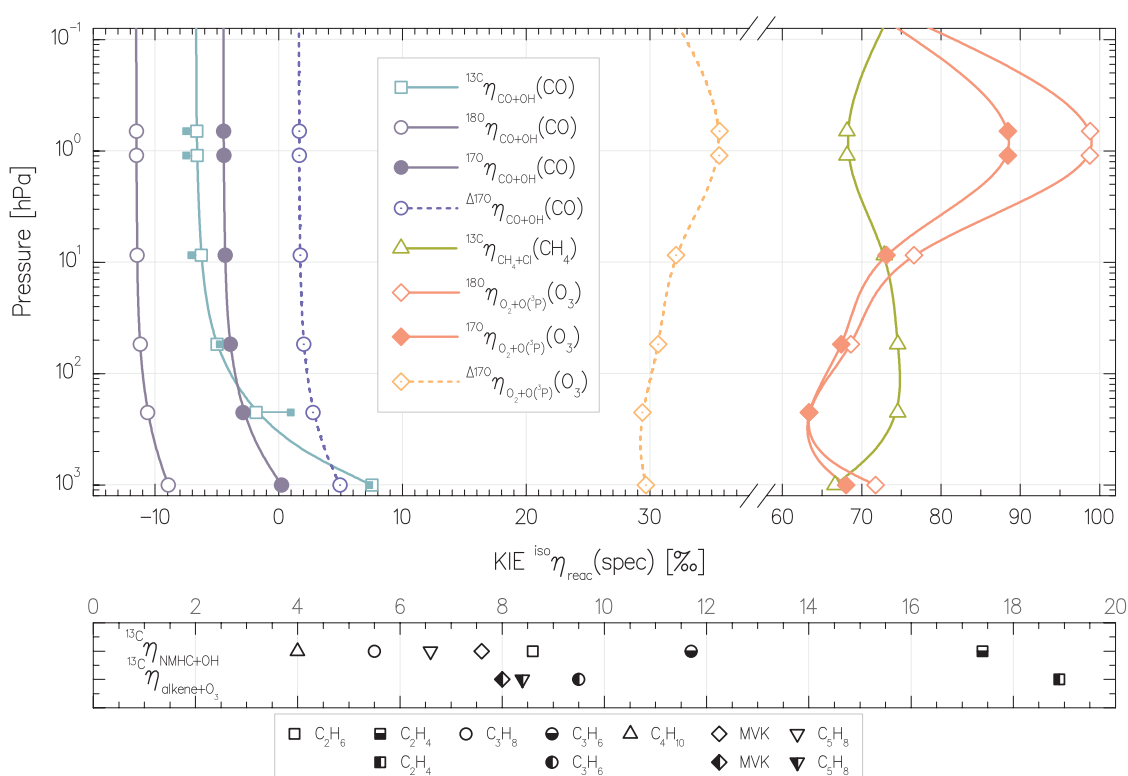


Figure 3.7 Top: Expected variation of heavy isotope enrichments in reactions escorted with pressure and temperature-dependent kinetic isotope effects. Values are plotted against the pressure/temperature profile of the Standard Atmosphere (ICAO^[1993]). Open and solid squares denote the values of the ^{13}C KIE in the CO+OH reaction calculated with the conventional and revised approaches, respectively (see text for details). Bottom: Variation of ^{13}C KIE enrichments in reactions of NMHCs with ozone and hydroxyl radical.

3.5 Box-model simulations of the stable isotope chemistry with CAABA

To assess whether the parameterisation introduced in the current study is capable of adequately reproducing the isotope chemistry kinetics with respect to the relevant atmospheric compounds, a set of evaluation simulations was designed within the framework of the CAABA box-model. Specifically, these simulations are focused on reproducing the stable isotope composition of CO and related species. The following sections describe the model setup and the results of the simulations. A comparison of the simulated isotopic CO with the observational data is presented.

3.5.1 Model description and simulation setup

CAABA (Chemistry as a box-model application, Sander *et al.*^[2011]) is the atmospheric chemistry model that represents an air parcel with given physical conditions (temperature, pressure, humidity, *etc.*) at a given location (for instance, positioned in the boundary layer air at a certain latitude). CAABA is developed within the MESSy framework (Jöckel *et al.*^[2005]) and constitutes a *base model* coupling a desired set of *sub-models* by means of the MESSy interface.³⁹ The selection of submodels depends on the needs of a particular simulation; notwithstanding, the kinetic chemistry submodel MECCA is indispensable. For the simulations presented here, the submodels JVAL and SEMIDEP are employed additionally. The submodel JVAL calculates the rates J [s^{-1}] of photolytical reactions, which are subsequently provided to MECCA in every integration timestep. CAABA allows adjusting the longitudinal/latitudinal position of the box (on the surface), thus affecting the solar zenith angle and the incident radiation intensity, hence altering the J -values respectively.

The submodel SEMIDEP (simplified emission and deposition) parameterises in- and out-mixing of the chemical species from the isolated CAABA's air parcel due to exchange process like air entrainment (emission) or dry/wet deposition. Essentially, CAABA's box has no size, as the model operates with concentrations explicitly. To translate the in- and out-fluxes in [$\text{cm}^{-2} \text{s}^{-1}$] into the respective concentration change in [$\text{cm}^{-3} \text{s}^{-1}$], the box is assumed to contain a well-mixed portion of air, represented by the specific boundary layer, or scale height z_b . Thus, for example, the emission flux E into the box is converted into the respective concentration change Δc as

$$\Delta c = E \cdot (z_b)^{-1} . \quad (3.18)$$

Conformably, the removal term is quantified with the specific deposition velocity v_d in [cm s^{-1}], defining the proportionality of Δc to the species' abundance in the box:

$$\Delta c = c \cdot v_d (z_b)^{-1} . \quad (3.19)$$

Here, c denotes the species concentration [molecules cm^{-3}]. Customarily, z_b is taken as 1000 m and the emission/removal terms are appropriately scaled to obtain the reasonable chemical regime in the parcel. Species concentrations are updated upon emission and deposition processes in the box before every MECCA integration step starts.

A comprehensive chemistry scheme comprising ozone- and non-methane hydrocarbon chemistry was selected for the simulations with MECCA. The chemical mechanism resembles the one used in the EMAC evaluation simulation (EVAL) performed by Jöckel *et al.*^[2006], with reduced halogen and stratospheric chemistry parts.⁴⁰ The simplification is not found to notably alter the results, as the tropospheric part retains its functionality in CAABA. The stable carbon-12/13 and oxygen-16/17/18 isotope configurations were introduced by means of the MECCA-TAG submodel, following the parameterisation described in Sects. 3.3 and 3.4. Noteworthy, only the chemical isotope effects are accounted for in the simulations, thus any supplementary KIEs (*e.g.* accompanying the species deposition from the box) are disregarded.

³⁹ For conciseness, the reader is referred to the detailed description of the MESSy given in Sect. 5.1.2 (p. 108). The description of the JVAL submodel, as well as respective references is to be found therewith.

⁴⁰ The ECHAM5/MESSy1 evaluation study (Jöckel *et al.*^[2006]) is implied. The emission setup of EVAL resembles those described thoroughly in Sect. 5.2 and used for the 3D model simulations performed in this work. The detailed chemical mechanisms used in this and the current study can be found in the supplement to Jöckel *et al.*^[2006] and in Appendix A (p. 225).

The model setup comprises a tropospheric chemistry box with prescribed trace gas emissions. For consistency, these were derived from the original surface emission fluxes for the 3D model simulations of the EVAL study.⁴⁰ The monthly averaged global gridded source data were averaged with respect to the domain represented by the box, which was assumed to be the latitudinal band spanning $\pm 30^\circ$ from the given box location. In this way, the averaging is an attempt to partly compensate for the air mass transport and mixing effects manifestly missing in the box. The EVAL emission fluxes for the year 2000 were selected as the periodic temporal conditions for the CAABA simulations. To avoid an abrupt transition between monthly averages, these were linearly interpolated to daily values.

Originally, the emission data consist of the offline (prescribed) and online (calculated during the simulation) parts. The offline emission comprises influxes of CH₄, CO, HCHO, CH₃OH, HCOOH, C₂ to C₄ alkanes, C₂ to C₃ alkenes, acetaldehyde, acetone, acetic acid and MEK. The online emission fluxes for NO, SO₂ and isoprene were diagnosed from the EVAL calculations. Since the emission data is segregated into various categories, it is possible to assign corresponding isotopic compositions to every category according to the estimates⁴¹ (see Table 3.7). The species' initial abundances were derived from the averages of EVAL-simulated surface mixing ratios. Similarly, the background abundances of H₂O, CH₄ and O₃ (the latter is expected to be more realistically represented in EVAL) and temperature were set using the pre-calculated surface average values at the given latitude for the year 2000 throughout the simulations.⁴² The air pressure in the box was kept at 1 atm. The tracers' initial isotope compositions were set to 0‰ with respect to the given isotope standards, to assure that the simulated ratios reach adequate and stable, annually recurrent behaviour. Exceptionally, owing to their little variability, the isotope compositions of $\delta^{13}\text{C}(\text{CH}_4) = -47.2\text{‰}$ and the mass-dependently fractionated $\delta^{18}\text{O}(\text{H}_2\text{O}) = -20\text{‰}$ ⁴³ and $\delta^{18}\text{O}(\text{O}_2) = +23.5\text{‰}$ were kept constant throughout the simulations.

Table 3.7 Emission and in-situ sources and their signatures used in the box-model simulations

Trace gas emission source ^a	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	Reference ^b
Biomass burning, waste burning	-24.5	+17.2	0	c
Biofuel usage	-27.5	+17.2	0	d
Fossil fuel combustion	-27.5	+23.5	0	e
Biogenic emission	-27.0	0	0	f
Oceanic emission	-13.5	0	0	g
Chemical (in-situ) sources and KIEs for CO				
CH ₄ oxidation	-51.2	-5.0	0	h, i
NMHCs oxidation	-27.0	-8.0	0	f, i
Alkenes ozonolysis (O ₃ signature)	-	+90.0	+30.0	j
CO oxidation by OH ^k	+6.5	-9.4	+4.7	l

^a) Direct surface emission of CO and relevant species is implied. For the emission sources classification, see Jöckel *et al.*^[2006], Jöckel *et al.*^[2010] and Sect. 5.2, (p. 118) for emission sources classification.

^b) For a common reference, see Brenninkmeijer *et al.*^[1999b], Röckmann *et al.*^[2002].

^c) Kato *et al.*^[1999], Brenninkmeijer^[1993]

^d) Assumed average value for $\delta^{13}\text{C}$, biomass burning for $\delta^{18}\text{O}$.

^e) Stevens *et al.*^[1972].

^f) Brenninkmeijer and Röckmann^[1997], Conny^[1998].

^g) Manning *et al.*^[1997], $\delta^{18}\text{O}$ assumed equal to the biogenic signature.

^h) Derived from $\delta^{13}\text{C}(\text{CH}_4) = -47.2\text{‰}$ (Quay *et al.*^[1999]) and CH₄+OH KIE of $^{13}\text{C}\eta(\text{CH}_4) = +3.9\text{‰}$ (Saueressig *et al.*^[2001]).

ⁱ) Following the estimates of Gros *et al.*^[2002]; yields ca. -9‰ accounting for removal KIEs (see Table 3.4, p. 44).

^j) Röckmann *et al.*^[1998a], see also Sect. 3.4.3 (p. 45).

^k) Listed are the nominal enrichments (depletions) η in CO due to the sink KIE.

^l) Conventional KIE parameterisation value at 1 atm. pressure (see Sect. 3.4.4, p. 47).

⁴¹ A more comprehensive estimate of the ^{13}C emission strengths and signatures is given in Sect. 5.2.

⁴² Species concentrations were relaxed towards EVAL-simulated values, with a variable-specific relaxation coefficient of 1 day. The original (not temporally averaged) EVAL output data were linearly interpolated for every CAABA integration time step.

⁴³ The average composition of atmospheric H₂O is taken from Criss^[1999] (p. 90). Although the atmospheric vapour may be much more depleted, compositions below -20‰ in $\delta^{18}\text{O}$ are rarely found in the boundary layer air (Craig and Gordon^[1965]).

The removal from the box was accounted for the following species (their respective deposition velocities in $[\text{cm s}^{-1}]$ are given in brackets): O_3 (0.04), CH_3OH (0.08), NH_3 , NO_2 and CH_3OOH (0.1), HCHO , H_2O_2 and SO_2 (0.5), N_2O_5 , HCOOH , $\text{CH}_3\text{SO}_3\text{H}$ and DMSO (1.0), and HNO_3 and H_2SO_4 (2.0). The deposition velocities generally reflect the overall effect of the dry/wet deposition removal, depending on the properties of a particular species. Thus, for example, the highly soluble H_2SO_4 is characterised with an intensive removal ($v_d = 2.0 \text{ cm s}^{-1}$).

The simulations were performed for a period of three years, conventionally starting in January 1st of 1996. To note, the first simulation year is spent for the model spin-up, so that the simulated compartments become adequately altered by the kinetic isotope effects and refilled by the emissions into the box and concurrent chemical interchanges. Due to the low share of the minor isotopologues in the overall species abundances, the isotope ratios require a longer spin-up time than the species concentrations itself. For instance, for CO the period of 9–10 months was found to be sufficient to renew the isotope ratios after the model initialisation.

3.5.2 Results and discussion

The purpose of the box-model study is the reproduction of the carbon and oxygen isotopic compositions of the atmospheric tracers, particularly in view of the different factors that determine the isotope ratios in CO. We briefly outline these:

- Variations in carbon monoxide abundance and composition are chiefly controlled by the surface emissions and the hydroxyl radical. During autumn and winter periods, when OH is virtually absent in the extratropics, surface emissions refill the CO inventory causing its mixing ratio grow almost linearly. In spring and summertime available OH triggers in-situ CO production and sink accompanied by the KIE. As CO quickly becomes broken down, its isotopic composition becomes more sensitive to the current sources. The different phases of OH presence result in various amplitudes of the isotope ratio variations, as well as the average values. Longer available OH at lower latitudes smoothes the variability and favours in-situ production of CO, compared to the high-latitude cases, where OH peaks briefly.
- Considering carbon isotopes, there are two distinct isotope signatures of the surface emission and in-situ sources of trace gases, *viz.* biogenic and fossil-fuel derived CO (with $\delta^{13}\text{C}$ of approximately -27‰) and methane-derived CO (depleted by as much as -51.2‰). The relative contribution of these sources, superposed with the CO removal KIE of $+6.5\text{‰}$ determines the annual variability of $\delta^{13}\text{C}(\text{CO})$. The latter is highly sensitive to input from CH_4 , as this major in-situ source of CO exhibits a large exclusive ^{13}C depletion.
- The oxygen isotope compositions of the sources contrast isotopic carbon: the in-situ sources such as NMHCs and CH_4 are characterised by lower $\delta^{18}\text{O}$ values ($\sim 0\text{‰}$) compared to the enriched surface sources ($+17\text{‰}$ to $+23.5\text{‰}$). The ^{18}O KIE escorting CO removal is inverse, inducing as much as 9‰ depletion in $\delta^{18}\text{O}(\text{CO})$. Besides, the ozonolysis of NMHCs opens the way for a largely enriched O_3 composition ($\sim +90\text{‰}$) to enter the subsequent products and particularly CO.
- The third independent signal, namely the oxygen mass-independent fractionation (MIF) in CO, is attributed exclusively to the chemical reactions. All surface and in-situ sources are mass-dependently fractionated, thus they dilute the MIF signal in CO with $\Delta^{17}\text{O}(\text{CO}) = 0\text{‰}$. An exception is the ozone whose $\Delta^{17}\text{O}(\text{O}_3)$ is $\sim +30\text{‰}$. The CO sink via oxidation by OH induces a $\Delta^{17}\text{O}(\text{CO})$ enrichment of $+4.7\text{‰}$, which is expected to be the dominant effect. The contribution of mass-independently fractionated O_3 , however, can add a significant portion to $\Delta^{17}\text{O}(\text{CO})$, depending on the amount of CO produced from NMHCs ozonolysis and isotope exchange between O_3 and CO via the secondary pathways. Röckmann *et al.*^[1998a] estimated $\Delta^{17}\text{O}$ of CO produced in reactions of alkenes and O_3 to be considerable, 25‰ – 40‰ ; thus assessing ozone oxygen input to CO is one of the primary objectives of this box-model study. The simulated mechanism accounts for the oxygen isotopic transfer through other intermediates, in addition to direct source effects.

The simulations were carried out in four different setups. To examine the sensitivity of the CO isotope composition to the O_3 input, the ozone KIE was set to be either anomalous (*reference* setup) or mass-dependent (MDF- O_3 setup) in the different simulations. The mass-independently fractionated O_3 with $\Delta^{17}\text{O}$ of $\sim 0\text{‰}$ is

thus produced with the $\delta^{17}\text{O}(\text{O}_3)$ value lowered from +78‰ to +46.5‰, while $\delta^{18}\text{O}(\text{O}_3)$ remains unaltered. To assess the sensitivity of the model to the OH levels, each setup was simulated in two distinctive regimes of OH seasonality emerging in the box positioned at the NH latitudes of 70°N (*high-latitude* setup, HL) and 30°N (*low-latitude* setup, LL). For the ease of the analysis, a subsidiary tagging configuration of the mechanism was introduced to estimate the fractions of the carbon in CO and its precursors originating from the two distinct $\delta^{13}\text{C}$ in-situ sources, namely CH_4 and remaining non-methane hydrocarbons.⁴⁴

Figures 3.8 throughout 3.12⁴⁵ present the detailed simulation results for the reference setup at high- and low-latitudes. The model adequately reproduces atmospheric background mixing ratios, displaying a dynamic equilibrium in the second and third simulation years. The isotope compositions fall within the expected ranges, reflecting the annual dynamics of the sources and kinetic effects. Notably, the intermediates of the $\text{CH}_4 \rightarrow \text{CO}$ chain, such as CH_3O_2 , CH_3OOH and HCHO , are largely influenced by the methane input, comprising up to 70% of the CH_4 -derived carbon during summer. For HCHO , the fraction of the methane source amounts to 0.45–0.65, which is in a good agreement with the estimates of Stavrakou *et al.*^[2009]. Shorter-lived species like CH_3O_2 show large isotope ratio variations, being rapidly refilled by the sources with contrasting compositions, switching between the day (dominated by CH_4) and night (driven by NMHCs and surface emissions) conditions. The annual dynamics of the compositions is larger in the HL box, where the chemical interchanges are largely inhibited in the winter time. On the contrary, the influence of the surface sources on the LL box ratios is smaller.

Generally, the variations of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signals in tracer compositions are well correlated, which is not the case for $\Delta^{17}\text{O}$ controlled only by the dynamics of the oxygen arriving from O_3 . An exceptional case is the composition of methyl glyoxal (CH_3COCHO), which has a small $\delta^{13}\text{C}$ variability (due to the CH_4 input via CH_3O_2 of less than 1%) but a large, clearly ozone-derived oxygen composition in winter. This is a consequence of the missing OH in the HL box, when leftover ozone reacts with the remaining NMHCs in the winter time. A similar effect can be noted also in the quite large MIF of H_2O_2 and HCHO . Despite that the effect for formaldehyde is amplified by its low concentrations, it is not insignificant for the CO MIF signal. Analogously, in the HL box the peculiar MIF peaks for CH_3O_2 , CH_3OH and CH_3OOH are similar to those in HNO_3 , denoting that a significant portion of their MIF oxygen is secondarily derived from NO_3 during winter time, whereas in summer the OH-mediated oxygen contribution dominates. The simulated nitrate oxygen enrichments in HL become elevated in winter with sharp drops in summer, very similar to what is observed in the Arctic atmosphere (Morin *et al.*^[2008]). Interestingly, the isotope composition of OH itself is merely determined by its abundance, because higher OH concentrations boost the isotope exchange between atmospheric water and O_3 -derived OH, as denoted by the characteristic relation $\delta^{18}\text{O}(\text{OH}) \approx \Delta^{17}\text{O}(\text{OH})$. The intensive equilibration results in similar enrichments of +1.5‰ in both setups in summer, whereas in winter the HL box enrichments reach ~+8‰ which is 2‰ higher than in the LL box. The latter also peaks earlier, denoting that OH concentrations reach the levels when isotope exchange becomes significant earlier.

The simulated oxygen isotopic composition interchanges are substantially perceptible in the triple-isotope plot (Figures 3.8 and 3.12, right panels), where the mass-independent enrichment in $^{17}\text{O}/^{18}\text{O}$ is proportional to the vertical deviation from the MDF-line. Ozone and CO bulge out as remarkable outliers, displaying unrelated characteristic MIF. The remaining compositions reflect the effect of the chemical “mixing” via the intermediates and the isotope exchange reactions. Thus the HO_x and NO_x groups “move” along mixing lines of “dilution” with the end members being ozone and the two main oxygen reservoirs of air O_2 and H_2O . For example, the H_2O_2 composition is generally “positioned” on the O_2 – O_3 mixing line; however, the deviation towards an equilibrated mixture of H_2O and O_3 compositions in the winter time is prominent in case of the HL box.

⁴⁴ These diagnostic tagging configurations are described in detail in Sect. 5.1.4.1 (p. 113).

⁴⁵ Figures 3.11 and 3.12 (on pp. 63 and 65, respectively) aggregate the simulation results for relevant carbonaceous and oxygenated species.

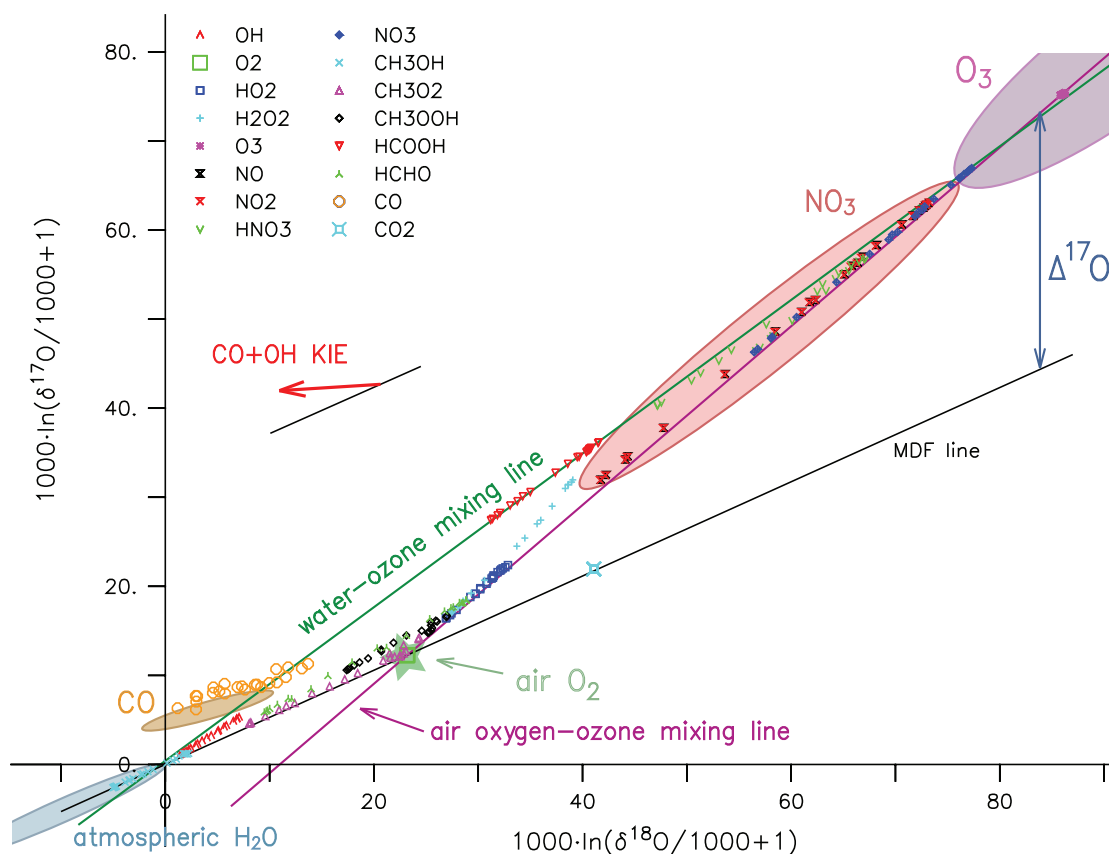


Figure 3.8 Triple-isotope plot of the main oxygen-bearing gas-phase species compositions simulated in the reference setup, HL box. The shaded areas indicate typical compositions observed for certain species reported by Brenninkmeijer *et al.*^[2003] and Thiemens^[2006]. The red arrow denotes the depletion in CO induced by the oxygen CO+OH kinetic isotope effects.

Generally, the box-model reproduces observational data of CO and its isotopic composition well (see Figure 3.9). The average $\delta^{13}\text{C}(\text{CO})$ value for the LL box is lower due to greater input from methane (estimated from 19% in the late winter to 37% in summer) compared to the HL box (10% to 31%, correspondingly). Since the latter has much less OH, the maxima and minima in $\delta^{13}\text{C}(\text{CO})$ are less pronounced and shifted in time towards summer. During the fall-winter season the HL box reflects the signature of the primary sources in a characteristic “shoulder” at around -27.5‰ . The annual dynamics of the CO sources (surface and in-situ) effect estimated for the HL box is presented in Figure 3.10 (upper left). The in-situ sources account for up to 50% of CO in August, when CO production and removal are comparable. The fraction of photochemically derived CO progressively lowers until April to half of that value due to the surface emissions in fall and winter. The detailed analysis of the simulation results confirms that only the CH_4 source and the CO sink KIE are influential for the $\delta^{13}\text{C}(\text{CO})$ dynamics. Figure 3.10 (lower left) displays the de-convolution of these signals derived using the diagnostic tagging results and the isotope mass balance of the sources. Considering the mixture of non-methane sources, one receives a fairly stable composition of -26‰ to -25.5‰ throughout the year (dashed line). Upon adding CH_4 , sources become depleted by 4‰ to 8‰ , depending on the fraction of the methane contribution to CO (*cf.* the dashed and dotted lines). The CO+OH KIE conversely enriches CO in ^{13}C , becoming prominent at least one month earlier than the effect of CH_4 , owing to the buffering of the depleted carbon by the intermediates of the methane chain. The effective enrichment due to the sink fractionation becomes largest in June and amounts to its nominal value ($+6.5\text{‰}$), denoting that virtually all CO is currently “exposed” to the sink. The buffered CH_4 signal peaks in August taking over the fading removal KIE, thus defining the fall minimum in the annual $\delta^{13}\text{C}(\text{CO})$. The observed CO composition, however, reflects sufficiently larger $\delta^{13}\text{C}(\text{CO})$ amplitudes ($\sim 4\text{‰}$ observed *vs.* 2‰ simulated) in the HL box. That is due to the effect of mixing of CO from lower latitudes, which is longer exposed to the OH during transport. The low-latitude CO is less influenced by the transport effect and the LL box captures this. Similarly, the simulated CO mixing ratio peaks later in the HL box due to the absence of the admixed fresher CO.

The oxygen composition of CO is more influenced by the source signatures change during the year. The overall sources (including in-situ) vary within $\sim 6\%$ in $\delta^{18}\text{O}(\text{CO})$, as it is seen after subtracting the contribution of the KIE (Figure 3.10, upper right). In the winter-spring season, CO is progressively refilled with heavier surface sources, whereas the depleted methane and NMHCs oxygen outbalances the emissions in the summer-fall period. The depletion is enforced by the inverse ^{18}O KIE, whose actual magnitude varies within 4% – 9.5% , depending on the balance of the CO production and removal terms. Analogously to the ^{13}C case, due to the absence of transport, $\delta^{18}\text{O}(\text{CO})$ in the HL box starts to decrease with a delay, as OH appears later.

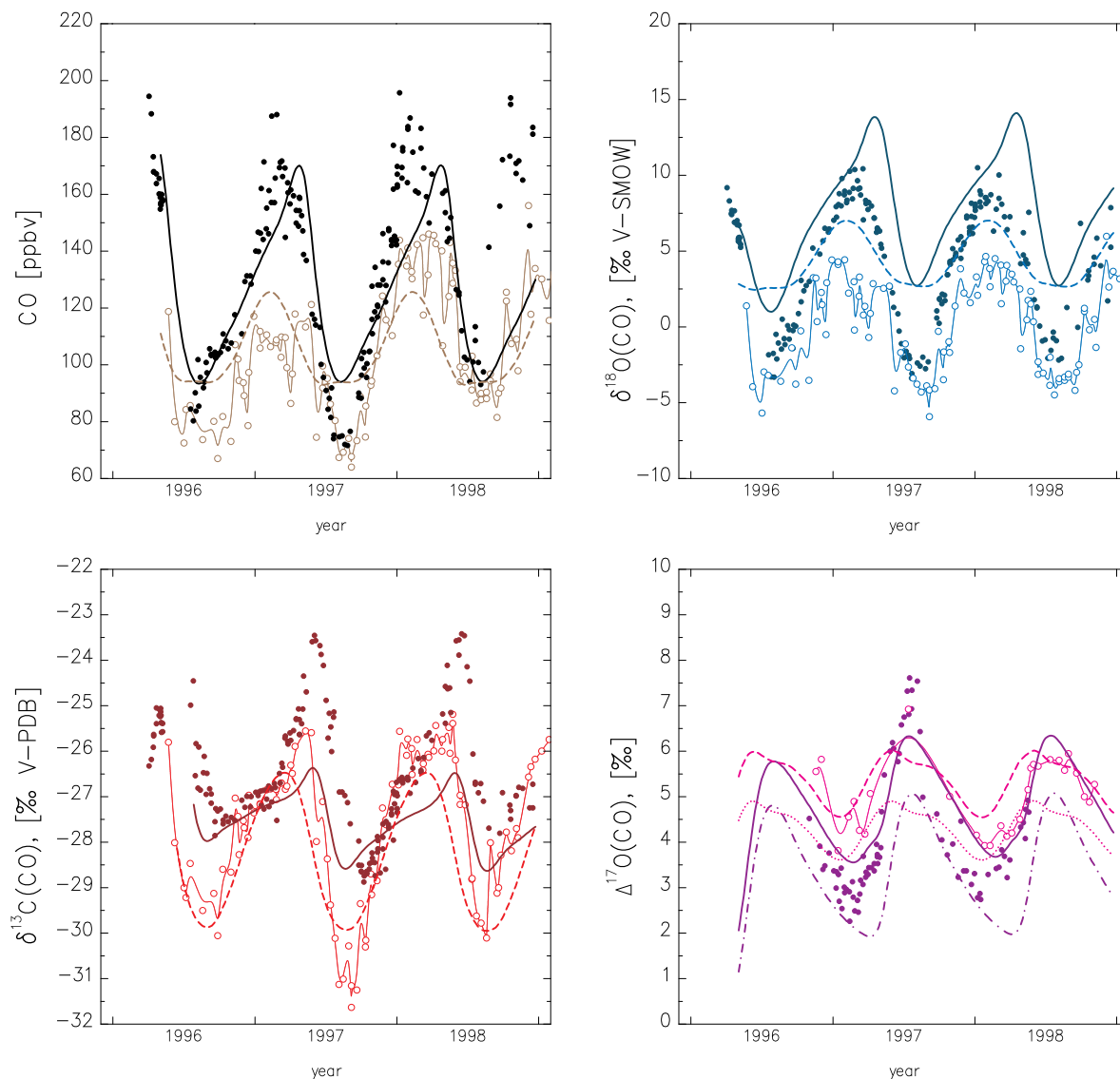


Figure 3.9 Simulated CO mixing ratio and isotopic composition in the box. Solid and dashed lines refer to the HL and LL box setups, respectively (see text). Symbols denote the observations (Gros *et al.*^[2001], Röckmann *et al.*^[2002]) for CO for high (80°N , filled symbols) and low latitudes (30°N , open symbols). The lower right panel presents the mass-independent fractionation signal ($\Delta^{17}\text{O}$) in CO and additional results of the mass-dependently fractionated O_3 setup for high latitude (dash-dotted line) and low latitude (dotted line) simulations. The unpublished observational data for $\Delta^{17}\text{O}(\text{CO})$ at low latitudes (Izaña, 28°N) are kindly provided by T. Röckmann, Institute for Marine and Atmospheric research Utrecht (IMAU).

The simulated $\delta^{18}\text{O}(\text{CO})$ signature in both boxes (Figure 3.9, upper right) is overestimated considerably by 5% – 7% . This can be attributed to the underestimated signatures of the main sources (Table 3.7). One reason may be that the CO from CH_4 and NMHCs is significantly more depleted compared to the assumed compositions. The isotope mass balance requires these sources to be additionally depleted by as much as 10% , taking into account the current compositions of all other sources. The underestimation may partly result from neglecting the O_3 input to CO in the previous estimates (*e.g.* Conny^[1998]). Ozone effects the overall $\delta^{18}\text{O}(\text{CO})$ by as much as $+4\%$ (*cf.* the solid and dashed lines in Figure 3.10, upper right), which is not negligible for the isotope mass-balance calculations. Notably, the model predicts a nearly uniform O_3 signal in

CO throughout the year. That is because the alkenes emitted in the box (particularly C_2H_4 and C_3H_6) continue to react with ozone in winter, whilst OH chemistry is at a low level. In spring, appearing OH starts to compete with ozone for alkenes, thus ozonolysis contributes with nearly the same input to CO as in the winter.

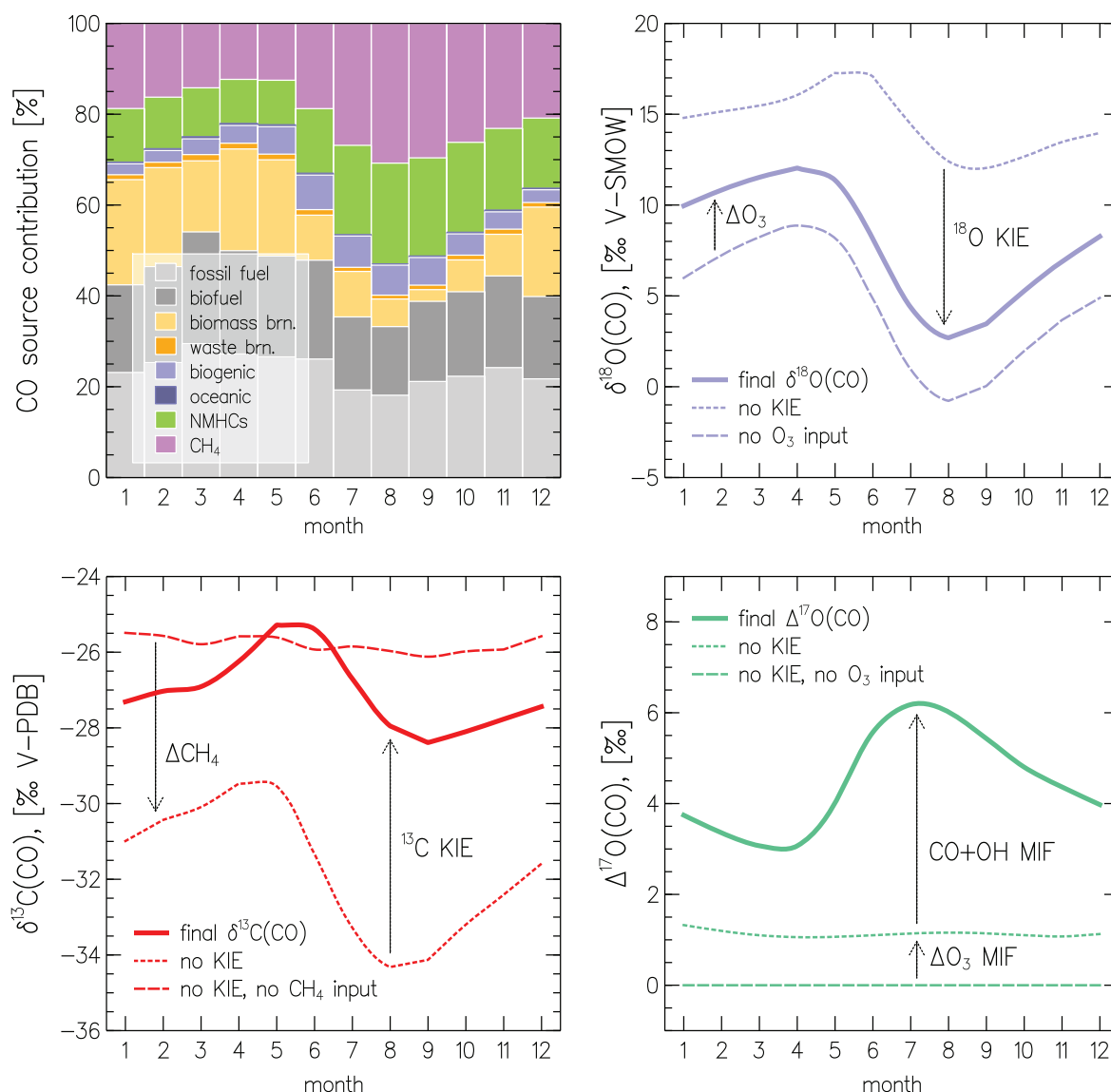


Figure 3.10 Estimated contributions of the various sources and kinetic isotope effects to the CO isotope composition simulated in the HL setup. Left top: Fraction of each source category (see Table 3.7). Left bottom: Estimated ^{13}C composition of the CO sources: All sources except CH_4 (dashed line), including light CH_4 (dotted line) and resulting $\delta^{13}C(CO)$ accounting for the CO+OH KIE (thick line). Right panel: estimated ^{18}O (top) and anomalous oxygen (bottom) CO compositions and effective enrichments due to the KIEs. Shown are the overall CO source composition (dotted line) minus the contribution of the CO+OH KIE and ozone MIF (dashed line). Thick lines denote the resulting $\delta^{18}O(CO)$ and $\Delta^{17}O(CO)$ upon summing all effects, respectively.

The CO oxygen isotope anomaly is reproduced well and can be attributed dominantly to the reaction with OH. The isotope effect for ^{17}O is uncommonly not of about half that of ^{18}O , but is nearly absent as discussed before. Thus, during the OH-driven removal of CO, $C^{17}O$ accumulates stronger than expected for an MDF process. The simulated $\Delta^{17}O(CO)$ maxima occur in May (LL box) and June (HL box) and are weakened during the fall-winter seasons (Figure 3.9, lower right) because of surface and in-situ sources dominating. The seasonal cycle in the HL box is delayed and the maxima are weak due to the low OH regime. In the fall-autumn seasons, $\Delta^{17}O(CO)$ in the HL box is overestimated by up to 1‰, which is a consequence of the imbalance between in situ MIF sources and MDF in-situ and surface sources. Indeed, the latter are not sufficiently large to dilute MIF in airborne CO, as can be seen comparing the simulated and observed abundances in the HL box for January-April. Conversely, the summer 1997 maximum of $\Delta^{17}O(CO)$ in the HL box is underestimated on top of too high CO mixing ratios. Here, however, the underestimated sink, or, analogously, the absence of mixing of aged air (bringing lower CO concentrations with higher $\Delta^{17}O(CO)$) into the box is most likely to be the cul-

pruit, rather than the underestimated emissions. Comparing the reference case with the MDF-O₃ setup, it becomes clear that the large ozone MIF signal contributes to the CO anomaly with additional 1‰ in the presented regime (Figure 3.10, lower right). Similar to $\delta^{18}\text{O}(\text{CO})$, the effective ozone signal in $\Delta^{17}\text{O}(\text{CO})$ is virtually constant. This is in contrast to the HO_x and NO_x compounds, whose $\Delta^{17}\text{O}$ values are more directly related to that of O₃. The comparison with the observations for the low-latitude box $\Delta^{17}\text{O}(\text{CO})$ is presented for the first time. Evidently, the model adequately represents the $\Delta^{17}\text{O}(\text{CO})$ seasonality upon switching between the distinct OH regimes. The simulated CO MIF in the LL box is reproduced better than in the HL box, again owing to the smaller influence of the transport effects. The low-latitude data furthermore points to the underestimation of the winter surface emissions of CO, as particularly seen for the winter 1997–spring 1998 period. However, in the 1998 summer–fall, the simulated CO mixing ratios are close to the observed values, and synthesised $\Delta^{17}\text{O}(\text{CO})$ agrees well with the measurements.

Obviously, important processes such as transport and mixing cannot be represented by a box-model, which is especially noted for the comparison with the high latitude observations that are difficult to reproduce because of the “arctic haze” conditions ruling in the winter. The underestimation of the emission sources generally leads to the incorrectly simulated isotope CO ratios. The problem is principal, as this tracer is short-lived and hence its isotope compositions are rather sensitive to the *balance* of the direct and in-situ sources. Apart from that, one can conclude that the developed comprehensive isotopic chemistry mechanism is able to capture the main features of seasonal changes in the compositions as well as the “chemical mixing” feature. The analysis of the CO+OH sink fractionation dynamics confirms that the seasonal amplitude and timing of this important effect are concordantly represented for atmospheric conditions. The further part of this study focuses on a better estimation of emission strengths and signatures, as well as the realisation of consistent AC-GCM simulations employing the here developed isotope chemistry extension.

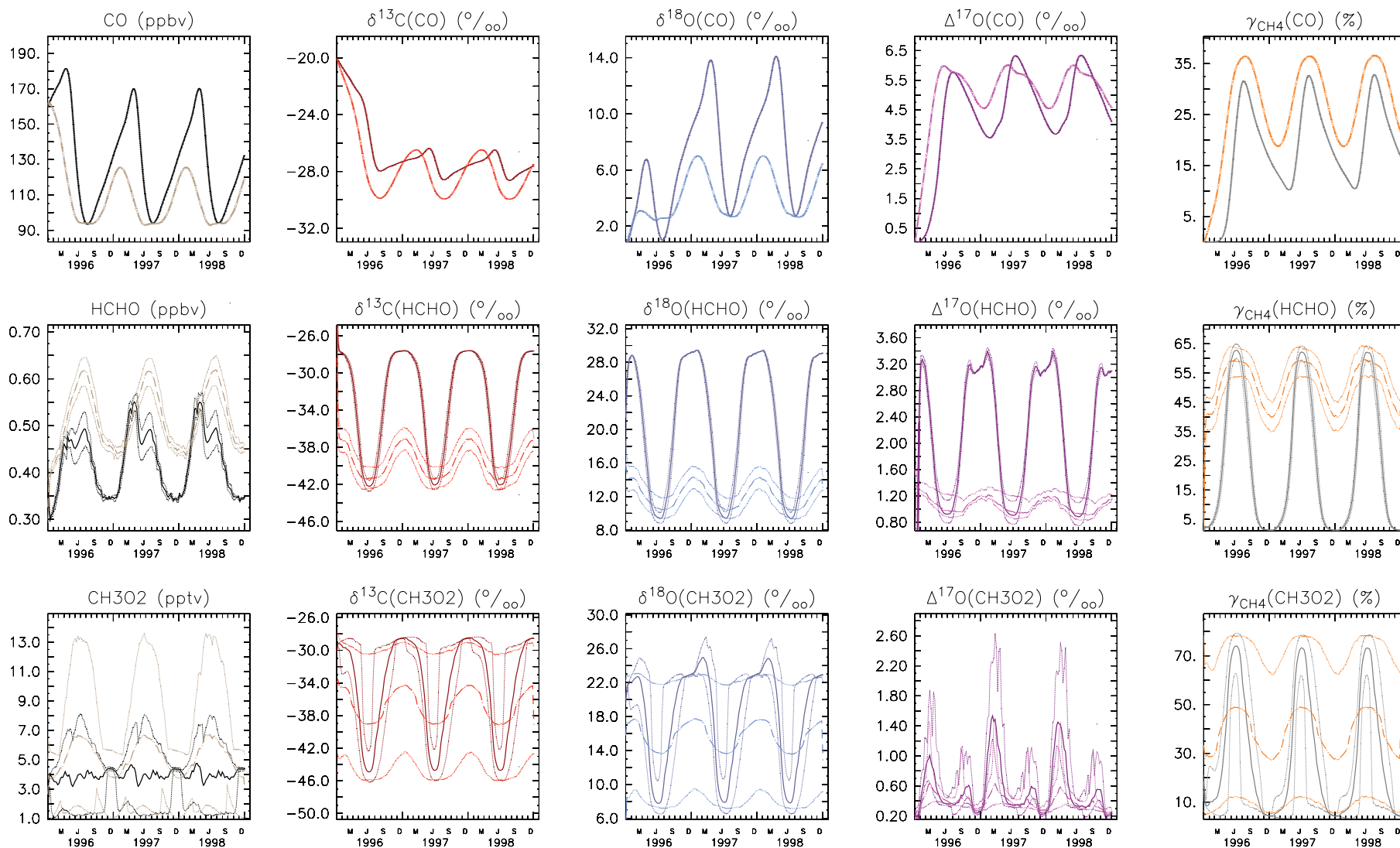


Figure 3.11 Box-model simulation results for CO, formaldehyde and methyl peroxy radical. Columns (left to right) denote species concentrations, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$ and fractions γ_{CH_4} of methane-derived carbon, respectively. Thick lines represent the high-latitude (HL, solid lines) and low-latitude (LL, dashed line) setups. Thin dotted lines mark the diurnal variability of the values.

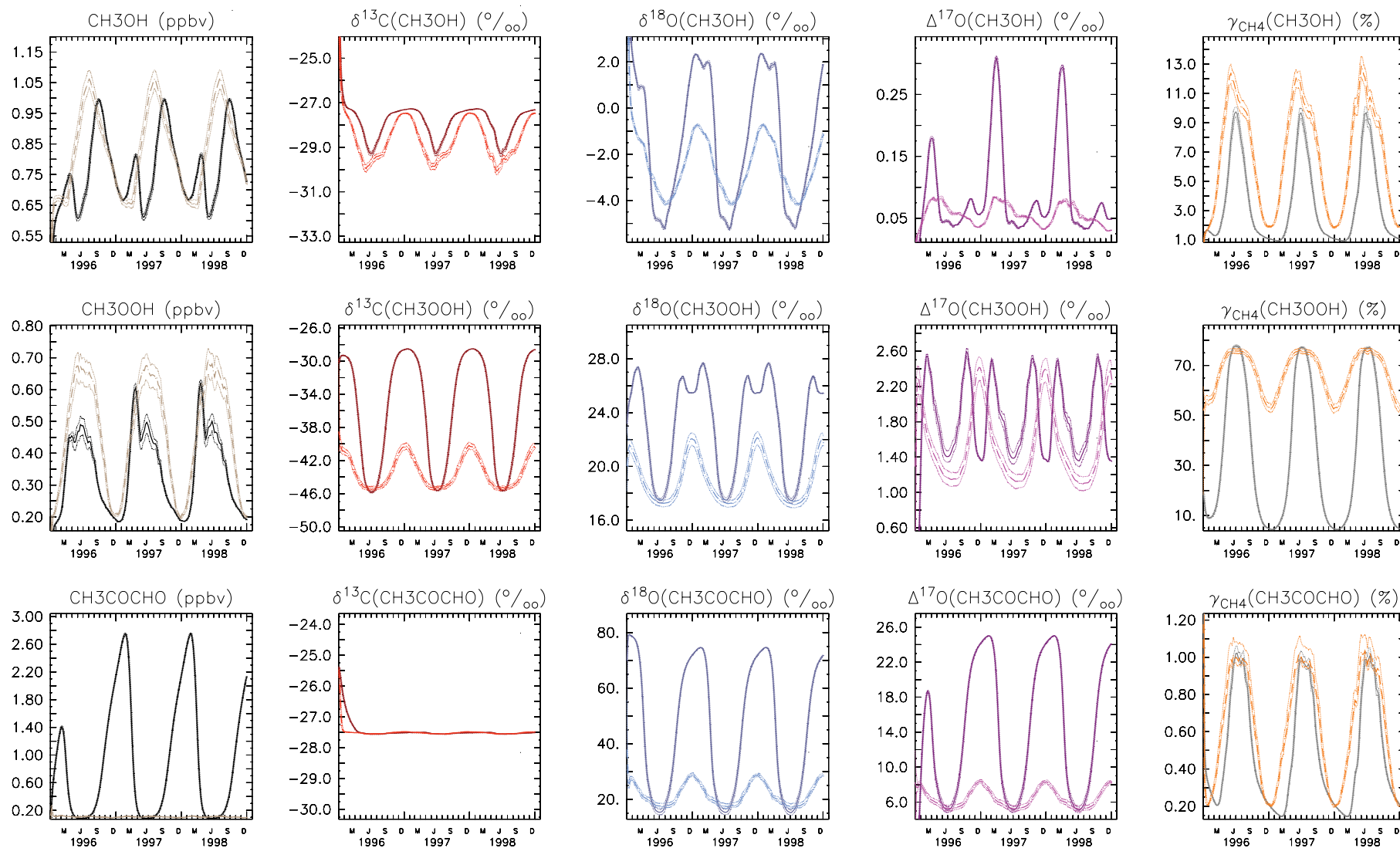


Figure 3.11 (continued) Box-model simulation results for methanol, acetic acid and methyl glyoxal, the primary carbonaceous intermediates and sources of CO.

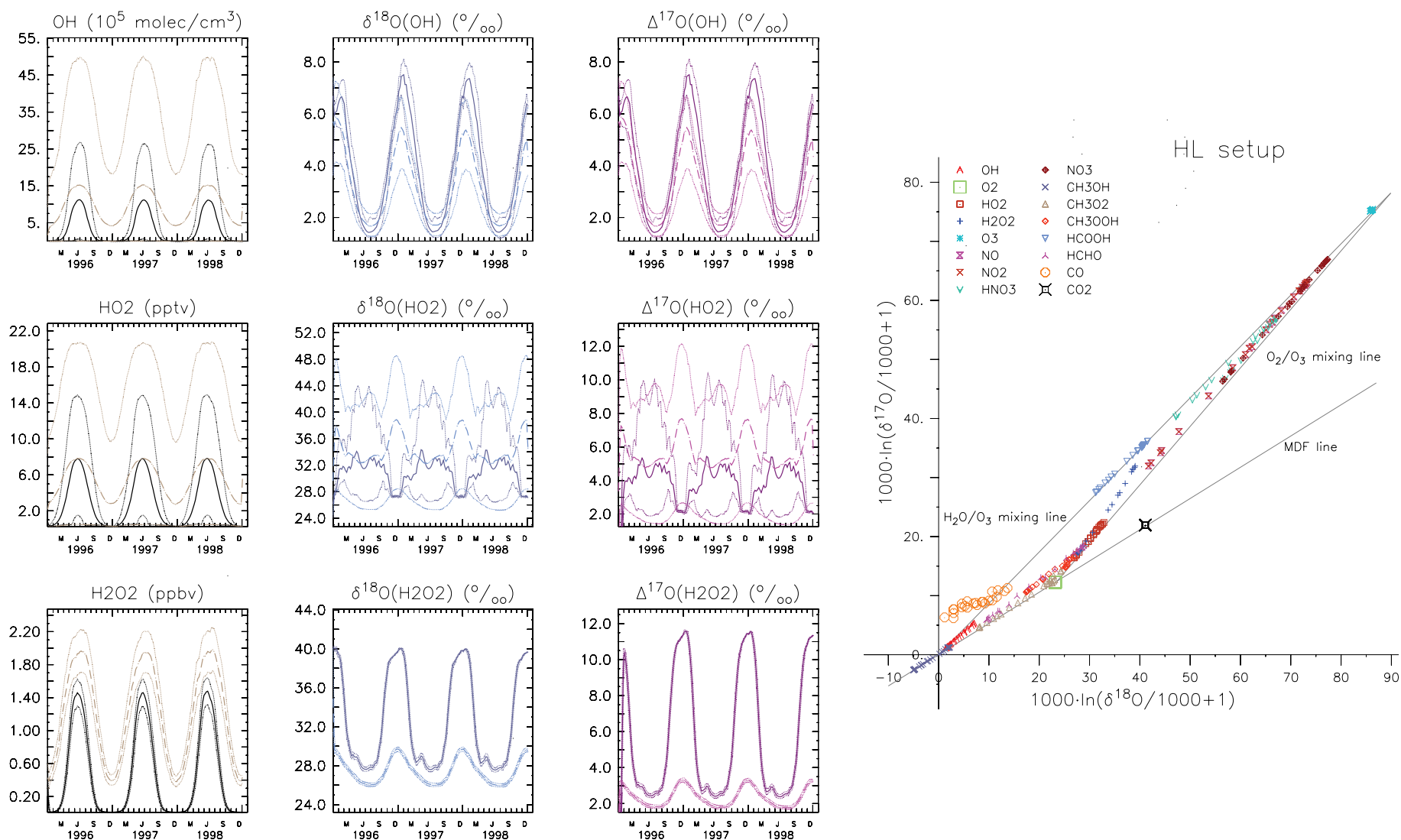


Figure 3.12 Box-model simulation results for oxygenated compounds. Left: columns (left to right) denote concentrations, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ for OH, HO₂ and H₂O₂ species. The outline follows that of Figure 3.11. Right: three-isotope plot of the principal oxygen-bearing compounds simulated in the mechanism in the high latitude (HL) setup.

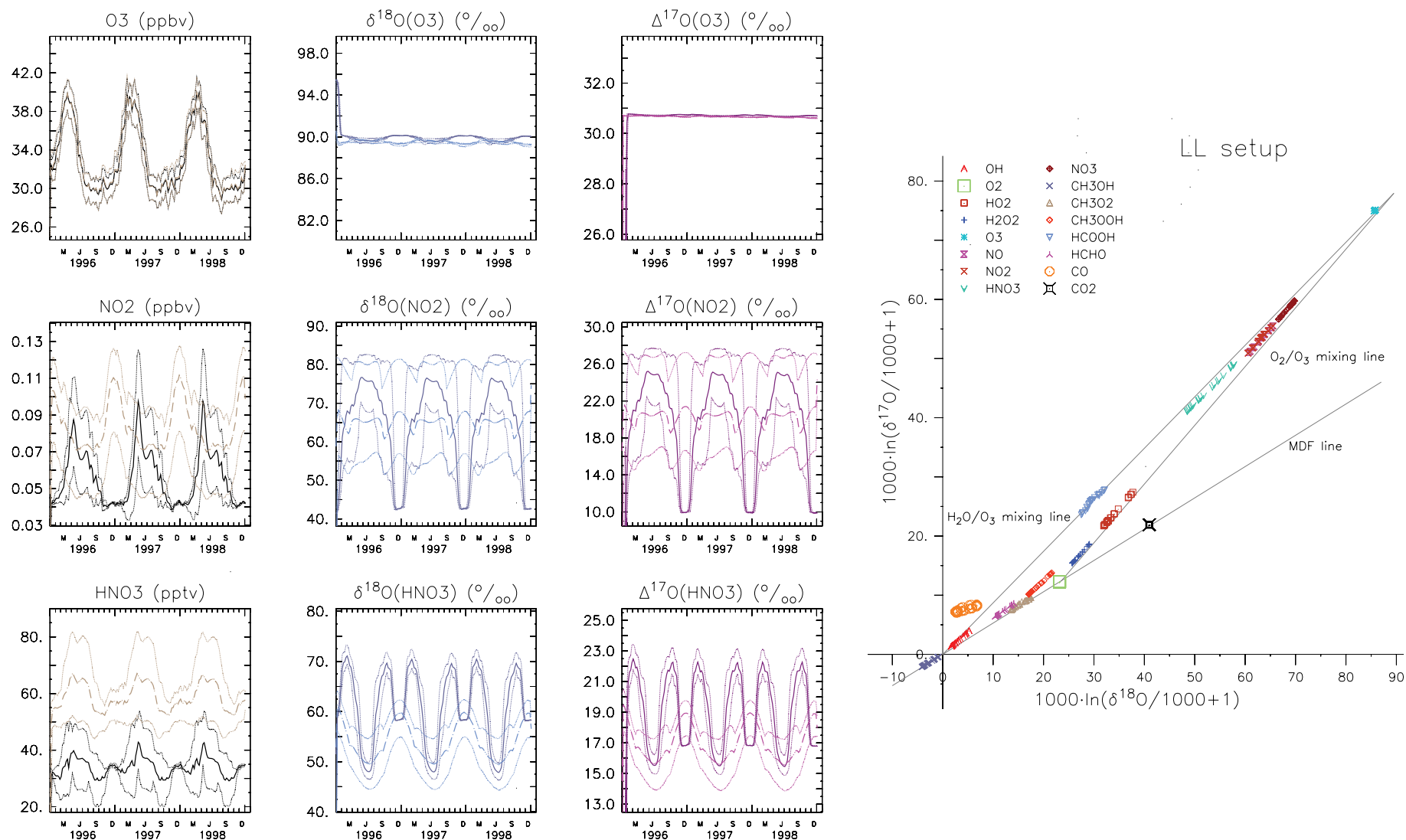


Figure 3.12 (continued) Left: simulations results for ozone, nitrogen dioxide and nitric acid. Right: three-isotope plot of the principal oxygen-bearing compounds simulated in the mechanism in the low latitude (LL) setup.

4

Isotope CO observations

In the following chapter an overview and analysis of the observational data used for the model evaluation is given. Because this study specifically features the isotope composition of CO, only the simultaneous CO mixing ratio and isotope composition observational data is regarded. The available data pertains to two general domains, *viz.* (1) surface level observations from several research stations (described in Sect. 4.1) and (2) upper troposphere/lower stratosphere (UTLS) observations obtained by the CARIBIC platform (Sect. 4.2, p. 96). Each set of data was analysed and processed in a way to make a comparison with the global modelling results consistent, as described in the following.

4.1 Surface CO

The surface isotope CO time series were obtained for ten observational sites, each covering a period of at least one year. Table 4.1 (supplemented by Figure 4.1) lists the locations, the selected isotope data sampling period and statistics, as well as the abbreviations used to identify each particular site. Measuring atmospheric CO is a laborious task when the isotope ratios are to be investigated. In particular, isotope measurements of CO are not available as *in-situ* results; rather air samples have to be collected for the retrospective isotope analysis in the laboratory, based on the separation of the CO content from the air matrix. Although an enormous improvement has been achieved through the application of the “continuous flow mass-spectrometry” which allows on-line ^{13}C , ^{18}O and lately ^{17}O analysis of atmospheric CO, the available data all were obtained using the conventional off-line technique. Moreover, most results are based on the analyses of very large air samples (greater than 100 L) because consequently ^{14}CO was analysed, which has an abundance of only 10 molecules per cm^3 of air STP. Conformably, all observational data referenced here are the analysis of the large air samples collected on a monthly to weekly basis in the best case. We note that out of ten observational sites only two are located in the Southern Hemisphere; however, these confer the longest record of ^{13}CO observations to date. Compared to $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$, the body of $\Delta^{17}\text{O}(\text{CO})$ data is very small, covering few years of observations at three NH sites. The reported overall uncertainty of the sample data is generally small, not exceeding $\pm 2\%/\pm 0.2\text{‰}$ (SPI, ALE, KMW, SBK, HAP and IZA), $\pm 4\%/\pm 0.1\text{‰}$ (MOP, BAR) and $\pm 4\%/\pm 0.2\text{‰}$ (BHD and SCB, prior to 1994; $\pm 7\%/\pm 0.8\text{‰}$ since 1994) for $[\text{CO}]/\delta^{13}\text{C}(\text{CO})$, respectively (see Table 4.1 for the references). The uncertainty in $\Delta^{17}\text{O}(\text{CO})$ data is reported to be $\pm 0.2\text{‰}$ (Röckmann *et al.*^[2002]).

Table 4.1 Isotope CO surface observational data

Abbr.	Site	Location / elevation [m.a.s.l.]	Isotope data	Observational period	Samples number ^a	References
ALE	Alert, CAN	82.5°N, 62.3°W / 210	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$ $\Delta^{17}\text{O}$	08/96–01/98 11/96–12/97	70 (1–13) 31 (0–5)	R02
SPI	Spitsbergen, NOR	78.9°N, 11.9°E / 474	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$ $\Delta^{17}\text{O}$	04/96–08/01 11/96–02/99	192 (7–40) 55 (1–8)	R02 ^b
KMW	Kollumerwaard, NLD	53.3°N, 6.2°E / 0	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	10/97–01/01	54 (2–8)	MB00 ^c
SBK	Mt. Sonnblick, AUT	47.1°N, 13°E / 3106	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	09/96–08/01	132 (4–18)	G01 ^{b,d}
MOP	Montauk Point, Long Island, USA	41.1°N, 71.9°W / 45	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	10/96–10/97	46 (3–6)	MK99 ^c
HAP	Happo, JPN	36.7°N, 137.8°W / 1840	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	02/97–12/99	52 (2–7)	K00 ^f
IZA	Izaña, Tenerife, ESP	28.3°N, 16.5°W / 2370	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$ $\Delta^{17}\text{O}$	05/96–04/01 11/96–11/98	90 (5–11) 26 (0–4)	MB00 ^b RB98 ^{g,h}
BAR	Ragged Point, BRB	13.2°N, 59.4°W / 45	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	06/96–04/00	125 (6–15)	M03 ^c
BHD	Baring Head, NZL	41.4°S, 174.9°E / 85	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	06/89–11/05	351 (25–34)	B93 ⁱ
SCB	Scott Base (Arrival Heights), ATA	77.8°S, 166.7°E / 184	$\delta^{13}\text{C}$, $\delta^{18}\text{O}$	06/91–09/05	217 (11–24)	B93 ⁱ

References: R02 – Röckmann *et al.*^[2002], MB00 – Bräunlich^[2000], G01 – Gros *et al.*^[2001], MK99 – Mak and Kra^[1999], K00 – Kato *et al.*^[2000], RB98 – Röckmann *et al.*^[1998], M03 – Mak *et al.*^[2003], B93 – Brenninkmeijer^[1993].

- ^{a)} Indicates the number of (filtered) samples used to construct the climatological season cycle used in the model comparison. Numbers in braces denote the minimum and maximum number of samples falling within the particular month. The data is filtered for consistency of the model comparison (see text), except otherwise stated (*e.g.* model fit is used).
- ^{b)} Referenced are observations prior to 2000. The later unpublished data is provided by P. Jöckel, MPI-C.
- ^{c)} Referenced are observations from 1997–1998. The later unpublished data is provided by C.A.M. Brenninkmeijer, MPI-C.
- ^{d)} The results of the fitting through the background data are used.
- ^{e)} Reported data is processed with three- (BAR) and four- (MOP) week running average. Data from MOP is filtered additionally (see text).
- ^{f)} Model calculation fitting the data is used (scenario with the KIE value for carbon of 1.006, see text).
- ^{g)} Partly unpublished data on $\Delta^{17}\text{O}(\text{CO})$ are provided by T. Röckmann, Institute for Marine and Atmospheric research Utrecht (IMAU).
- ^{h)} Model fit applied to substitute missing $\Delta^{17}\text{O}(\text{CO})$ data (see text).
- ⁱ⁾ The 1994–2005 data from BHD and SCB are provided by Dr. D. Lowe (d.lowe@niwa.co.nz) and R. Moss, G. Brailsford, and R. Martin from National Institute of Water and Atmospheric Research (NIWA), Wellington, New Zealand ([ftp://ftp.niwa.co.nz/tropac/](http://ftp.niwa.co.nz/tropac/)).

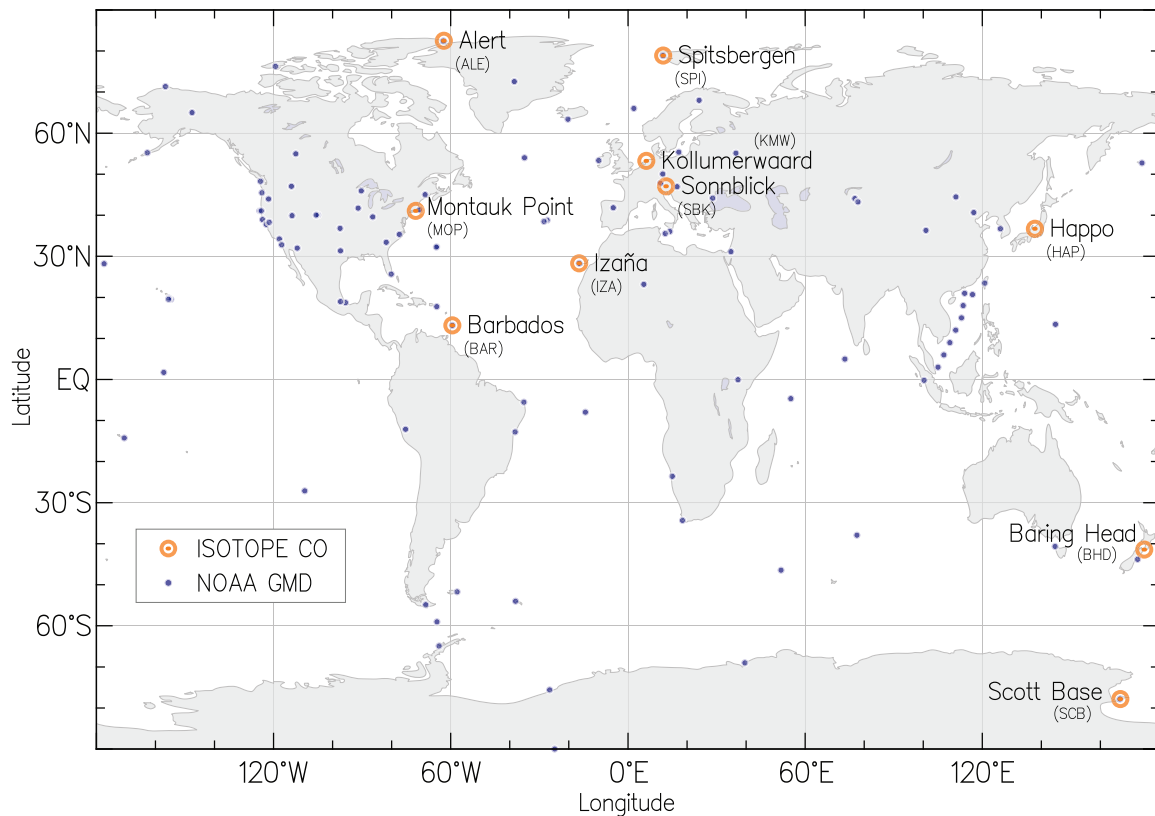


Figure 4.1 Overview of the CO surface mixing ratio observational sites. Isotope-inclusive data are marked with encircled symbols, the remaining symbols pertain to the Carbon Cycle Cooperative Global Air Sampling Network (NOAA ERSI GMD, Novelli and Masarie^[2010]).

The time series of available observations generally span over several years, however, for the majority of sites it is not continuous, *e.g.* interruptions of one or more months occur. Moreover, the simulated CO within this study with the EMAC model corresponds to the emissions for the year 2000 (see Sect. 5.2, p. 118), which is not covered entirely (*i.e.* containing at least one representative sample per calendar month) by the observational series from any of the sites. Therefore, to obtain a consistent record of seasonal CO variations for the comparison with model simulations, average seasonal cycles of $[\text{CO}]$, $\delta^{13}\text{C}(\text{CO})$ and $\Delta^{17}\text{O}(\text{CO})$ were derived for each site. Here, an assumption is made that a particular observation is representative for the sampling calendar week and month of the year, thus contributing to the “climatological” record of the CO annual variation. The “climatological” mixing ratios are calculated as the median of the observed values falling in a particular month, whereas the seasonality for $\delta^{13}\text{C}(\text{CO})$ or $\Delta^{17}\text{O}(\text{CO})$ is derived from the respective averages of the minor and major CO isotopologues’ abundances. Not all data were assimilated in the constructed climatological series, however. For the background sites, samples obviously containing contaminated air (local pollution) were discarded. The methodology of identification of polluted compositions (*e.g.*, selecting outliers with strongly elevated $[\text{CO}]$ and/or drastic changes to the isotope composition, back-trajectory analysis, *etc.*) varies from site to site and hence the reader is referred to the literature cited in Table 4.1 for the details omitted here. Notably, the large bulk of excluded data pertains to the period spanning from fall 1997 to spring 1999, when a large-scale perturbation in CO from its regular (*i.e.* representing the typical background conditions for the year 2000) seasonal cycle was observed (see WDCGG^[2010] and references therein). The latter is attributed to the extensive biomass burning events at both, NH high latitudes (boreal forest fires, Röckmann *et al.*^[2002], Simmonds *et al.*^[2005]) and tropical Pacific Asia (wildfires following the extreme El Niño–Southern Oscillation (ENSO) event) that had an impact on both, tropical and extra-tropical CO compositions (Novelli *et al.*^[2003], Duncan *et al.*^[2003]). The perturbation in 1997/1998 is the only ENSO-related event that occurs within the time span of the NH isotope CO observational data. The consequent disturbance of the CO seasonality is marked in the series from the background sites SPI, ALE, IZA and BAR, but are not much prominent in the ETSH data and at SBK (Röckmann *et al.*^[2002]). We further focus on the mixing ratio, $\delta^{13}\text{C}(\text{CO})$ and $\Delta^{17}\text{O}(\text{CO})$ data series specifically.

4.1.1 CO mixing ratio and $\delta^{13}\text{C}(\text{CO})$ observations

Considering the CO stable carbon isotope data “climatology”, in addition to the assumptions above, it is presumed that the long-term trends in CO mixing ratio and respective isotope compositions are too small to introduce any significant disagreement between the observations prior to 2000 (commonly beginning in fall 1996) and the derived climatology. For the case of ^{13}CO in the ETSH, this is confirmed by the longest records of the isotope-inclusive observations at BHD and SCB extending beyond a decade: The linear fits through their data as a function of time yield slopes not exceeding $\pm 0.3 \text{ ppb yr}^{-1}$ for $[\text{CO}]$ and no significant trends for $\delta^{13}\text{C}(\text{CO})$, respectively. The NH compositions, however, may be subject to an appreciable trend, first of all due to the changes in emission strengths after 1990, particularly for Europe and Asia (see Wotawa *et al.*^[2001], Novelli *et al.*^[2003], Duncan *et al.*^[2007] and references therein). Trend estimates essentially depend on the time window considered; for instance, the global $[\text{CO}]$ decline rate between 1991 and 1996 derived by Novelli *et al.*^[1998] was revised from $-2.3 \pm 0.2 \text{ ppb yr}^{-1}$ to $-1.8 \pm 0.2 \text{ ppb yr}^{-1}$ in the subsequent study encircling 1991–2001 (Novelli *et al.*^[2003]). Congruous to the trends inferred here for the regarded isotope CO series, these authors also conclude much of the changes to the global CO burden pertain to the ETNH (north of 30°N), with no significant trend over 1991–2001 observed in the SH. Compared to the ETSH observations, NH isotope CO data series are short (spanning within 1–5 years) and do not provide a strictly consistent record for the assessment of the long-term trends, being additionally worsened by the discontinuity of the data. This is seen from the statistics calculated for the ^{13}CO -inclusive and concurrent continuous non-isotope observations (referred to hereafter as “regular” for convenience) at selected sites compared in Table 4.2. Thus, the median and spread of CO mixing ratios from the “isotope” and “regular” series are very well comparable, nonetheless the resulting $[\text{CO}]$ slopes for the former amount to few to tens of ppb yr^{-1} , whereas the long-term trends obtained with the regular data are much less significant. In the isotope-inclusive observational data, both $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ slopes progressively diminish with increasing length of the data record, hence a $\pm 0.2\text{‰ yr}^{-1}$ trend in $\delta^{13}\text{C}(\text{CO})$ appears to be

the upper limit for the data from SPI, ALE⁴⁶, KMW, SBK, HAP, IZA and BAR, which cover three and more years of observations. The large slopes for [CO] and $\delta^{13}\text{C}(\text{CO})$ derived for MOP and ALE are, however, not representative based on insufficiently long series of data. The reader is further referred to Figure 4.3 for the overview of the ^{13}C -inclusive observations of [CO] at the surface.

Although NH isotope data do not confer a substantial evidence for small long-term trends in $\delta^{13}\text{C}(\text{CO})$, for the background sites one can surmise that these accompany small or negligible [CO] trends, analogously to the undisputable case for the ETSH compositions. In actuality, the long-term regular observations of CO mixing ratios (depicted in Figure 4.2) show much uniform multi-year variations at SPI, ALE, BAR and IZA, similar to those registered at BHD and SCB. A different example are the observations at HAP and KMW sites capturing a significant fraction of regionally polluted air (Pochanart *et al.*^[2004], Zvyagintsev *et al.*^[2010], Zondervan and Meijer^[1996]), where systematic negative long-term trend is evident even on top of greatly variable CO mixing ratios. Whilst [CO] trends at these sites generally reflect altering surface sources strengths, the principal cause for the concomitant changes in $\delta^{13}\text{C}(\text{CO})$ is the repartitioning between the highly ^{13}C -depleted methane and relatively enriched other sources. The rate of increase of the relative contribution of CH_4 to CO due to the reduction of the surface sources is, nonetheless, likely to be slow, thus introducing small negative trends in $\delta^{13}\text{C}(\text{CO})$ comparable to the other (non-polluted) sites. For example, the estimate of the changes to the CO budget over Europe by Mészáros *et al.*^[2005] suggest an increase of the CH_4 source share in the European inventory on the order of +2% during 1996–2000. This translates into $-0.3\% \text{ yr}^{-1}$ and $-0.2\% \text{ yr}^{-1}$ rates for the European sources and BL air $\delta^{13}\text{C}(\text{CO})$ signatures, respectively.⁴⁷ Notably, this estimate outweighs the observed trends at the continental European sites, KMW and SBK.

Unfortunately, for a few sites (SBK and MOP) there are no concomitant long-term regular observations or estimates of the CO source partitioning available for the comparison with the isotope CO data. Concerning the MOP series, the observed elevated [CO] and $\delta^{13}\text{C}(\text{CO})$ at this site are identified with the large influence of the anthropogenic sources (Mak and Kra^[1999]). Moreover, this observational window is short (covering the period from fall 1996 to fall 1997) and thus least representative for the current model results inferred with the emissions for 2000. On the other hand, the $\delta^{13}\text{C}(\text{CO})$ data at this and other non-background sites (HAP and KMW) show a small scatter and a much more pronounced (compared to the mixing ratios) seasonal variation, which is expedient to compare with the modelling results at least qualitatively. The observations at SBK also grant a clear $\delta^{13}\text{C}(\text{CO})$ seasonal cycle on top of [CO], comparable to the background levels, despite the considerable portion of the data is attributed to polluted episodes (Gros *et al.*^[2001]). Overall, the relatively long series of SBK data SBK (five years) yields a small long-term negative trend for [CO] and insignificant trend in $\delta^{13}\text{C}(\text{CO})$, which are calculated at even smaller values when the samples representing only background conditions are selected (this is done later for constructing the seasonal climatology of CO for this station, see below). At last, Table 4.2 also lists a rough estimate of the discrepancies introduced into the derived seasonality of CO for 2000 due to augmenting the non-2000 data and neglecting the trends in it. The error terms e_s are calculated as the sum

$$e_s = \sum_i (b_s \cdot (i - 2000)) ,$$

where b_s stands for the slope (for [CO] or $\delta^{13}\text{C}(\text{CO})$, in respective units per year) of the linear fit to the data, and summation is performed for every year i the data is available at a particular site. Thus the calculated terms represent the annual average error for 2000, and can be virtually considered as the lower limit on the uncertainty associated with the derived climatologies. Except of the series from HAP, the expected errors are generally low and do not exceed the appreciable uncertainty of the EMAC-simulated CO composition of $\pm 9\%$ for [CO] and $\pm 1.8\%$ for $\delta^{13}\text{C}(\text{CO})$ (see Sect. 6.1.5, Table 6.3), as well as the uncertainties associated with the monthly averages derived for every station (Figure 4.4).

The resulting “climatological” seasonal cycles of [CO] and $\delta^{13}\text{C}(\text{CO})$ applied in the comparison with the model results are presented in Figure 4.4 (p. 74). Figure plates also include the aggregate of the single observations plotted against the respective calendar date of the measurement along with the monthly statistics of the

⁴⁶ Although the length of these data series is insufficient to derive an adequate estimate, it is surmised that the trends at ALE are comparable to those at SPI, as these two sites confer very close mixing ratio and isotope composition of CO accumulated at high NH latitudes (Röckmann *et al.*^[2002]).

⁴⁷ In this calculation it is assumed that the isotope composition of the inflow source (estimated from 39% to 44% of the total inventory of CO over Europe) remains unchanged; the $\delta^{13}\text{C}$ of the sources are taken from the estimates obtained in this study (REF, see Table 6.3).

integrated data. For means of the analysis, the observational sites are categorised as the remote high-latitude (SPI, ALE, BHD, SCB), background NH (SBK, IZA, BAR) and polluted NH (KMW, MOP, HAP), which is clearly reflected in the $[\text{CO}]$ averages and scatter. The observations from the remote high latitude sites offer a very clear seasonal variation of both, $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$, with single observations arranging in a very compact distribution around the monthly means. The characteristic phase shift in CO seasonality between the NH and SH is attributed to the hemispheric alteration of the chemistry regimes and seasonality in surface emissions. The seasonal variation in the median $[\text{CO}]$ at the remote NH sites is more than 3 times larger than that of the SH, ranging from 80 ppb (June) to 170 (February), whereas the SH cycles are constrained within 45 ppb (March) to 70 ppb (October) at BHD (at SCB the dynamics is similar with the mixing ratios being commonly $\sim 5\text{--}7$ ppb lower throughout the year). The concurrent seasonal changes in $\delta^{13}\text{C}(\text{CO})$ at these sites are, in contrast, well comparable, covering $\sim 4\text{‰}$ of minima-to-maxima variation, but around substantially different averages, *viz.* -28‰ to -24‰ at SPI/ALE compared to -31.5‰ to -27.5‰ at BHD (at SCB, generally 0.5‰ higher). The difference in CO burden renders a rather different timing between the $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ extrema in the NH and SH data. Thus, the maxima in the SH $\delta^{13}\text{C}(\text{CO})$ are delayed only by 4–6 weeks (November) with respect to the maxima in the mixing ratio, whereas in the remote NH these are delayed by at least 4 months (June), respectively. Because of the much lower SH CO abundance, the $\text{CH}_4 + \text{OH}$ source activated in austral summer re-fills the CO reservoir with highly ^{13}C -depleted CO much quicker than in the NH, causing the rapid decrease in $\delta^{13}\text{C}(\text{CO})$ only a month later, after the OH starts effectively breaking down CO. A longer and noticeable delay between $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ maxima observed at the extratropical NH sites is due to less intensive chemistry and greater effect of transport governing the remote high-latitude compositions (see below, p. 85).

Table 4.2 Surface [CO] and $\delta^{13}\text{C}(\text{CO})$ statistics for selected sites

Site	regular observations				isotope-inclusive observations							error e_s ^c	
	CO [ppb]			period ^b	CO [ppb]			$\delta^{13}\text{C}(\text{CO})$ [‰]			record length [yr]		
	m	iqr ^a	slope [yr ⁻¹]		m	iqr ^a	slope [yr ⁻¹]	a	iqr ^a	slope [yr ⁻¹]		CO [%]	$\delta^{13}\text{C}(\text{CO})$ [‰]
ALE {	138	59	-0.52	01/'92-12/'09 [†]	134	54	—	-27.1	1.5	—	1.4	+8.5 [†]	—
	128	56	-1.87	01/'92-12/'09 [‡]								+2.4 [‡]	
SPI	139	57	-1.15	02/'94-01/'09 [†]	143	55	-6.83	-26.5	2.1	-0.051	5.3	+1.4 [†]	+0.09
KMW	255	79	-4.19	10/'96-06/'09 [§]	186	69	-11.25	-26.6	1.4	-0.106	3.3	+5.7 [§]	+0.32
SBK					131	39	-2.55	-26.7	2.3	-0.023	5.1	+3.6	+0.04
MOP					182	57	—	-28.2	1.6	—	1.0		
HAP	186	55	-7.95	01/'96-12/'99 ^d	175	88	-21.10	-26.2	2.0	-0.161	2.8	+17.8 ^d	+0.64
IZA	105	33	-0.31	11/'91-10/'09 [†]	99	30	+0.93	-27.4	2.4	+0.187	4.9	+0.7 [†]	-0.42
BAR	92	27	-0.40	03/'92-02/'09 [†]	105	25	-0.57	-28.4	2.9	-0.123	3.8	+0.9 [†]	+0.28
BHD					59	16	-0.12	-29.6	2.4	+0.002	16.4		
SCB					52	15	-0.32	-28.9	1.5	-0.020	14.2		

Notes:

The isotope-inclusive observations statistics for background sites are calculated from filtered data, *i.e.* excluding samples identified to pertain to the polluted conditions. Record length denotes the span between the first and last collected sample. Where possible, trends are calculated from series spanning over the whole number of years, excluding incomplete year residues.

- ^a) Given are the median value (*m*) and the interquartile range (*iqr*, the difference between the upper and lower quartiles) of all samples constituting the series. For regular observations, monthly means are used, except for the data from KMW represented by the daily means. For isotope-inclusive series, the event data is taken in the calculation.
- ^b) Time span the statistics and slopes are derived for. Symbols denote the data obtained from the World Data Centre for Greenhouse Gases (WDCGG, <http://gaw.kishou.go.jp/wdcgg/>) pertaining to the following contributors: (†) NOAA/GMD, (‡) CSIRO and (§) RIVM.
- ^c) Estimated discrepancy introduced into the “climatological” averages for 2000 due to neglecting the long-term trend in non-2000 data.
- ^d) Based on monthly data from Pochanart *et al.* ^[2004]; incomplete series from the year 1997 is excluded from the calculation.

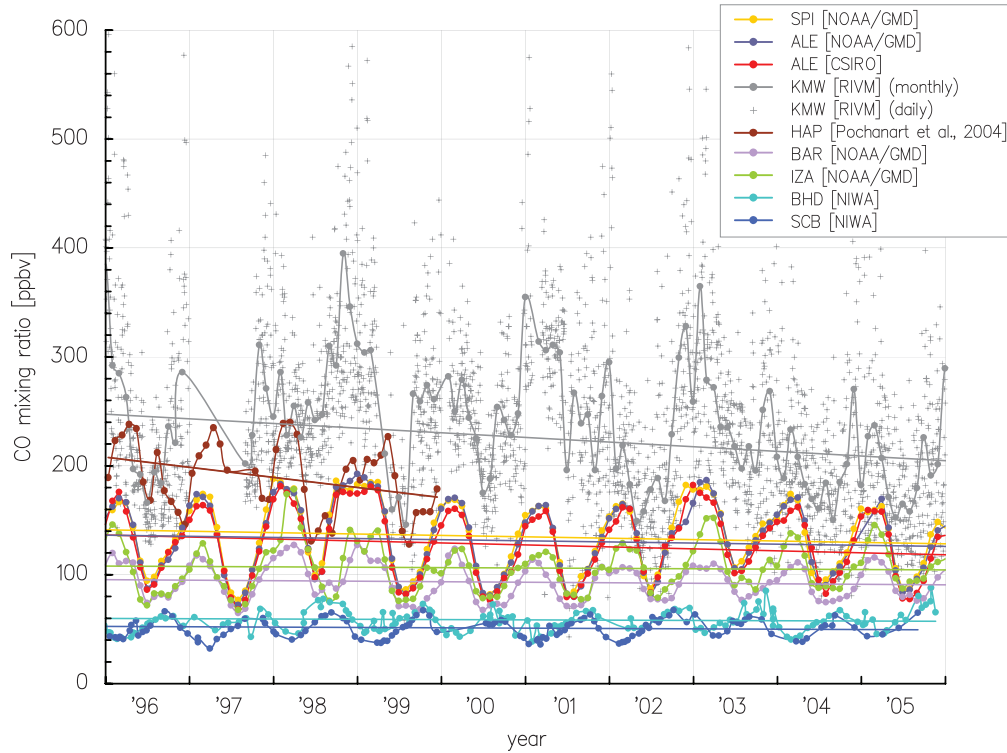


Figure 4.2 (accompanies Table 4.2) Continuous record of the regular (non-isotope) observations of CO mixing ratio at several sites the isotope CO data is available from. All data points are monthly means except of daily and event data presented for KMW and BHD/SCB, respectively. Data from BHD and SCB are from the simultaneous mixing ratio and isotope composition observations (referenced in Table 4.1). Linear fits are derived for the entire data span (differs for each site, only 1996–2005 period is depicted).

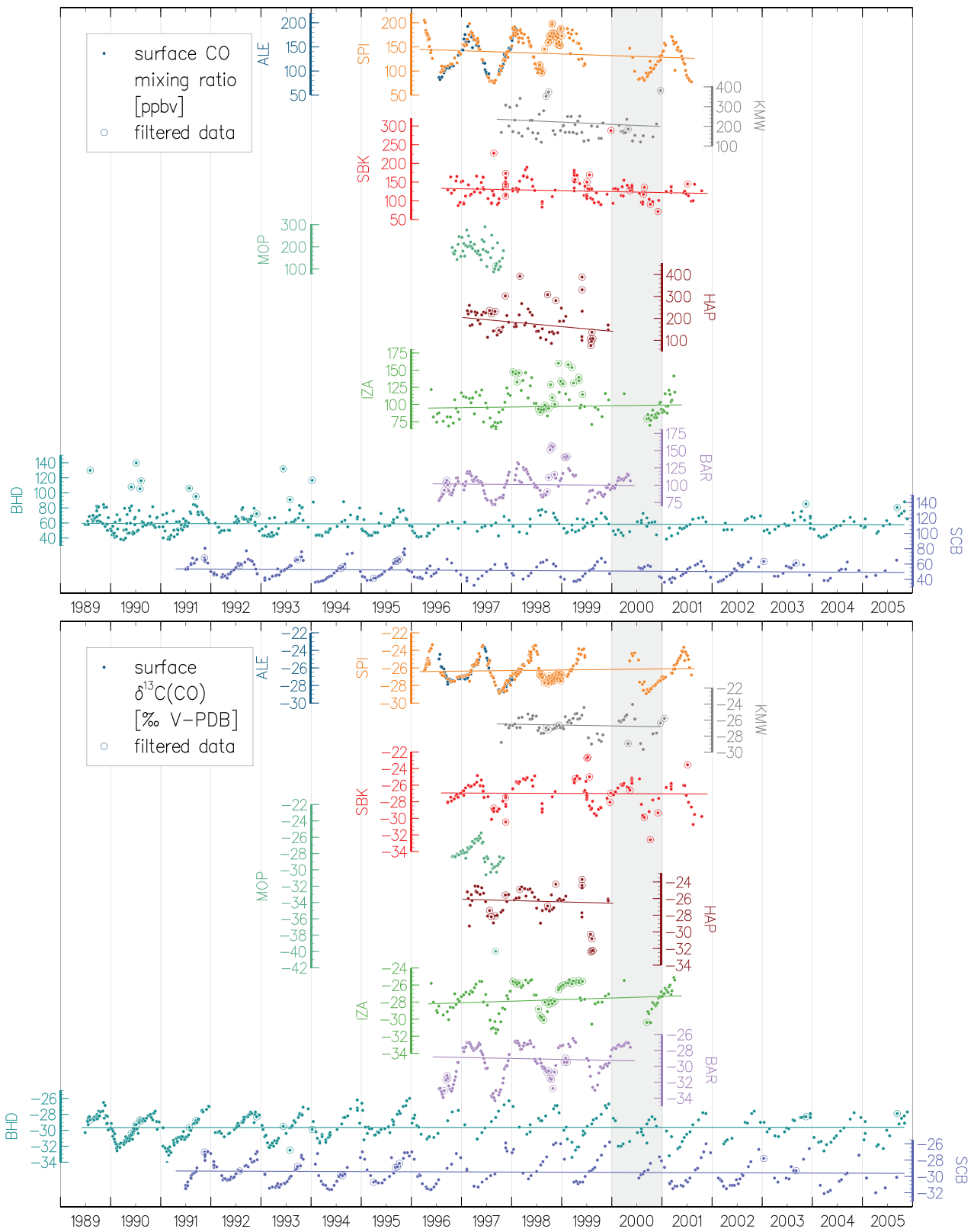


Figure 4.3 Temporal coverage of the simultaneous observations of CO mixing ratio and ^{13}C at the surface available to date. Different colours denote different observational sites, solid symbols mark the flask samples collected, open circles denote the samples disregarded (see text). Solid lines are the linear fits to the data as a function of time.

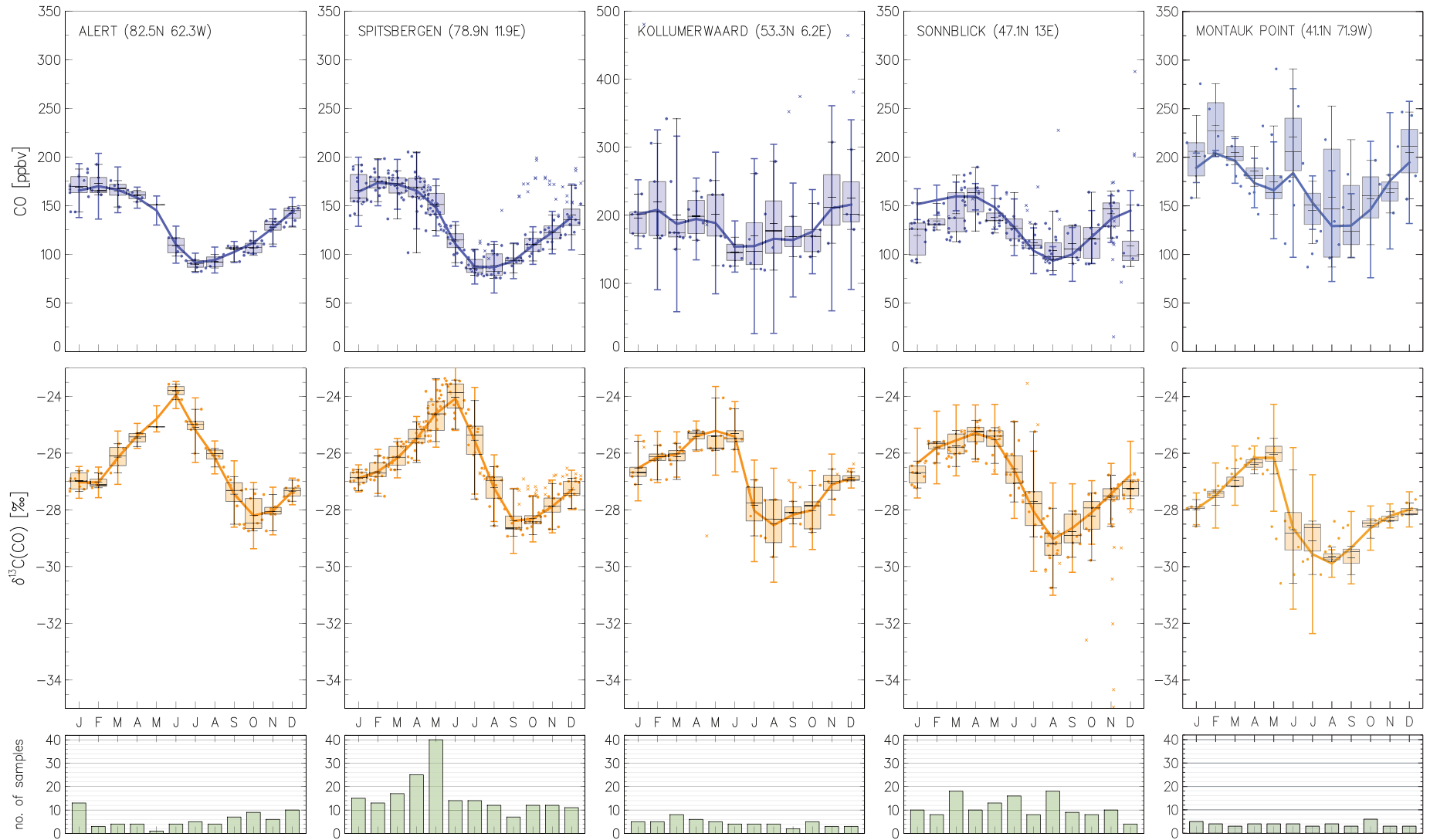
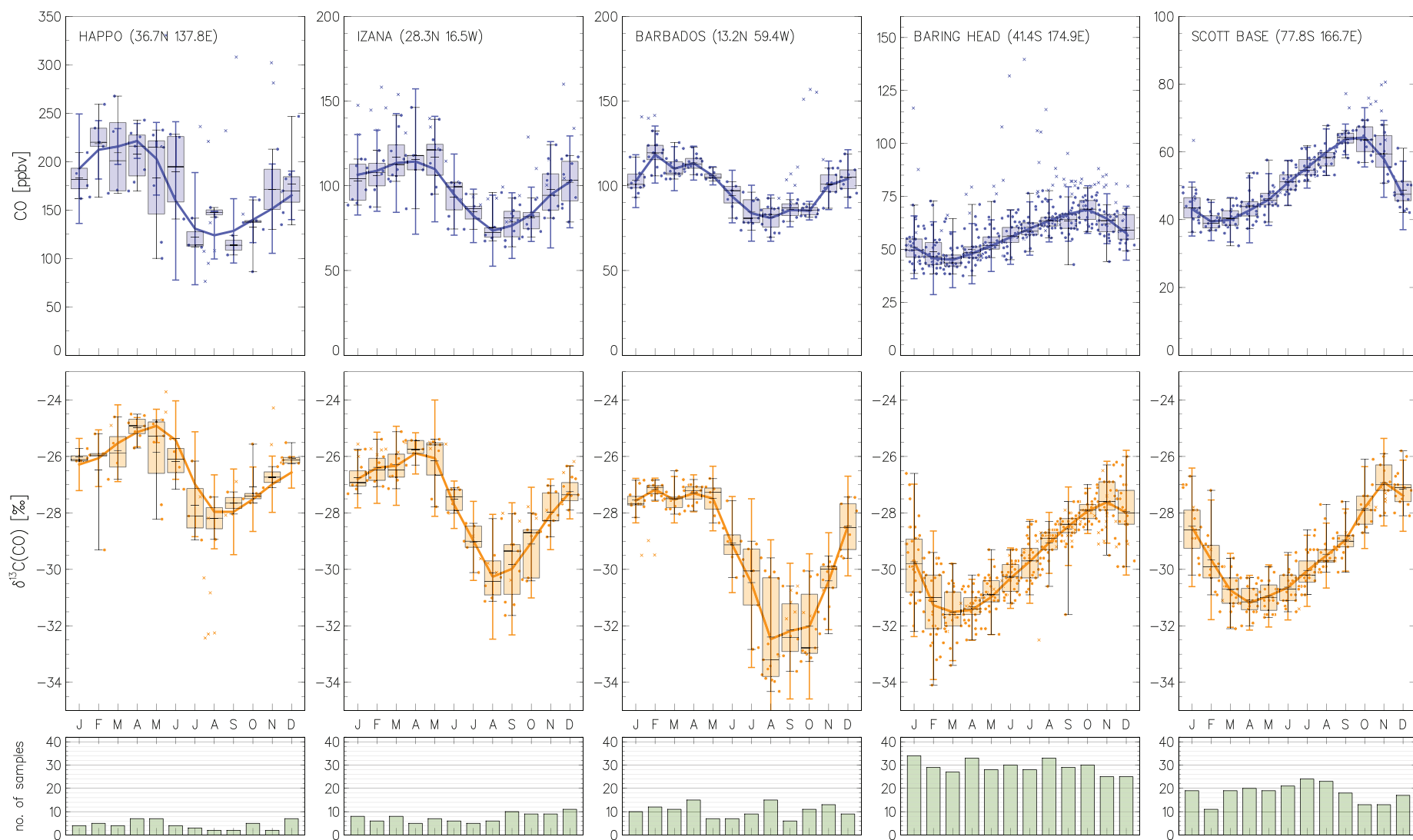


Figure 4.4 Seasonal cycles (solid lines) of the surface CO mixing ratio (top panel) and corresponding $\delta^{13}\text{C}(\text{CO})$ (middle panel) constructed from the observational series at particular sites (see Table 4.1). Error bars are given as ± 2 standard deviations of the monthly data. Symbols denote the single observations taken into account (solid) and disregarded (crosses) while constructing the climatologies.

(continued on next page)



Generally all surface $\delta^{13}\text{C}(\text{CO})$ data show a distinct seasonal variation, even at the polluted sites where the $[\text{CO}]$ seasonality is obscured by the large scatter, which is generally the case for the series characterised with a scant amount of data. For instance, the least average number of representative samples (~ 4 per month) pertains to ALE, KMW, MOP and HAP series, with the number of samples comprising half or more of the seasonal means being below this average. Notwithstanding that, for several sites, where possible, the derived climatologies were amended with the aid of the ancillary analysis of the data conferred by the authors. Thus, for HAP series, the results obtained with the isotope-inclusive box model study (Kato *et al.*^[2000]) designed to reproduce CO mixing and isotope ratios at this site were used. Their simulated compositions (adopted in the seasonal curves) suggest a smoother transition of $[\text{CO}]$ during its annual minima (June to September) than the spread of 10–25 ppb inferred from the actual representative samples. The actual sample number is low (2–3 per month), hence it is likely that they favour the compositions with significantly different shares of the polluted/background air that do not represent the typical conditions expected from the model. The difference between the average samples' $\delta^{13}\text{C}(\text{CO})$ and the climatology are congruous with those for $[\text{CO}]$. For example, higher and lower $[\text{CO}]$ in June and July both are associated with lower $\delta^{13}\text{C}(\text{CO})$, which in effect is the similar response to the different factors determining the ^{13}C content. In the first case, elevation of $[\text{CO}]$ causes a lower effective ^{13}C enrichment in the $\text{CO}+\text{OH}$ sink compared to the seasonal dynamic equilibrium value. The other case is a source effect, as the lower $[\text{CO}]$ from much cleaner air bears a larger fraction of ^{13}C -depleted methane-derived CO. The temporal superposition of these two disturbances inadvertently results in a generally better agreement of the seasonality of $\delta^{13}\text{C}(\text{CO})$ with the actual data than that for $[\text{CO}]$. Importantly, in the results of Kato *et al.*^[2000] the best fit to the $\delta^{13}\text{C}(\text{CO})$ data was achieved assuming higher effective enrichment induced in the CO sink, with the fitted value for the 3 km altitude-average of $\sim 6\text{‰}$ *vs.* $\sim 4.5\text{‰}$ calculated from the conventional ^{13}C KIE formulation implemented in the reference model setup. This is in line with the fact that the authors used earlier ^{13}C KIE data of Stevens *et al.*^[1980] favouring lower KIE magnitudes, and supports the conclusions drawn below (see Sect. 6.1.4.2, p. 152) that the atmospheric ^{13}C KIE in $\text{CO}+\text{OH}$ sink is expected to be larger. Indeed, the EMAC-simulated enrichment for the composite KIE in the BL ($\sim 6\text{‰}$ in AK setup, *cf.* Table 6.2, p. 154) is in a good agreement with the findings of Kato *et al.*^[2000].

The seasonalities at SBK were amended with the help of the low-pass convolution filtering (Jöckel^[2001]) of the mixing ratio and $\delta^{13}\text{C}(\text{CO})$ data. Curve fittings are performed for the background compositions that comprise nearly 50% of the complete SBK record (Gros *et al.*^[2001]). The uncertainties assigned to the climatologies are calculated from the variability of the multi-year weekly values of the fitted curves and are hence larger than those reported for the curves themselves. Similarly to the series from HAP, one remarks smaller disagreement between the actual sample data and the seasonality for $\delta^{13}\text{C}(\text{CO})$ compared to that of $[\text{CO}]$. The inferred climatology (monthly means calculated from the fitted curves) accounts for higher CO mixing ratios and their smoother transition in the winter period, retaining $[\text{CO}]$ maxima at the end of March. Because of the lowest importance of the sink enrichment throughout winter time, lower actual $\delta^{13}\text{C}(\text{CO})$ values reflect a smaller contribution of the enriched composition from ^{13}C -enriched sources.

An alternative post-processing routine was applied by Mak and Kra^[1999] (“MK99”) and Mak *et al.*^[2003] (“M03”) to the observational data from MOP and BAR, respectively. Because these records comprise weekly event data, the running averages of three- (BAR) and four-week (MOP) time windows were derived to better identify the seasonal variations of CO. The record from MOP is characterised by the large week-to-week variability in $[\text{CO}]$ driven predominantly by the input from anthropogenic CO sources and additionally further promoted by the atmospheric stability inhibiting the admixing of the marine background air in summer. This is reflected in the statistics on CO mixing ratios in unprocessed data from June to October in Figure 4.4. Nonetheless, the authors single out the intrinsic seasonality from the lower part of the $[\text{CO}]$ monthly distributions by means of the filtered floating average (FFA) analysis. The latter is calculated by discarding the samples with $[\text{CO}]$ outlying one standard deviation range of the ordinary floating average. The monthly means of thus obtained FFA results are adopted here as the seasonalities for $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ at MOP. Conformably, these suggest monthly CO mixing ratios at the low end of the IQR⁴⁸ of the sample data distribution throughout the summer-fall period, with the monotonic increase until the maximum in February. This is unusually early and rather characteristic for the low tropics (see also Figure 4.8), whereas for mid-latitude NH locations one expects

⁴⁸ The interquartile range (IQR) is equal to the difference between the upper and lower quartiles of the data distribution and used throughout this analysis as a robust measure of the monthly data spread instead of the standard deviation. IQR is graphically represented by the size of the boxes in the box-whisker plots shown in Figure 4.4 and others.

the maxima to occur two months later, as it is observed at SBK, HAP and IZA, for example. The subsequent decrease in $[\text{CO}]$ until May is followed by the summer peak in June that propagates into the seasonality from the sample data regardless of filtering with FFA. From the similarity between the annual profiles of the regional energy consumption rate in 1996–1997 and changes in monthly $[\text{CO}]$, MK99 conjecture that CO variations are driven by the seasonal changes in anthropogenic emissions. However, the reciprocal dynamics of $[\text{CO}]$ and its isotope composition in February–May suggest, on the contrary, that they are likely to be of photochemical origin. To accompany the drop in $[\text{CO}]$ of ~ 20 ppb by an appreciable change of $+0.5\text{‰}$ in $\delta^{13}\text{C}(\text{CO})$ and -1.3‰ in $\delta^{18}\text{O}(\text{CO})$ per month, the effective fractionation in CO removal should be at least of $^{13}\text{C}\epsilon = +5\text{‰}$ and $^{18}\text{O}\epsilon = -11.5\text{‰}$, respectively, assuming the simplest case when no production but only the breakdown of CO takes place.⁴⁹ This is very close to the fractionations expected when predominantly CO+OH sink takes place (see Sect. 3.4.4), with somewhat lowered $^{13}\text{C}\epsilon$ and elevated $^{18}\text{O}\epsilon$ due to the production of CO from the ^{13}C - and ^{18}O -depleted photochemical sources, contrary to the effect of the input from the enriched surface sources (see further an example of that for KMW). The rates of change of $\delta^{13}\text{C}(\text{CO})$ and $[\text{CO}]$ in spring at MOP are the highest amongst all mid-latitude stations, thus prior to summer the seasonality at MOP clearly outruns the expected mid-latitude timing. Starting from June, the changes in CO resemble characteristic NH mid-latitude dynamics, with the average winter $\delta^{13}\text{C}(\text{CO})$ being 1–2‰ lower than that for other mid-latitude locations. MK99 interrelate the double peak in seasonal $[\text{CO}]$ with the highest regional energy consumption rate in June 1997; nonetheless, the majority of encountered elevated mixing ratios witnesses sufficiently low $\delta^{13}\text{C}(\text{CO})$ values that are unlikely to originate from the relatively enriched anthropogenic sources, thus the reoccurring $[\text{CO}]$ peak does not correlate with the continuous decrease in ^{13}C content from May to July. A plausible explanation assuming the observed CO compositions pertain to different source regions with much dissimilar ^{13}C signature remains ambiguous, since no analysis of the origin of air masses arriving at MOP was presented by MK99. The latter could potentially cast light on the peculiar “switching” of the CO seasonality between typical mid- and low-latitude profiles. Furthermore, the authors could not identify the origin of the systematically lower $\delta^{13}\text{C}(\text{CO})$ values observed throughout the year at MOP. These are generally lower by 1–2‰ compared to the body of other mid-latitude data.

Analogous to MOP, the observational data from BAR were smoothed with 3-week running averages, but not filtered (M03). In addition, about 8% of the samples unambiguously identified as polluted were disregarded in the constructed seasonalities (shown in Figure 4.4). The dynamics of tropical CO isotope composition at BAR is prominently different from that typically observed at mid- and high-latitude NH locations. The characteristic maxima in $\delta^{13}\text{C}(\text{CO})$ preceding its rapid decline in summer are absent, as well as the continuous enrichment of CO in ^{13}C from January to May. The inventory of CO in the tropics is much equilibrated due to intensive photochemistry, first of all due to the availability of OH and its weaker seasonal changes. Consequently, the variation in effective CO fractionation induced by the KIE in the OH sink is expected to be less extreme in the tropics than at higher latitudes, where the spring-autumn variation in $\delta^{13}\text{C}(\text{CO})$ is accentuated due to the shortage of OH in wintertime. On the other hand, OH-triggered photochemical production of CO, particularly from methane, also starts modifying $\delta^{13}\text{C}(\text{CO})$ in the tropics much earlier. At BAR, the flat $\delta^{13}\text{C}(\text{CO})$ shoulder in winter-springtime is a coincidental superposition of impacts from the increasing ^{13}C -depleted CO share stemming from the methane source, and the strengthening of the effective enrichment in the CO+OH sink, until the former takes over in June. Similarly to other mid-latitude NH stations, $\delta^{13}\text{C}(\text{CO})$ minima occur in August, presumably corresponding the greater share of photochemically derived CO in the atmospheric reservoir. February maxima in $[\text{CO}]$ at BAR appear to be an artefact from the multi-year large winter surface emission component, since the elevated mixing ratios correlate with both enhanced $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ characteristic for biomass burning and industrial/fossil fuel usage emission (not shown, see M03). The expected background seasonal maxima in tropical $[\text{CO}]$ at this latitude, however, are likely to occur in April, in accordance with the “regular” observations of MBL CO (see below, also Figure 4.8). Furthermore, in contrast to the observed annual span of 3‰ to 4.4‰ at the mid- and high-latitude NH locations, the observed seasonal variation of $\delta^{13}\text{C}(\text{CO})$ at BAR exceeds 5‰ (up to 7‰ in monthly means from particular years), which, as concluded by M03 and the model study they employ, cannot be explained exclusively by the larger input of

⁴⁹ Quoted are the averages of the sink fractionation enrichments of $+4.7\text{‰}$ to $+5.2\text{‰}$ for $\delta^{13}\text{C}(\text{CO})$ and -10.6‰ to -13.1‰ for $\delta^{18}\text{O}(\text{CO})$, respectively, calculated with respect to the February values. The enrichments ϵ are obtained using the Rayleigh fractionation process for the open systems relation $^{i}R/^{i}R_0 \approx f^{\epsilon}$, where $^{i}R_0$ and ^{i}R denote the isotope ratios of the i^{th} isotopologue (^{13}C or ^{18}O) in February and subsequent months, correspondingly; f is the fraction of the leftover CO compared to the value in February.

CH₄ to CO. To put it into perspective, the average ¹³C content at BAR is systematically lower than that at IZA, notwithstanding the comparable CO mixing ratios observed at these (sub-)tropical locations. To account for a typical 2–4‰ difference in summer $\delta^{13}\text{C}(\text{CO})$ between IZA and BAR, an equivalent increase of the CH₄ source share in the CO inventory at BAR relative to that at IZA should be on the order of 8% to 16%, which is unlikely regarding even slightly lower summer mixing ratios recorded at IZA⁵⁰. Moreover, the respective mass-balance of the C¹⁸O content at BAR does not yield signatures close to those expected for the CH₄-derived CO, but rather of an unknown and untypical ¹³C-depleted and ¹⁸O-enriched source. Ultimately, one year (July 1998 to June 1999) out of the four-year record of CO at BAR presents the $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ profiles very similar to those observed at IZA, however the remaining data deviates in an excursive manner. This is marked in large uncertainties associated with $\delta^{13}\text{C}(\text{CO})$ seasonality at BAR throughout July–October (Figure 4.4). One also notes the semblance between the low unexplained $\delta^{13}\text{C}(\text{CO})$ values in BAR and MOP data.

There is no specific analysis available for the isotope-inclusive observations at KMW, except of Bräunlich^[2000] who examines the $\delta^{18}\text{O}(\text{CO})$ data and suggests that CO variations at this continental station are generally driven by the input from local and regional sources. This inference is based on the relation between the observed mixing ratios and ¹⁸O content of CO in the two-component mixing model, which yields the $\delta^{18}\text{O}(\text{CO})$ signature of the admixed compositions in elevated CO close to the characteristic value of –23.5‰ associated with combustion processes (see Figure 4.5, right panel). From the tight correlation of $\delta^{18}\text{O}(\text{CO})$ and reciprocal [CO], it is concluded that admixing of CO from the surface sources overrules the effect of fractionation induced in the CO sink, *i.e.* the seasonal variations in effective enrichment due to CO+OH are negligible. The above stated is indeed valid in instances when observed CO mixing ratios are high and their variation is attributed exclusively to the pollution events. The latter, however, is not the case regarding the KMW record, as the variations in concomitant $\delta^{13}\text{C}(\text{CO})$ data indicate. The misjudgement in case of applying the mixing model approach (MMA) to $\delta^{18}\text{O}(\text{CO})$ may be caused by its incapacity to discern between similar effects of sink fractionation and photochemical production of CO on the final $\delta^{18}\text{O}(\text{CO})$ of the atmospheric reservoir. As the ¹⁸O KIE in CO+OH is inverse, and the $\delta^{18}\text{O}$ signature of the photochemically produced CO is lower than that of the surface emissions (~0‰ or lower *vs.* ~17‰ and higher, see Table 3.7, p. 56, for references), both processes deplete CO in ¹⁸O. Therefore, in case the effect of the OH sink is neglected (but actually present), the mixing model approach may overestimate the signature of admixed CO by underestimating the background $\delta^{18}\text{O}(\text{CO})$, and *vice versa*. The mid- and high-latitude NH stations are likely to be prone to that, because the effects of the sink fractionation and photochemical production are not simultaneously developed in the CO composition there. When OH appears in spring, breakdown of CO immediately starts to modify its isotopic composition, whereas the photochemical source, particularly from CH₄ oxidation, manifests itself somewhat later, after passing through the set of intermediates and diluting the large atmospheric burden (this is marked in the NH $\delta^{13}\text{C}(\text{CO})$ data, see above). This lag affects the consistency of the inferred dilution line slope: It does indeed reflect the mixing between the surface sources and a certain background composition, but the latter varies rapidly throughout the year, first with the increasing sink fractionation effect and later contained in a certain dynamical equilibrium with the photochemical sources. By chance, the equilibrium holds at a similar $\delta^{18}\text{O}(\text{CO})$ value, hence the resulting correlation of $\delta^{18}\text{O}(\text{CO})$ with reciprocal [CO] is compact. Nonetheless, if the significant part of variations in [CO] and $\delta^{18}\text{O}(\text{CO})$ pertains to the changes in background composition, the inferred $\delta^{18}\text{O}$ signature of the admixed CO becomes less certain.

Furthermore, if the sink effect were of least importance, a similar mixing-kind relationship would be observed for the $\delta^{13}\text{C}(\text{CO})$ data, which is not the case. On the contrary, ¹³C at KMW does not correlate with [CO]⁵¹, which can be explained only by the substantial role of the CO sink fractionation in the dynamical framework described above. In contrast to ¹⁸O, the ¹³C KIE in CO sink is positive, hence it enriches the atmospheric reservoir in ¹³C in spring, before the ¹³C-depleted photochemical CO sources outcompete it in summer. Such dynamics of CO, $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ at KMW is discernible in the two-isotope plot presented in Figure 4.5 (left panel). The polluted air samples with elevated [CO] in November–February are located around –27‰ and +16‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively, closest to the average composition of the surface CO sources. The observed compositions in March–June are clustered away from this point further towards more

⁵⁰ Surmising the only highly ¹³C-depleted source of CO capable to sufficiently deplete the atmospheric reservoir being the oxidation of CH₄ by OH.

⁵¹ The linear fit to the $\delta^{13}\text{C}(\text{CO})$ data as the function of reciprocal [CO] at KMW yields $R^2 = 0.0029$ compared to 0.8028 of that for $\delta^{18}\text{O}(\text{CO})$, respectively.

^{18}O -depleted and ^{13}C -enriched values, in concord with the anticipated influence of the sink fractionation. Later, from June to August, $\delta^{13}\text{C}(\text{CO})$ experiences a stark change towards more ^{13}C -depleted photochemical sources. These, however, keep $\delta^{18}\text{O}(\text{CO})$ virtually unaltered, being depleted in ^{18}O comparable to the background CO persisting in a dynamical equilibrium with the sink fractionation. From September on, the isotope compositions return along the approximate mixing line (dashed in Figure 4.5) between the photochemical and surface sources' averages, with continuously raising mixing ratios till late winter. Remarkably, the large variations of 6‰ in $\delta^{13}\text{C}(\text{CO})$ in summer samples with lowest $[\text{CO}]$ clearly reflect the dynamics between the photochemical sources and sink fractionation, but not the possible contamination from the admixed polluted compositions that are much effective at low mixing ratios. Should a polluted, ^{13}C -enriched sample, be encountered, it is expected to bear also an ^{18}O -enriched composition; the regarded samples are, however, all below 4‰ in $\delta^{18}\text{O}(\text{CO})$.

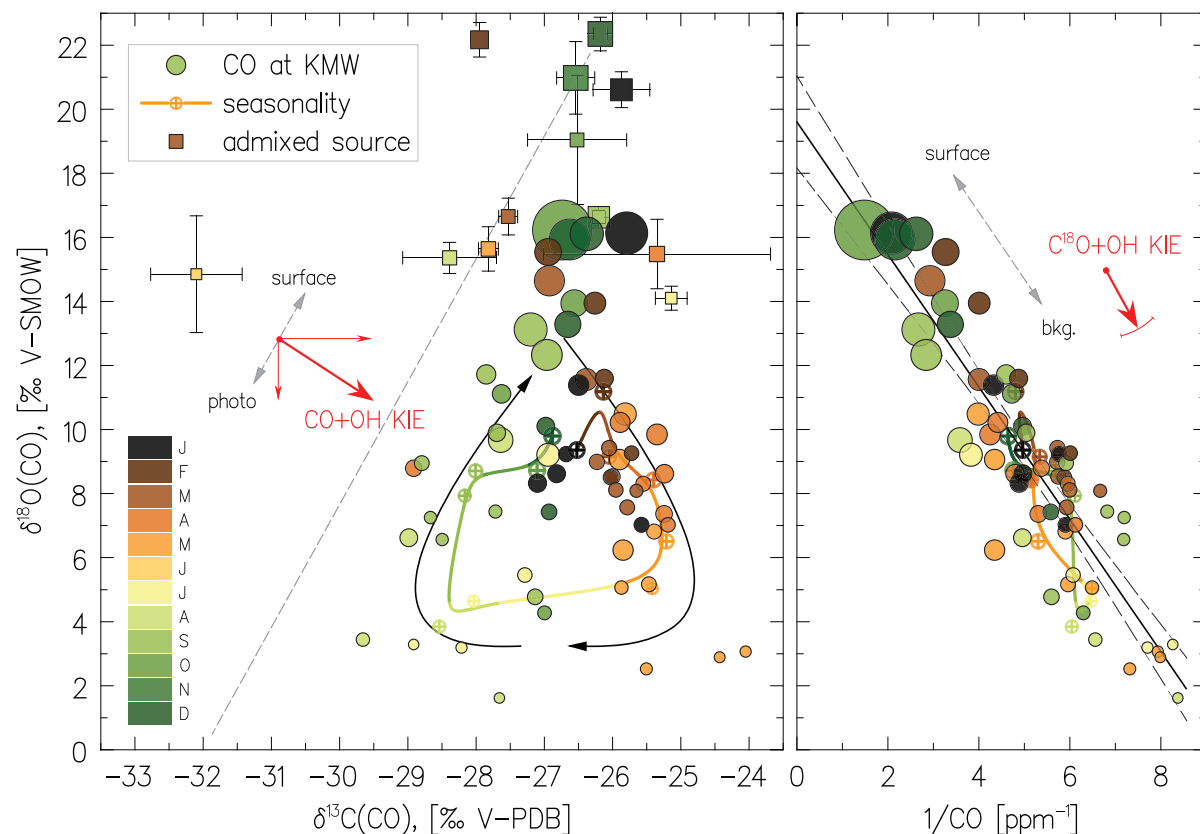


Figure 4.5 Isotopic composition of CO registered at KMW. Filled circles denote observations; symbol sizes scale proportionally to the mixing ratio (120–680 ppb), colours signify the calendar month. Coloured line navigates through the seasonal averages (crossed symbols). Red arrows denote the magnitude of the $\text{CO}+\text{OH}$ KIE (scaled as 1:5 to fit in the panels). Left: Seasonal variation of CO composition in the two-isotope plot. Solid arrows present the typical evolution of the isotope compositions throughout the year. Dashed line shows the approximate transition of the overall CO source mix composition from the surface (enriched in heavy isotopes) towards the photochemical (depleted, respectively) sources. This way the actual observed compositions are deflected on the graph towards bottom-right from the mixing curve by the $\text{CO}+\text{OH}$ sink KIE. Solid squares denote the signatures of the admixed compositions derived with the mixing model approach (Keeling plot) applied to particular month data (see text), with error bars indicating 95% confidence levels of the linear fit through $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ as the function of reciprocal $[\text{CO}]$. Right: Keeling plot showing the variations in $\delta^{18}\text{O}(\text{CO})$ as a function of inverse CO mixing ratio. The dilution curve (solid line and dashed lines denoting 95% confidence bands) is derived as the linear fit through all data (intercept at 19.6 ± 0.7 ‰, $R^2 = 0.80$). The red arrow exemplifies the average direction of the composition change upon the CO sink, with the error bar denoting its variation depending on the starting $[\text{CO}]^{-1}$ of $5 \pm 3 \text{ ppm}^{-1}$, respectively.

To note, the overall photochemical CO source $\delta^{13}\text{C}$ signature determining the low endpoint of the mixing line in Figure 4.5 is greater than that of the CH_4+OH source, owing to a considerable share of the ^{13}C -enriched NMHC-derived CO, whose $\delta^{13}\text{C}$ is higher and close to that of the surface sources. The here adopted value of (-32 ± 1) ‰ is derived from the annual estimates by Mészáros *et al.*^[2005] for the European CO inventory in 1995–2000 (see above, p. 70), corresponding to the share of the CH_4+OH source in the total photochemical CO source varying within ~20–25%, respectively, and the range of NMHC signatures from the literature (see Sect. 5.2.5, p. 131). It is difficult, nevertheless, to derive a similar estimate for $\delta^{18}\text{O}$, as the oxygen isotope composition of CO stemming from hydrocarbon oxidation sources is not known from laboratory experiments. Current estimates of the $\delta^{18}\text{O}(\text{CO})$ signatures from oxidation of both, CH_4 and NMHC, fall within -10 ‰ to

+10‰ range, likely being close to 0‰ or below this value (Gros *et al.*^[2004], Brenninkmeijer *et al.*^[1999b], see also Sects. 3.4.2, 3.5.1). Here, the median of these estimates (0‰) is accepted for the $\delta^{18}\text{O}$ signature of the photochemical sources, which still leaves all observed compositions below the surface-photochemical sources mixing line, denoting that each sample carries some nonvoid portion of the effective enrichment induced by the KIE of the CO sink. Along with the observations, Figure 4.5 (left panel) presents the isotope signatures of the admixed source calculated with the MMA for the observations falling in the particular calendar month, hence assuming monthly invariable background CO. The derived admixed source $\delta^{18}\text{O}$ is conspicuously higher in late fall and winter, when chemical alteration of CO is weak, stacking up above +20‰. Similarly, one notes elevated surface sources' carbon isotope signatures around -26‰ in $\delta^{13}\text{C}$. In the summer months, however, the MMA yields a wide span of $\delta^{13}\text{C}$ signatures which clearly outstrip the typical surface sources' range being deteriorated by the input from the sink enrichment and chemical production. Oddly enough, the concurrent $\delta^{18}\text{O}$ signatures are compacted around $(-15 \pm 1)\text{‰}$ and show tighter correlation with the reciprocal $[\text{CO}]$. Now, if we surmise in a plain case, that the actual (*i.e.*, not derived with the MMA) isotope composition of the admixed surface sources is invariable and is close to the winter values, straying of MMA-derived sources' $\delta^{13}\text{C}$ is likely to be the result of changing background $\delta^{13}\text{C}(\text{CO})$.⁵² A case in point are the inferred low June and high July values that are far and contrariwise deflected from the approximate mixing line, in an inverse relationship with the rapid drop in seasonal $\delta^{13}\text{C}(\text{CO})$ at KMW in this period (see Figure 4.4, p. 74). These over- and underestimated signatures are the artefact of the MMA, interpreted as the shift of the intercept point (at $[\text{CO}]^{-1} \rightarrow 0$) in the Keeling plot, when the background composition changes notably. In case of $\delta^{13}\text{C}$, the background signature varies around the actual composition of the admixed source, thus the MMA yields both, over- and underestimated signatures. By analogy, the admixed source $\delta^{18}\text{O}$ calculated with the MMA is expected to be influenced by the variations in the seasonal $\delta^{18}\text{O}(\text{CO})$. The profile of the latter, however, is different to that of $\delta^{13}\text{C}(\text{CO})$ and presents similar to $[\text{CO}]$ dynamics, with lower summer and elevated winter values (see also Figure 4.5, right panel), yet always below the expected ^{18}O -enriched surface compositions above +17‰. Therefore, due to the summer drop in seasonal $\delta^{18}\text{O}(\text{CO})$, MMA-derived $\delta^{18}\text{O}$ signatures of the admixed source appear to be overestimated, whereas the correct ones should be more negative, *i.e.* closer to the anticipated photochemical sources' signature of 0‰. The general conclusion from the above given analysis is that as long as the summer source $\delta^{13}\text{C}$ signatures inferred with MMA are inconsistent, it concerns the concurrent $\delta^{18}\text{O}$ signatures as well. The most reliable estimates of the admixed source composition are likely to be those inferred for the winter months, whereas based on the complete (*i.e.*, annual) set of the observations, the MMA will provide less certain $\delta^{18}\text{O}$ values. That is confirmed for the data at KMW: Applied to the entire observations dataset, the MMA yields the $\delta^{18}\text{O}$ of admixed sources at $(19.6 \pm 0.7)\text{‰}$, lower than the winter values of up to +23‰ that are close to the typical composition from the fossil fuel usage CO. Another example is the largest encountered $[\text{CO}]$ (~670 ppb) in November that bears $\delta^{18}\text{O}(\text{CO})$ of ~16.5‰ nearly matching the composition of CO from biomass burning. It is not possible in this case, however, to discern whether the MMA-inferred admixed source' $\delta^{18}\text{O}$ for November of +19‰ is the artefact from the varying background $\delta^{18}\text{O}(\text{CO})$ or results from admixing of more enriched (*e.g.* fossil fuel use) sources.

The characteristic triangular shape of the $\delta^{13}\text{C}(\text{CO})$ *vs.* $\delta^{18}\text{O}(\text{CO})$ distribution in Figure 4.5 is typically observed at the other sites as well, particularly background ones. This suggests that the data from KMW capture isotope ratio variations much comparable to that of the background compositions, however on top of generally elevated CO mixing ratios. The comparison of the statistics on CO mixing ratios from the isotope-inclusive record with the concomitant regular observations (shown in Figure 4.6) also supports that. The overall number of the isotope-inclusive data (event samples) amounts to roughly 5% of the number of regular data (daily means), with both datasets presenting different $[\text{CO}]$ distributions and median values.⁵³ The monthly averages of $[\text{CO}]$ derived from the isotope-inclusive data commonly fall in the lower quartile range of the regular data distribution, with the monthly midspreads (inter-quartile range and median) of the datasets showing a reciprocal relationship. The seasonal variations of $[\text{CO}]$ from both datasets are resembling, although the isotope-inclusive series show much weaker seasonal cycle compared the other polluted NH sites presenting similarly elevated mixing ratios. In particular, $[\text{CO}]$ minima clearly seen at high-latitude NH stations and SBK/MOP are less promi-

⁵² The term "background" here denotes the seasonal averages of CO mixing ratio (ranging within 150–210 ppb at KMW) and isotope composition taken as the state of the background reservoir into which the surface source is admixed in the MMA.

⁵³ The event sampling for CO isotope analysis was introduced at KMW to selectively pick background air in occurrences of low CO mixing ratios registered in the concomitant regular observations, hence the bias between the datasets' distributions is consistent.

nent at KMW, with July–August compositions retaining less clean air with additional 20–30 ppb from the surface sources and slightly risen $\delta^{13}\text{C}(\text{CO})$. On the other hand, the annual minima-to-maxima variations in $\delta^{13}\text{C}(\text{CO})$ are comparable to those at MOP/HAP and amount to $\sim 3\text{‰}$, that is expectedly lower than the typical 4‰ and larger variations at the background NH stations. As it is noted above, the variations in $\delta^{13}\text{C}(\text{CO})$ at KMW are surprisingly well discernible, in contrast to the only weakly apparent seasonality in CO mixing ratio.

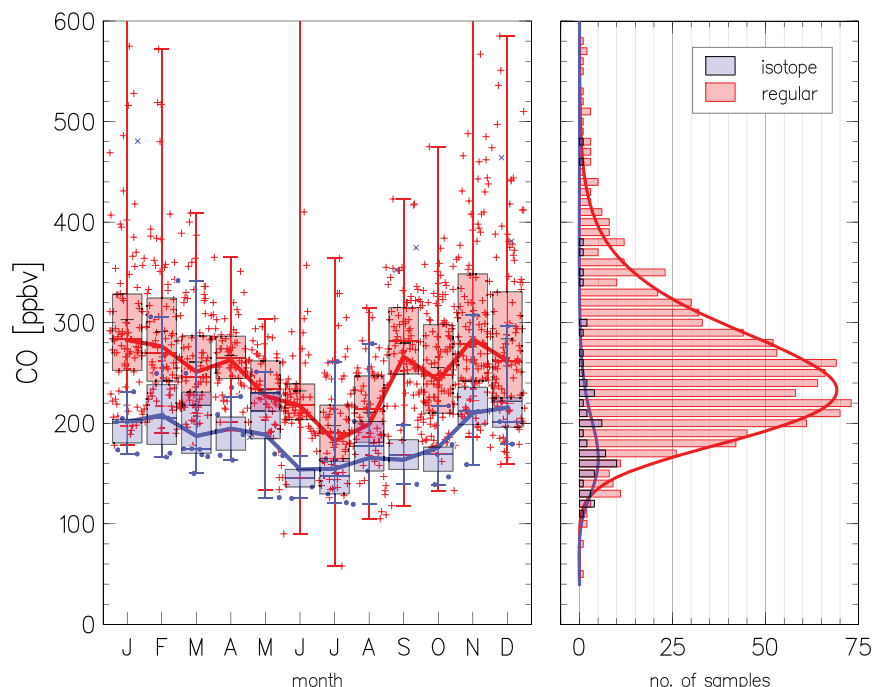


Figure 4.6 Left: Seasonal cycles (solid lines) of the surface CO mixing ratio observed at KMW from the regular continuous (red, RIVM daily data, ref. Table 4.2) and isotope-inclusive (blue, event data, ref. Table 4.1) observations. Solid lines connect monthly climatological medians; symbols denote the single observations plotted against the calendar date. Box and whisker plots present the distribution of the data for each calendar month, similar to that in Figure 4.4. Right: Distribution of the observed CO mixing ratios in 10 ppb bins for each dataset, respectively. Curves are lognormal approximations to the histogram data. Data for both, regular and isotope-inclusive series, cover the identical period (10/1997–01/2001). Note that the isotope-inclusive observations represent the samples with generally lower [CO] picked selectively.⁵³

4.1.2 Comparison with global CO observations

We further examine the isotope-inclusive data in the light of the regular observations of CO available from the NOAA ERSL data products (Novelli and Masarie^[2010], GLOBALVIEW-CO^[2009]) and free-troposphere measurements of isotope CO from various sampling campaigns by Mak and Brenninkmeijer^[1998]. Figure 4.7 (p. 83, upper panel) presents average CO mixing ratios registered at various surface locations as the function of latitude. The curves represent the Marine Boundary Layer (MBL) CO inventory derived in the GLOBALVIEW-CO product that exclusively integrates the observational data reckoned to pertain to the background conditions, thus representing the multi-year average background CO mixing ratios latitudinal “climatology”. Owing to the much larger surface emission component in the NH, average MBL [CO] exhibits a strong latitudinal gradient from ~ 125 ppb down to ~ 50 ppb in the NH and SH extra-tropics, respectively. Whereas the average SH and NH high-latitude mixing ratios relate as $\sim 1:2.5$, the seasonal variations in [CO] relate as $\sim 1:4$, conformably, signifying that the SH CO sources and sinks remain closer to their equilibrium throughout the year. This relationship holds for both, the averages of the complete time span of the data (1991–2008) and for the year 2000. The latter shows markedly moderate CO seasonal variations and generally 10–15 ppb lower mixing ratios in the NH, owing primarily to a reduction of the surface CO emission strength in the last two decades (see above, p. 69). Starting from $20^{\circ}\text{S}/40^{\circ}\text{N}$ latitudes, the lifetime of CO progressively increases poleward from roughly 1 month up to 1–2 years (see Sect. 6.2.2.1, p. 172, also note¹³¹), allowing efficacious zonal mixing of the high-latitude background CO inventory, as it is seen in flat MBL [CO] shoulders in Figure 4.7. A significant part of the data from the ERSL sampling sites (cross symbols in Figure 4.7) within 30°N – 60°N band indicates CO mixing ratios above the MBL levels that are associated with polluted conditions.

Similarly, in the isotope inclusive data, the compositions from HAP, MOP and KMW are markedly affected by the local or regional emissions that add up extra 40–50 ppb, or one-fourth, to the overall CO inventory at these sites. One notes, furthermore, the relatively small variations in [CO] at BAR and IZA, reaching only ~0.6 of the moderate MBL seasonal amplitude in 2000. Generally lower mixing ratios at IZA, and their minima coinciding with the low-end of the MBL mixing ratios span indicate that this station sees the air cleaner than expected from the MBL climatology. The elevated minima at BAR, on the contrary, suggest the presence of an additional source of ~20 ppb throughout the year (likewise noted above, p. 78). The large seasonal variations in [CO] at HAP and MOP are congruent with larger MBL amplitudes prior to 2000. The seasonal CO at SBK presents slightly elevated averages of the mixing ratios (due to the averaging over a weak negative trend throughout 1996–2001) and their annual variations much comparable to those of the MBL climatology; these data are expected to adequately reflect the background conditions. The [CO] from the isotope-inclusive records at the remote stations (ALE, SPI, BHD and SCB) is consistent with the regular data. Although the SH averages are comparable to the free troposphere observations, they are slightly elevated with respect to the background levels. In particular, the CO inventory at BHD and SCB appears to contain additional 5–7 and 3–5 ppb from the surface sources, respectively, which translates into equivalent ~15% and ~10% of the MBL-suggested background. Reckoning the much lower CO abundance in the ETSH, this additional surface component may strongly influence the $\delta^{13}\text{C}(\text{CO})$ values there, as the relative share of the CH_4 source in CO is considerably large.⁵⁴

The lower panel in Figure 4.7 presents the concomitant $\delta^{13}\text{C}(\text{CO})$ seasonalities from the isotope CO station data. The latitudinal distribution of $\delta^{13}\text{C}(\text{CO})$ in the NH resembles that of [CO], with a general tendency to decrease towards lower latitudes. The accompanying increase of the CH_4 oxidation source share in the CO inventory (γ_{CH_4}) is mainly responsible for the negative gradient of ~3‰ in the average $\delta^{13}\text{C}(\text{CO})$ throughout the NH tropics. Interestingly, despite the CO mixing ratios being generally lower in the SH and the γ_{CH_4} value is expected to continuously increase towards the pole due to the aging of CO with the transport to the higher latitudes, one does not remark the progressive lowering of $\delta^{13}\text{C}(\text{CO})$ at the SH sites and in the free troposphere data compared to the tropics. An illustrative example of the zonal average $\delta^{13}\text{C}(\text{CO})$ profile expected from the latitudinal variation in γ_{CH_4} is given by the supplementary curves in Figure 4.7. The latter are synthesised from the MBL CO data, assuming approximately one-third of the overall CO budget (median of the estimates listed in Table 6.3, p. 158) is being produced from the $\text{CH}_4 + \text{OH}$ source and distributed as a ~26 ppb integral equivalent in the near-surface mixing ratio throughout the latitudinal span. The remaining fraction of the CO inventory accounts for the other sources that are relatively enriched in ^{13}C (we take the average $\delta^{13}\text{C}$ of -25.5‰ reckoned in this study) compared to the CH_4 -derived carbon (-51.2‰, respectively). From this standpoint, the $\delta^{13}\text{C}$ of the source CO becomes merely a function of γ_{CH_4} , however, the composition of the atmospheric reservoir is further modified by the effective isotope fractionation in the CO sink, $^{13}\text{C}\epsilon_{\text{CO}+\text{OH}}$, that primarily depends on the [CO] and [OH] distributions. Reckoning for the best proxy, the magnitude of the MBL $^{13}\text{C}\epsilon_{\text{CO}+\text{OH}}$ used for the synthesis in Figure 4.7 is diagnosed from the sensitivity simulation (referred to as “Z”, see Sect. 6.2.5 below) employing the conventional CO+OH KIE parameterisation in this study (see Sects. 3.4.4, p. 47, and 6.1.4.2 below, respectively). The profile of $^{13}\text{C}\epsilon_{\text{CO}+\text{OH}}$ shows a reciprocal relationship to the average [CO], with lower magnitudes and variability in the NH and nearly invariable enrichments around +4.6‰ in the SH resulting from the superposition of the chemical sink and, more importantly, transport and mixing effects.

⁵⁴ Changes to the overall $\delta^{13}\text{C}$ composition of the atmospheric reservoir are sensitive to its initial composition. For example, admixing of 6 ppb of the surface CO (with the average $\delta^{13}\text{C}$ of -25.5‰) to the background reservoir of 50 ppbv with either 30% or 50% of CH_4 -derived CO component will result, respectively, in quite different enrichments of 0.85‰ and 1.43‰ of the final reservoir composition with respect to the initial background $\delta^{13}\text{C}(\text{CO})$. Thus, compared to the NH, the SH compositions are more sensitive to the surface emission due to lower expected background $\delta^{13}\text{C}(\text{CO})$ and generally lower background mixing ratios.

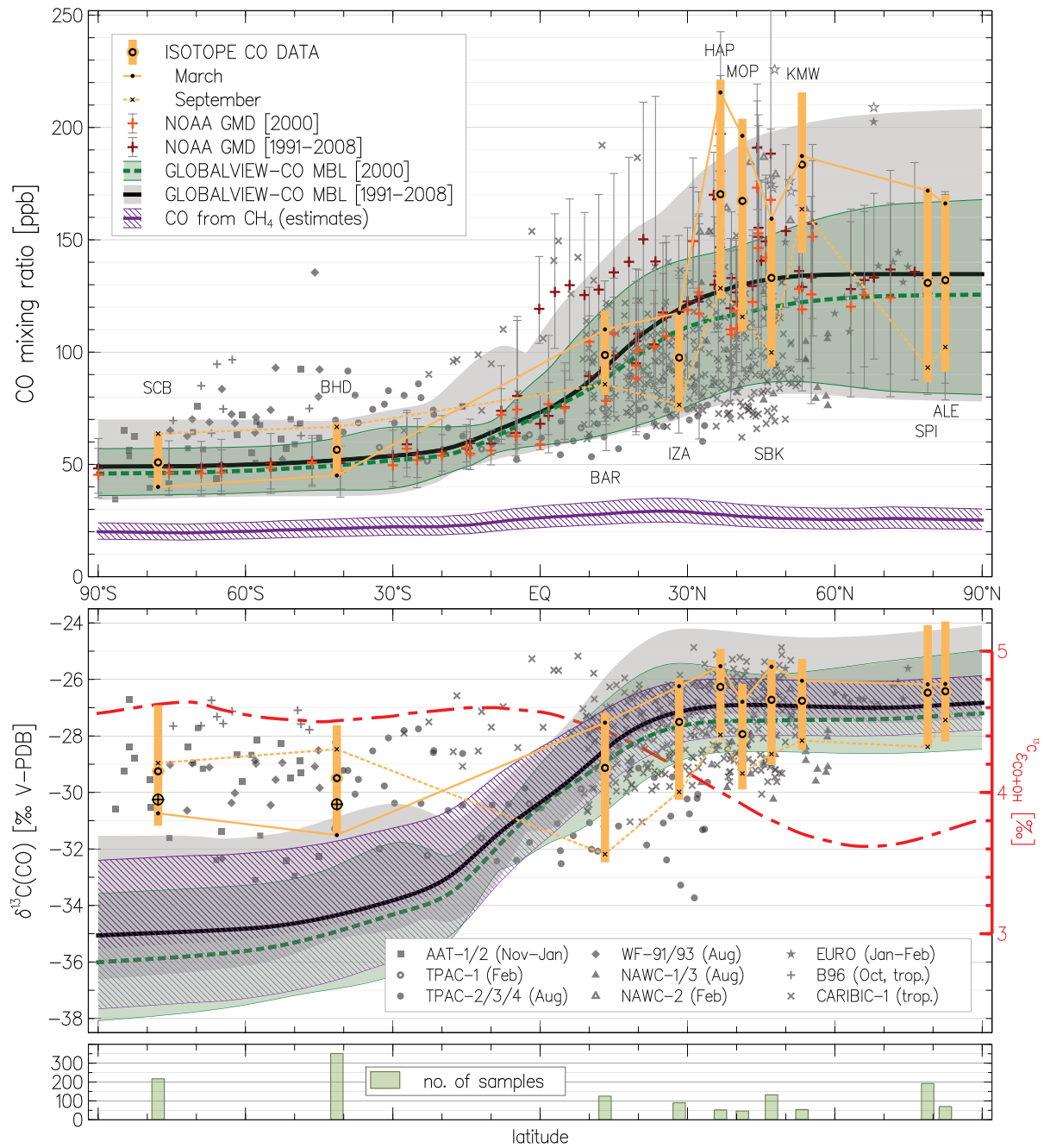


Figure 4.7 Latitudinal distribution of the CO surface mixing ratio (upper panel) and respective ^{13}C isotope composition (middle panel). Symbols denote the multi-year averages, with the error bars indicating their seasonal variation. The regular observational data is from the Carbon Cycle Cooperative Global Air Sampling Network (NOAA ERSI, Novelli and Masarie^[2010]); the isotope CO data presents the seasonalities discussed in the text. Grey symbols denote the BL and free troposphere observations from various sampling trips in 1991–1993 (see Mak and Brenninkmeijer^[1998] for details), B96 and CARIBIC-1 represent the aircraft observations in the UTLS (see Brenninkmeijer *et al.*^[1996] and further Sect. 4.2, p. 96). The reader is referred to Figure 4.1 (p. 68) for the overview of the surface observational sites' locations. Curves denote the MBL CO abundance derived in the GLOBALVIEW-CO product (GLOBALVIEW-CO^[2009], <http://www.esrl.noaa.gov/gmd/ccgg/globalview>). The regular data are shown for two periods: monthly averages for the year 2000 and for 1991–2008. Thin solid and dashed lines connect the monthly averages for March and September from the isotope CO observations, respectively. The latitudinal distribution of $\delta^{13}\text{C}(\text{CO})$ (curves) is an approximation (see text) based on MBL CO data and the effective ^{13}C enrichment in CO due to OH sink, obtained in this study assuming the conventional KIE parameterisation (annual zonal average of $^{13}\text{C}_{\text{ECO-OH}}$ is shown as dash-dotted line on the separate scale). The hatched area denotes the variation in the synthesised average $\delta^{13}\text{C}(\text{CO})$ (lower panel) within given estimates of the CH_4 -derived component in the CO budget (upper panel). Crossed circles denote the average background (MBL) $\delta^{13}\text{C}(\text{CO})$ expected from the isotope mass-balance of the compositions observed at BHD and SCB (see text). Lower panel presents the overall number of the station isotope CO data samples collected. This figure is complemented by Figure 4.16 (p. 103 below) reviewing the UTLS isotope CO data.

Despite the synthesised curves ensue from somewhat crude approximation, they clearly anticipate a progressive lowering of the $\delta^{13}\text{C}(\text{CO})$ towards higher southern latitudes, as well as much depleted compositions compared to those registered in the SH. From the difference between the curves calculated for 2000 and the entire MBL CO data, one acknowledges an appreciable sensitivity of the $\delta^{13}\text{C}(\text{CO})$ in the remote SH to the changes in mixing ratio. For example, lowering of $[\text{CO}]$ at SCB (78°S) by mere 3–5 ppb⁵⁵ (apropos equal to the estimate of the extra surface component at this station) results in a decrease of up to 1‰ in the final $\delta^{13}\text{C}(\text{CO})$. Analogously, less clean air at BHD is expected to carry supplementary ~0.9‰ in $\delta^{13}\text{C}(\text{CO})$ from the surface sources on top of the average background value expected at this latitude. Furthermore, the hatched area in Figure 4.7 presents the span of the MBL-synthesised average $\delta^{13}\text{C}(\text{CO})$ profiles within the range of current estimates of average γ_{CH_4} from 24% to 35% (see Table 6.3, p. 158). Under the above given assumptions (*i.e.*, selected average surface sources' $\delta^{13}\text{C}$ and MBL $[\text{CO}]$ profile, plus the conventional KIE in CO+OH sink) none of these reconcile the observed $\delta^{13}\text{C}(\text{CO})$ in the SH: Even with a less likely small γ_{CH_4} value of 24% (see Sect. 6.1.1) the MBL-synthesised $\delta^{13}\text{C}(\text{CO})$ is still 1.3‰ (BHD) to 2‰ (SCB) lower than the background values anticipated from the observational data. The expected MBL $\delta^{13}\text{C}(\text{CO})$ at BHD and SCB are nearly levelled off, contrary to the apparent gradient in the synthesised SH profiles. Overall, a befitting explanation for this discrepancy is the sufficiently larger ^{13}C enrichment of the leftover CO, induced by the KIE in the CO removal, which also has to strengthen southward to overcompensate for the effect of the increasing contribution from the ^{13}C -depleted CH_4 oxidation source. An alternative to this may be a modest ^{13}C -enriched source of CO in the higher latitudes, however this hypothesis is not upheld by the current notion on the distribution of the SH surface sources which suggests these being amassed outside of the ETSH (*i.e.* lower than 40°S, see Sect. 5.2.2 and Figure 5.3, p. 122). Within the ETSH, the longer CO lifetime and mixing of its inventory renders the background $\delta^{13}\text{C}(\text{CO})$ gradient being primarily dependent on γ_{CH_4} (and presumably sink fractionation) altering with latitude, furthermore being insensitive to the $\delta^{13}\text{C}$ of the surface sources that might have been erroneously assumed in this inquiry. The estimated change to the background CO inventory between BHD and SCB corresponds to the increase of the γ_{CH_4} value by ~2%, or an equivalent decrease of ~0.5‰ in $\delta^{13}\text{C}(\text{CO})$ ⁵⁶. To compensate for the consequences of the increased CH_4 -derived CO share, the effective sink enrichment $^{13}\text{C}\epsilon_{\text{CO+OH}}$ at SCB must be of at least 0.6‰ larger than that at BHD. The results of the sensitivity simulations with EMAC within this study attest that a difference of 0.64‰ is reproduced in the model setup implementing the revised composite CO+OH KIE parameterisation (AK), whereas the conventional KIE approach (REF setup) predicts a lower value of 0.4‰ only.

It is furthermore difficult to prospect the NH data for the discrepancies that may similarly be caused by the underestimated CO sink fractionation, because the sensitivity of the NH isotope compositions to the chemical alteration of CO is dampened by the greater CO burden ensuing from the large surface emission term. For instance, the observed NH $\delta^{13}\text{C}(\text{CO})$ averages (including the data presenting significantly polluted compositions) on the whole comply with the range of γ_{CH_4} estimates; the latter also yield much smaller range of possible NH MBL $\delta^{13}\text{C}(\text{CO})$ profiles. An attempt to find somewhat pronounced photochemistry-related features in $\delta^{13}\text{C}(\text{CO})$ may be based on scrutinising the compositions at the remote NH sites, which are expected to observe the CO with the longest atmospheric residence time originated and transported from the lower latitudes. Thus, from Figure 4.7 one picks two particularities: (1) The averages of $\delta^{13}\text{C}(\text{CO})$ at SPI and ALE are higher than those given by the synthesised MBL curves, whilst the averages of $[\text{CO}]$ itself are positioned between the 2000 and entire MBL levels. That is typically not the case for the other NH locations (excluding questionable low $\delta^{13}\text{C}$ data from BAR/MOP), where lower CO mixing ratios correlate with lower $\delta^{13}\text{C}(\text{CO})$ values as compared to both MBL averages. Elevated $\delta^{13}\text{C}(\text{CO})$ hence suggests that the remote compositions should carry an additional photochemically-induced enrichment which correlates with $[\text{CO}]$ lowering due to the photochemical sink. (2) In addition, seasonal variations of $\delta^{13}\text{C}(\text{CO})$ at SPI/ALE clearly outsize those given by the MBL curves, and, judging by the comparable spans of the observed and synthesised MBL data for 2000, the discrepancy lies in the observed maxima that are at least 1‰ higher. The latter are essentially promoted by the sink fractionation enriching CO in ^{13}C in spring-summer in the remote NH, because one can likely rule out possibly underestimated $\delta^{13}\text{C}$ signatures of the NH winter surface sources on top of which the sink fractionation develops in spring: Analogously to the SH case, NH emissions are accumulated lower than 60°N, thus similarly ele-

⁵⁵ At the expense of the surface component, thus retaining the CH_4 -derived $[\text{CO}]$ invariable.

⁵⁶ That is the difference in atmospheric $\delta^{13}\text{C}(\text{CO})$ subtracting the sink fractionation effect. See Sect. 6.2.7 (p. 199) for the details on the analysis of the observed compositions at BHD/SCB in comparison with EMAC results.

vated $\delta^{13}\text{C}(\text{CO})$ should be observed in both, high- and mid-latitude data (*e.g.*, SBK). On the contrary, the maxima in SPI and ALE $\delta^{13}\text{C}(\text{CO})$ are markedly (by at least 1‰) higher compared to the observed compositions at HAP, SBK and KMW.

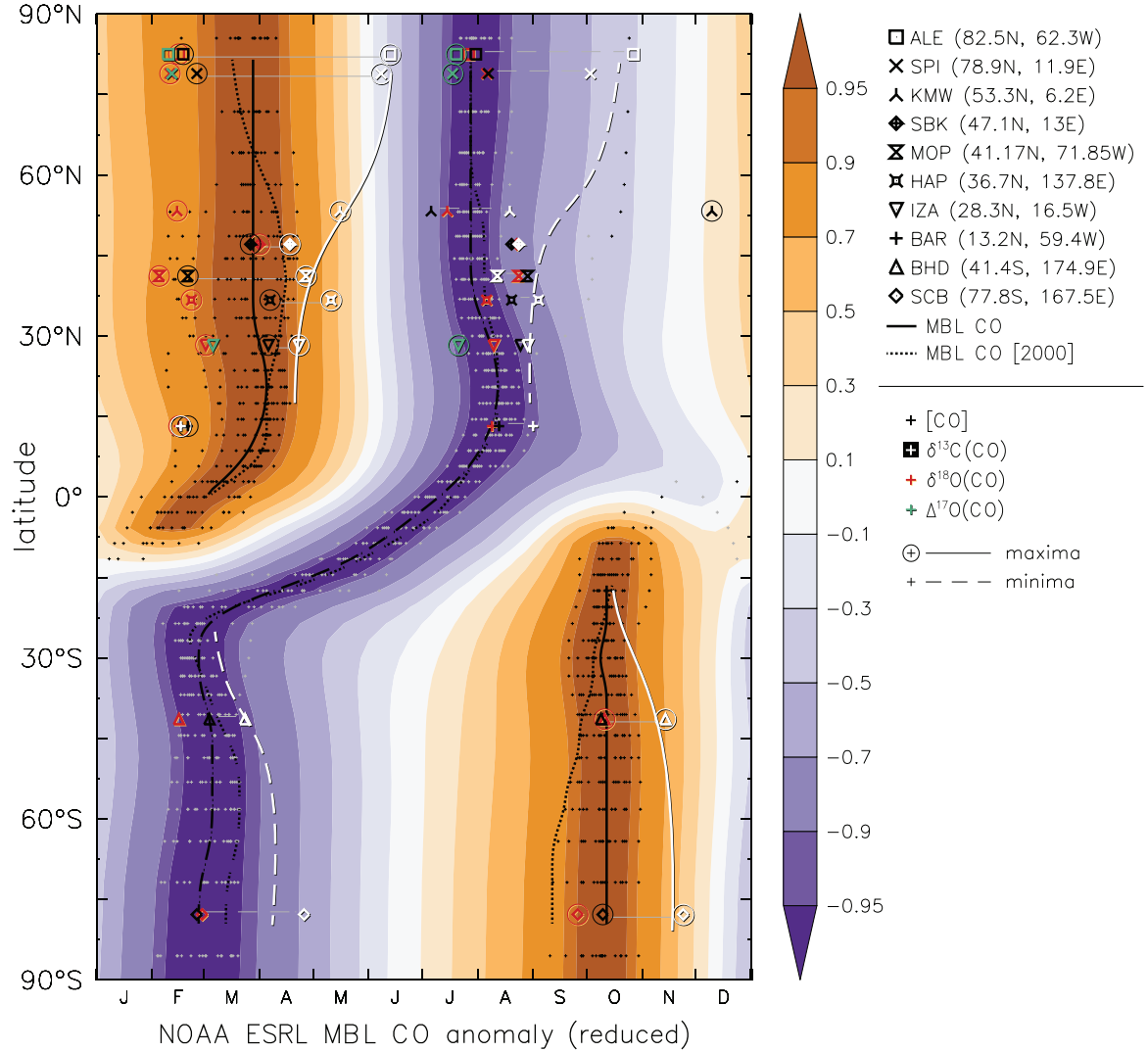


Figure 4.8 Latitudinal timing of surface CO mixing and isotope ratio maxima and minima. The colour-shade plot presents the specific (reduced) anomaly of the 1991–2008 climatology of the MBL $[\text{CO}]$ from the NOAA ESRL GLOBALVIEW-CO product (GLOBALVIEW-CO^[2009], see Figure 4.7). Large symbols denote the minima (plain) and maxima (encircled) in CO mixing ratio (black), $\delta^{13}\text{C}(\text{CO})$ (white), $\delta^{18}\text{O}(\text{CO})$ (red) and $\Delta^{17}\text{O}(\text{CO})$ (turquoise), respectively, encountered in the isotope-inclusive observations' climatologies. Solid and dashed lines navigate through the maxima and minima of the respective MBL characteristics. Dotted lines refer to 2000 MBL data (not shaded) which highlights slightly earlier $[\text{CO}]$ maxima in the high latitudes. Typical latitudinal profiles for $\delta^{13}\text{C}(\text{CO})$ timing (white lines) are derived from the MBL CO simulated in the REF setup of this study. Small symbols denote maxima (black) and minima (grey) in the MBL $[\text{CO}]$ for particular years. For example, the untypical ETNH October maxima and tropical November–December minima refer to the year 1998, when the large-scale perturbation of the global $[\text{CO}]$ due to the El-Niño event was observed (see above, p. 69).

The importance of the sink fractionation in CO is further emphasised by the asynchronous development of the $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ extrema. Figure 4.8 presents the specific anomaly of the MBL CO mixing ratio as a function of latitude, overlaid with the minima and maxima in CO mixing ratio, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ from the isotope-inclusive data seasonalities. The specific anomaly a_r is calculated as an absolute anomaly reduced by the modulus of the residue between the average and respective seasonal extrema of the series, that is

$$a_r = \frac{[\text{CO}] - [\text{CO}]_{ave}}{|[\text{CO}]_{ave} - [\text{CO}]_{ext}|},$$

where $[\text{CO}]$ denotes the current CO mixing ratio, $[\text{CO}]_{ext}$ equals either minima or maxima of $[\text{CO}]$ when current $[\text{CO}]$ is below or above its annual average $[\text{CO}]_{ave}$, respectively. This way a_r indicates the transition between the seasonal minima (−1) and maxima (+1) in $[\text{CO}]$ at a specific latitude, with values around zero denot-

ing mixing ratios in proximity to the annual mean. From Figure 4.8 one notes that the transition period from maxima to minima in the climatological MBL [CO] is nearly invariable with latitude in the extratropics. The maxima in the ETNH typically develop in the end of March followed by the minima in the beginning of August. Relative to the corresponding austral seasons, the ETSH extrema occur 2–4 weeks later and lag by additional 2–3 weeks compared to that in the ETNH, owing to more moderate [CO] dynamics driven by significantly lower SH abundances and surface emission terms. The timing of the tropical and northern mid-latitude maxima is furthermore subject to large variability due to changes in the surface emission seasonal development, *e.g.* the instant of the biomass burning component strengthening in particular years. The example of the MBL [CO] in 2000 presents only slight deviations of the NH maxima within two weeks from the climatological average. The unusual early maxima in the ETSH, however, are also likely to be unexceptional, resulting from the lower SH CO abundance established in 2000 and hence earlier [CO] reduction with the commencing OH sink. In contrast to the largely variable maxima, MBL [CO] minima fit much tighter in a period of one month, coinciding with timely cessation of the CO sink triggered by the seasonal disappearing of OH.

The [CO] dynamics similar to those of the MBL data are observed in the isotope-inclusive seasonalities, with an exception for KMW, MOP and BAR. At KMW, early [CO] extrema are brought by the augmented surface component in the CO inventory, added on top of the regular background variations. Both regular and isotope data, however, present similar monthly [CO] averages throughout November–February at the series' maximum levels (*cf.* Figure 4.6, p. 81). The late July minima occurring in the regular data one month later than in the isotope series are more congruous with the MBL seasonality. The early [CO] maxima at MOP and BAR, as discussed above, are untypical and are likely to be the artefact of the scarce amount of data available in these series. In the case of BAR, simultaneous maxima in [CO] and $\delta^{13}\text{C}(\text{CO})$ clearly point to their non-background origin.

Notably, the delay between the corresponding mixing ratio and $\delta^{13}\text{C}$ extrema systematically increases with latitude, whilst the $\delta^{13}\text{C}(\text{CO})$ signals themselves remain equidistant, in a similar fashion to [CO]. For the locations within the 30°S–45°N span, a typical delay between the [CO] and $\delta^{13}\text{C}(\text{CO})$ maxima does not exceed 3–4 weeks. Such close development of the mixing and isotope ratio extrema is propelled by the strengthening of the surface component in the CO inventory. Conversely, as the seasonal photochemical production and sink of CO become influential, they lead to near minima in [CO] and its $\delta^{13}\text{C}$ in August: Lowest mixing ratios promoted by the sink correlate with the largest fraction of the ^{13}C -depleted CO from the methane oxidation source, with both processes being mediated by the presence of the OH. In the extratropical regions, however, the interval between peaking [CO] and $\delta^{13}\text{C}(\text{CO})$ becomes conspicuously protracted: Seasonal extrema of $\delta^{13}\text{C}(\text{CO})$ at SPI/ALE are delayed by 2–4 months (1–2 months at BHD/SCB) with respect to that of [CO]. The dynamics of $\delta^{13}\text{C}(\text{CO})$ extrema are intricate, and depend on the timely superposition of the effects caused by the in-situ sink and production of CO, each in turn leading to increasing and lowering of $\delta^{13}\text{C}(\text{CO})$, respectively. The major factor promoting the misphasing between [CO] and $\delta^{13}\text{C}$ in the extratropics is, however, the transport effect, *i.e.* a continuous supply of the CO from the tropics and mid-latitudes to the high latitude regions. Due to the virtual absence of the surface sources and photochemical production of CO north of 50°N (45°S), poleward transport may be regarded as another source contributing to the remote inventory, although with the isotope compositions of the airborne CO, that is notably different from that of the surface sources. The variations in the $\delta^{13}\text{C}$ signature of such “transport” source are such that they are capable to significantly alter the seasonal development of the high-latitude $\delta^{13}\text{C}(\text{CO})$. For example, the heaviest in ^{13}C NH low-latitude CO encountered in the beginning of April–May becomes apparent in the Arctic $\delta^{13}\text{C}(\text{CO})$ two–three months later, in June (when the current [CO] there is below its annual average), but not shortly after the inventory becomes at filled most with the ^{13}C -enriched CO from the surface sources. Analogously, the CO with lowest $\delta^{13}\text{C}$ from the lower latitudes in August subsequently contributes to the inventory at SPI and ALE, shifting the $\delta^{13}\text{C}(\text{CO})$ minima to October. That is much later than the timing of the local [CO] minima, when the greatest share of the CH_4 -derived CO component is expected to yield the lowest $\delta^{13}\text{C}(\text{CO})$ value. One notes, furthermore, that the extent of the delay between the [CO] and $\delta^{13}\text{C}(\text{CO})$ extrema in high latitudes is correlated with the average abundance of the tracer. The lag is notably shorter in the ETSH than at the high NH latitudes, because the CH_4 source requires longer refilling of the much larger NH inventory with ^{13}C -depleted CO.

Interestingly, there is no marked latitudinal shift in the high-latitude [CO] extrema itself. The “transport” source has no effect on mixing ratio extrema owing to comparable [CO] dynamics with those at the destination region. In other words, the air introduced to the remote regions has a similar [CO] but a much dissimilar $\delta^{13}\text{C}(\text{CO})$ temporal development. During the transport, CO progressively undergoes photochemical

sink, whilst its in-situ production becomes inhibited. The ratio between the total CO sink and in-situ production terms in the boundary layer sets at $\sim 1:1$ within the 35°S – 40°N span, and grows continuously poleward up to $\sim 4:1$ in the Antarctic and $\sim 7:1$ in the Arctic, respectively.⁵⁷ The prevailing sink lowers the mixing ratio, but elevates the $\delta^{13}\text{C}$ of the “transport” source owing to the positive sink ^{13}C fractionation, especially in spring and summer. Such dynamics of the CO composition is similar to that of the above analysed KMW record (p. 79): Variations in $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ do not correlate timely, thus $\delta^{13}\text{C}$ first peaks and then falls during a continuous drop in mixing ratio. In a superposition with transport, the spring-summer enrichment promotes and retards the $\delta^{13}\text{C}(\text{CO})$ maxima. The minima, subsequently, also become delayed, as the inventory needs more time to return back to the lowest seasonal $\delta^{13}\text{C}(\text{CO})$ value. Oppositely, the tight relationship between the $\delta^{18}\text{O}(\text{CO})$ and $[\text{CO}]$ (resulting from the aggregate negative effect on $\delta^{18}\text{O}$ of the *inverse* sink KIE and more ^{18}O -depleted sources) leads to their synchronous extrema, as the data from SPI, ALE, SBK, BHD and SCB witness (see Figure 4.8, red symbols). Analogously to the KMW record, coincidental similar changes to $[\text{CO}]$ and $\delta^{18}\text{O}(\text{CO})$ conceal the peculiarities of latitudinal transport seen in $\delta^{13}\text{C}(\text{CO})$ otherwise.

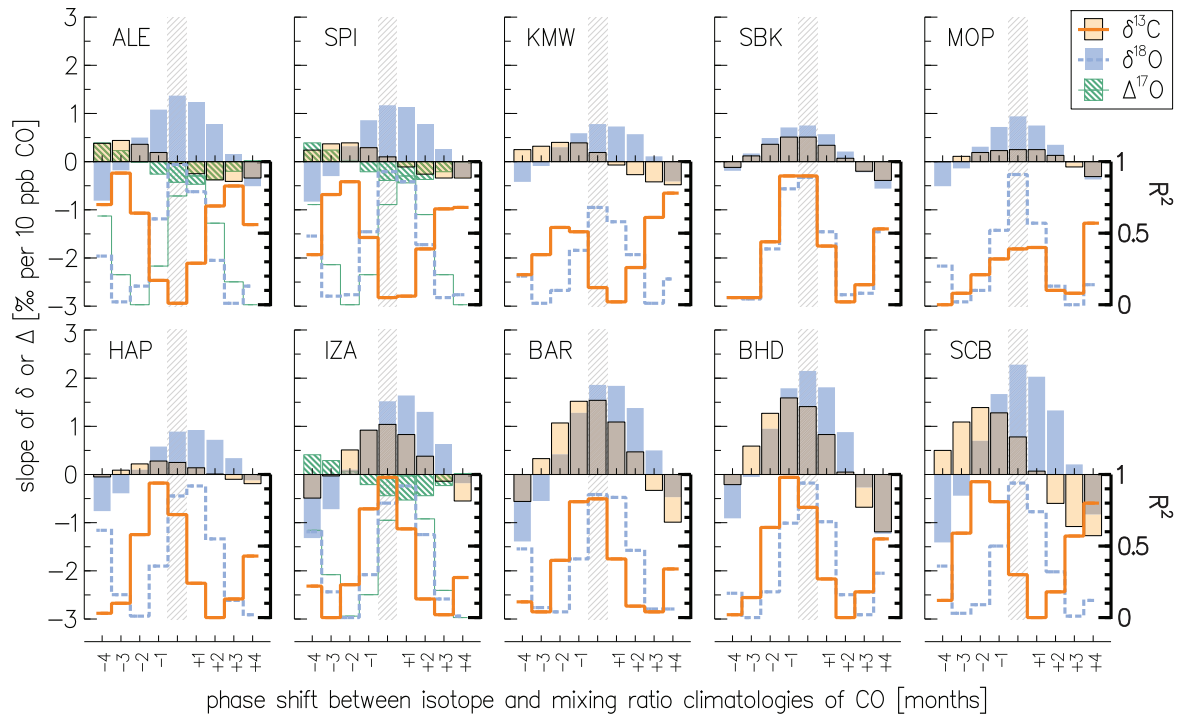


Figure 4.9 Correlation between the observed CO isotope and mixing ratio seasonalities as a function of $[\text{CO}]$ phase shift. Lower insets accommodate the R^2 value (denoted with lines, right scale), solid bars represent the slopes of the linear regression fit through respective isotope ratio data ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$) as a function of $[\text{CO}]$. Maxima of the slope and R^2 found to the right from the centre of the panel denote the that isotope ratio changes forestall (anticipate) corresponding changes in $[\text{CO}]$. Likewise, shifts of the highest R^2 and slope to the left from the centre signify changes in isotope ratio following variations in $[\text{CO}]$ with the corresponding delay.

A further interesting observation is the minima and maxima in $\Delta^{17}\text{O}(\text{CO})$, whose development coincides with the greatest and smallest magnitudes of the effective sink fractionation in CO, respectively (see details in the following section on $\Delta^{17}\text{O}(\text{CO})$). The timing of $\Delta^{17}\text{O}(\text{CO})$ minima suggest that the seasonal photochemical processing of CO begins to cease nearly simultaneously at both high- and low-latitude NH locations in July, with the start of the seasonal drop in $[\text{OH}]$, respectively. At the remote locations, corresponding $[\text{CO}]$ and $\delta^{18}\text{O}(\text{CO})$ maxima and $\Delta^{17}\text{O}(\text{CO})$ minima, as well as their counter-extrema, develop synchronously, hence indicating that the transport and surface sources of CO play an integral role in determining the oxygen isotope ratio variations. In the tropics, however, early (relative to the peaking $[\text{CO}]$) extrema in $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ at IZA (and likely at HAP) are rather triggered by the commencing CO sink and photochemical production. This is better seen in Figure 4.9 presenting the analysis of the correlation between the isotope ratios variations and the $[\text{CO}]$ seasonality cyclically shifted forward and back in time from its original timing. Thus, $\delta^{13}\text{C}$ and $[\text{CO}]$ at

⁵⁷ According to estimates from the current study with EMAC, REF simulation (see Sect. 6.2). Prevalence of the CO photochemical sink over production ensues from the ambient high-latitude conditions: At lower temperatures, reaction of CO with OH, being primarily pressure-dependent, proceeds more readily than the majority of the temperature-sensitive reactions yielding CO.

IZA show tight timely correspondence, whereas $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ best correlate with $[\text{CO}]$ from one month later (*i.e.*, anticipating changes in mixing ratio). This is explicable in view of the opposite ^{13}C and ^{18}O KIE in $\text{CO}+\text{OH}$ sink: Despite changes to $[\text{CO}]$ are not yet pronounced (the overall sink is balanced with the sources), the removal of ^{13}CO and C^{18}O alters the isotope ratios in the atmospheric reservoir quicker than the sources equilibrate them. Roughly one month is required for the photochemical CO sources at IZA to stop $\delta^{13}\text{C}(\text{CO})$ growing due to the sink and further enforce the drop in $\delta^{18}\text{O}(\text{CO})$ by the in-situ production of CO with lower $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures. Surprisingly, the “transport source” liable for the large misphasing between $\delta^{13}\text{O}(\text{CO})$ and $[\text{CO}]$ apparently leads to slightly better synchronisation between $\delta^{18}\text{O}(\text{CO})$ and $[\text{CO}]$ in the high latitudes. Finally, one remarks much similar profiles at SPI, ALE and IZA for $\Delta^{17}\text{O}(\text{CO})$ indicating its likely latitude-invariable correlation with mixing ratio. The latter maximises about a month ahead of peaking $\Delta^{17}\text{O}(\text{CO})$. Due to the absence of the $\Delta^{17}\text{O}(\text{CO})$ observations in the ETSH, one can only reckon that the $\Delta^{17}\text{O}$ signal develops similarly to that in the ETNH; in this case the development of $\delta^{18}\text{O}(\text{CO})$ and $[\text{CO}]$ may be used as indirect proxies for the effective sink fractionation magnitude. The analysis in Figure 4.9 also confirms the ill-defined seasonalities at KMW and MOP concluded in previous sections. A case of very synchronous $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $[\text{CO}]$ signals is presented by the SBK record, which may imply a strong source effect that requires further analysis however outside the scope of this work. It is necessary to mention that the untypical correlation of the isotope and mixing ratio seasonalities at this free troposphere site is not an artefact of the data post-processing applied (see above, p. 76).

Recapitulating, the series of the surface observations on CO mixing ratio and $\delta^{13}\text{C}(\text{CO})$ presented here offer a qualitative dataset for the subsequent comparison with the model results. Four out of ten series (*viz.* KMW, HAP, MOP and BAR) are to various degree subject to artefacts due to infrequent or irregular sampling, exposure to polluted air masses and compositions bearing an appreciably large surface emission component. A comparison with the concomitant regular CO observations confirms that the remaining isotope-inclusive series represent the background variations of the surface $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ adequately and are in accordance with the alternative regular estimates of the MBL CO abundance, particularly for the year 2000. Notwithstanding the deteriorated data, distinct seasonal variations in $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ enable one to construct the seasonal climatologies of $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ for all series, with the proviso that some of them pertain to non-background conditions. A simplified ^{13}CO isotope mass-balance assimilating the estimates of the MBL CO abundance from the regular data, the range of its CH_4 -derived component and the sink isotope fractionation magnitude based on the conventional $\text{CO}+\text{OH}$ KIE approach underestimates the $\delta^{13}\text{C}(\text{CO})$ in the ETSH in contrast to the observational data. Reprising the conclusions drawn in previous sections, this analysis suggests that most likely the missing ^{13}CO ensues from the underestimated magnitude of the fractionation in the CO sink, as neither the surface source $\delta^{13}\text{C}$ nor the CH_4 -derived CO component underestimation can explain the small latitudinal gradient in the observed background $\delta^{13}\text{C}(\text{CO})$ in the ETSH. As for the NH data, similar conclusions can be drawn for the observational record in the Arctic; the remaining data pertain to the locations subject to large surface emissions attenuating the photochemical signal in CO. Nonetheless, the analysis of the mixing and isotope ratio extrema timing suggests that a large photochemical sink component develops in the high-latitude remote conditions, an effect seen in the data in the augmenting delay between the $[\text{CO}]$ and ^{13}CO extrema, but not marked in the oxygen isotopes composition. The latter, however, may be used as the proxies for the intensity of the CO photochemical processing.

4.1.3 $\Delta^{17}\text{O}(\text{CO})$ observations

In addition to the ^{13}CO and C^{18}O data, three records from SPI, ALE and IZA offer the simultaneous observations of the C^{17}O isotope composition of CO in surface air. Unfortunately, no trend analysis similar to that for the $\delta^{13}\text{C}(\text{CO})$ is feasible for the $\Delta^{17}\text{O}(\text{CO})$ data due to the short span of the series sporadically covering one (IZA) and two (SPI, ALE) years of observations (shown in Figure 4.10). The most consecutive data period (above 40% of all available $\Delta^{17}\text{O}(\text{CO})$ samples) pertains to the remote NH stations and encompasses observations throughout December 1996 to July 1997, however, the August and September compositions from these sites are represented only by the samples at SPI. Similarly, the least represented months at IZA are September and December. The originally reported $\Delta^{17}\text{O}(\text{CO})$ data are derived from the respective $\delta^{18}\text{O}(\text{CO})$ and $\delta^{17}\text{O}(\text{CO})$ values using the linear-approximate formulation (Eq. (3.6), see Sect. 3.2, p. 30) employing the slope coefficient β of 0.52. To comply the exact, logarithm-based formulation (*ibid.*, Eq. (3.5)) and the universal value of $\beta = 0.528$ used in the present study, the reported values were recalculated. The mutual variations of $\delta^{18}\text{O}$ and

$\delta^{17}\text{O}$ in atmospheric CO are such that the difference between the recalculated and the reported linearly-approximated $\Delta^{17}\text{O}$ values is levelled off when the latter is around +6‰, and varies from -0.1‰ to +0.08‰ at the lower- and upper-end of the observed $\Delta^{17}\text{O}(\text{CO})$ span of +2‰ to +8‰, respectively. The correction term this way roughly amounts to a half of the uncertainty in the $\Delta^{17}\text{O}(\text{CO})$ data reported at ± 0.2 ‰ (see references in Table 4.1).

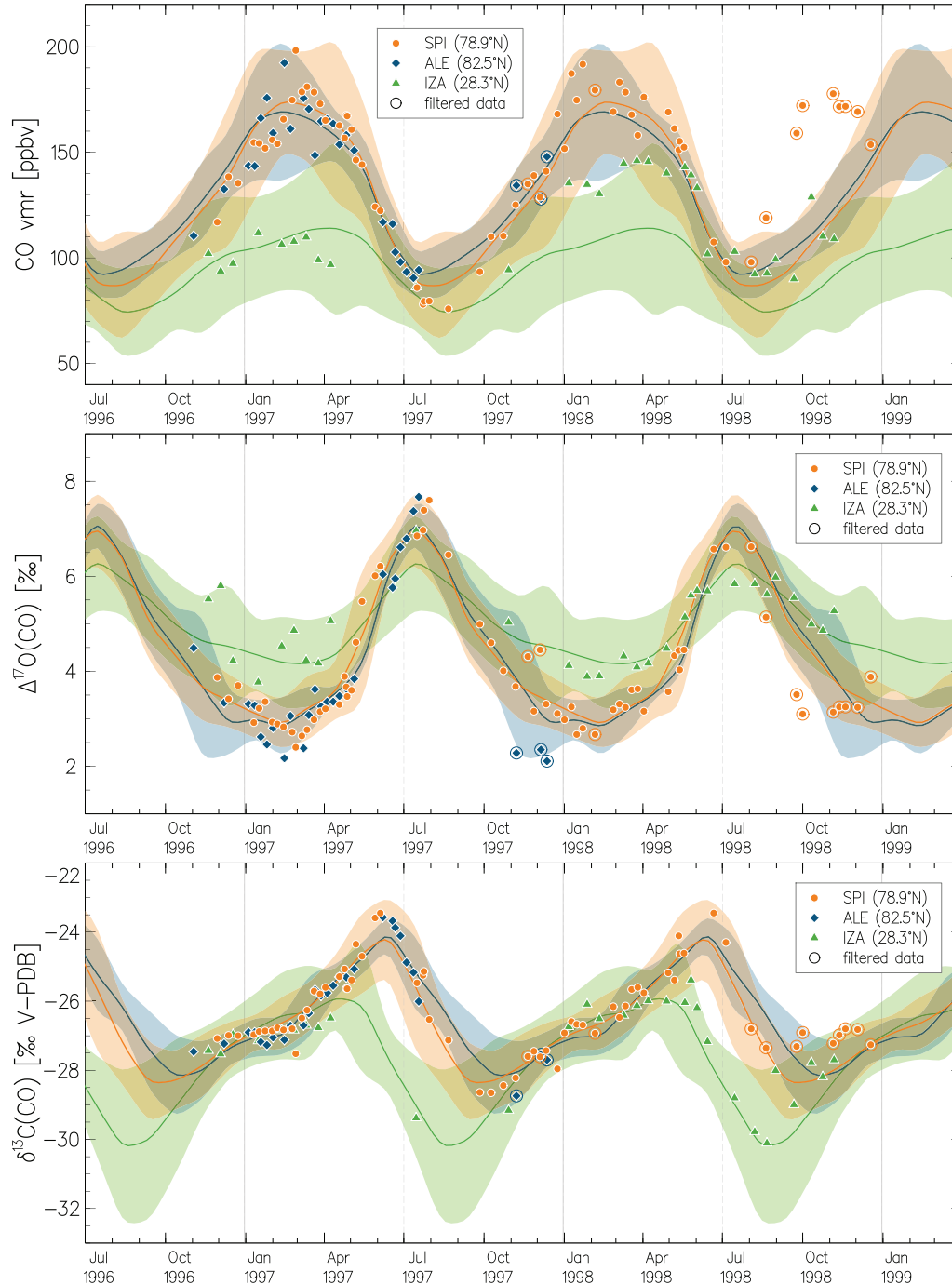


Figure 4.10 Temporal coverage of the available simultaneous observations of CO mixing ratio (upper panel), $\Delta^{17}\text{O}(\text{CO})$ and $\delta^{13}\text{C}(\text{CO})$ at the surface (middle and lower panels, respectively). Different colours denote different observational sites; solid symbols mark the flask sample data, open circles denote the samples disregarded (see text). Solid lines are the seasonal cycles (climatological monthly means) of the respective characteristics derived from the sample data; shaded areas denote ± 2 standard deviations of the seasonal monthly values.

Alike for $\delta^{13}\text{C}(\text{CO})$, variations of $\Delta^{17}\text{O}(\text{CO})$ present a distinct seasonal cycle, which is, however, interpreted differently than the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signals. The anomalous, or mass-independently fractionated (MIF) oxygen isotope composition signalled by non-zero $\Delta^{17}\text{O}(\text{CO})$ values is reckoned to be of exclusively photochemical nature, being principally propelled by the anomalous fractionation in the sink of CO via OH

that upholds a positive $\Delta^{17}\text{O}(\text{CO})$ value in the leftover atmospheric CO (see also Sects. 3.4.4 and 3.5). Conformably, the CO sink active in spring-summer leads to a prominent peak in $\Delta^{17}\text{O}(\text{CO})$ in July observed in all series. As a counterbalance to the MIF sink enrichment, the main photochemical and all surface sources of CO are characterised with non-MIF compositions with $\Delta^{17}\text{O}$ signature near 0‰⁵⁸, thus the atmospheric $\Delta^{17}\text{O}(\text{CO})$ is attenuated by the surface emissions, as it is distinctly seen in winter [CO] maxima and $\Delta^{17}\text{O}$ minima. A collateral source of the MIF in CO is found to be the ozonolysis of unsaturated hydrocarbons which yields in-situ CO with substantial positive $\Delta^{17}\text{O}$ signature inherited from the anomalous composition of O_3 (Röckmann *et al.*^[1998a]). Although the composition of thus produced CO may be as high as 25‰–40‰, ozone oxygen input to the overall $\Delta^{17}\text{O}(\text{CO})$ is expected to be rather minor and uniform, chiefly correlated with reciprocal CO abundance, *i.e.* attenuated by the non-MIF sources. Depending on the season, NH surface $\Delta^{17}\text{O}(\text{CO})$ at regarded data locations may receive additional 0.4‰–0.5‰ on average, with the seasonal variations not exceeding $\pm 0.3\%$.⁵⁹

The seasonalities of $\Delta^{17}\text{O}(\text{CO})$ for the model comparison (shown in Figure 4.11) are constructed using the same procedure described above for the $\delta^{13}\text{C}(\text{CO})$ climatologies (Sect. 4.1.1, p. 69). Similar to those in Figure 4.4, panels in Figure 4.11 present the distributions of the representative and disregarded $\Delta^{17}\text{O}(\text{CO})$ samples. The bulk of filtered data amounts to ~16% of the total record, being mainly represented by the observations past the second half of 1998, when global CO was subject to large-scale El-Niño perturbation (see above, p. 69). Notably, box-whisker plots in the upper panel of Figure 4.11 present the monthly distributions of [CO] from the $\Delta^{17}\text{O}(\text{CO})$ -inclusive data only, thus contrasting it with the background [CO] climatology derived from the complete observational record (shown as solid line). Evidently, a much better correspondence between the [CO] profiles is marked for the remote NH data, whereas the $\Delta^{17}\text{O}(\text{CO})$ from IZA pertains to the subset of mixing ratios generally 10–30 ppb higher than typically observed. Series with elevated CO may nonetheless show a consistent isotope ratio record capturing much of the background variation, as, for example, the analysis for the $\delta^{13}\text{C}$ data at KMW or HAP show. The inferiority of the tropical $\Delta^{17}\text{O}(\text{CO})$ record is, however, in a very low number of available samples at IZA whose [CO] either largely disperses around the climatological mean, or groups at the average value substantially elevated with respect to it. The exemplary cases are the March–April and August compositions (*cf.* right panel in Figure 4.11). A further comparison with climatologies was conducted for the available ^{13}C and ^{18}O data from the $\Delta^{17}\text{O}(\text{CO})$ -inclusive data only, surmising that similar isotope signatures indicate compositions close to the background conditions registered in the complete observational record otherwise. Regarding the IZA data, only February, March, June and October averages are found close to the $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ climatologies, whereas July, September, November and January compositions are clearly discarded by at least one of the isotope signatures.⁶⁰ The data from the remaining four months, unfortunately, has no relevant isotope information for such comparison. Concerning the joint SPI and ALE series, similar analysis yields a very good correspondence between the ^{13}C and ^{18}O isotope ratio monthly means from the $\Delta^{17}\text{O}(\text{CO})$ -only data and climatologies, with the average discrepancies of $\pm 0.17_{0.01}^{0.40}\%$ and $\pm 0.29_{0.06}^{1.37}\%$ in $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$, respectively. The only uncertain data is concluded to be the September value showing a large excess in $\delta^{18}\text{O}(\text{CO})$ of +1.37‰ and a concomitant departure in $\delta^{13}\text{C}(\text{CO})$ of –0.25‰ compared to the background climatology. The reciprocal isotope mass-balance suggests that a 5–10% share of this sample containing CO from biomass burning or fossil fuel usage source may explain such deviation, whilst other sources, *e.g.* photochemical, can be ruled out. Subsequently, the corresponding $\Delta^{17}\text{O}(\text{CO})$ value of +5‰ may appear by 0.25–0.5‰ lower than the background level, assuming a proportional dilution of the sample with the surface source CO of ~0‰ in $\Delta^{17}\text{O}(\text{CO})$.

⁵⁸ The remaining sources are attributed to the $\Delta^{17}\text{O}$ signatures of two major terrestrial oxygen reservoirs contained in meteoric waters and air oxygen of 0‰ and –0.455‰, respectively (see Sect. 5.2.8, also Barkan and Luz^[2005], Brenninkmeijer *et al.*^[2003], Meijer and Li^[1998]).

⁵⁹ Quoted is the range of estimates obtained in the current study with the box-model (Sect. 3.5, p. 55) and EMAC (Sect. 6.2.8.3, p. 216) simulations.

⁶⁰ As the rejection criterion, the departure of the monthly average δ larger than $\pm 1\sigma$ from the climatological averages is taken. For both locations, it is greater or equal to $\pm 0.4\%$ and $\pm 1\%$ in $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$, respectively, depending on the season.

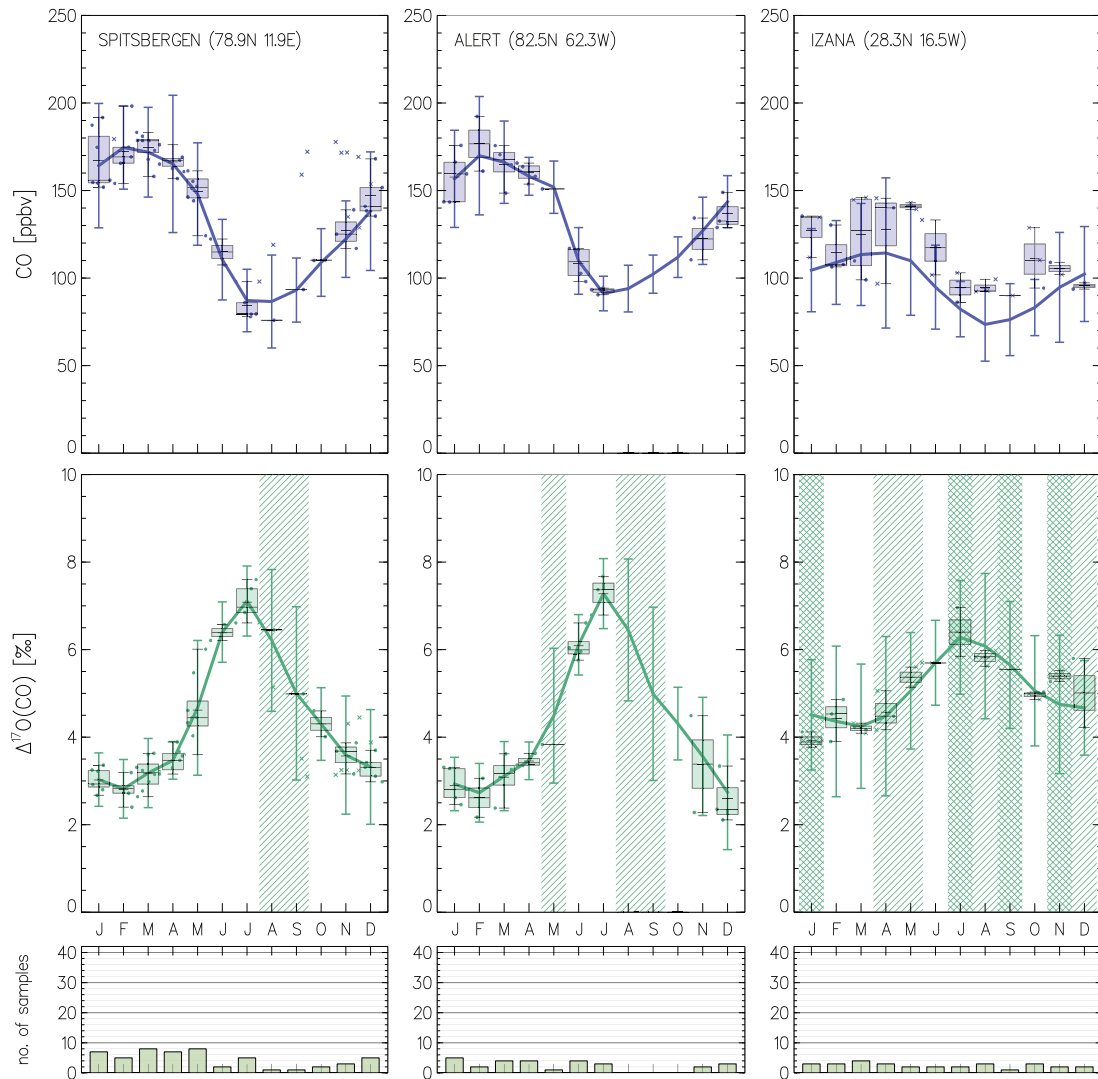


Figure 4.11 Seasonal cycles and single observations of the surface CO mixing ratio (top panel) and corresponding $\Delta^{17}\text{O}(\text{CO})$ (middle panel) constructed from the observational series at particular sites (see Table 4.1, p. 68). Plot outline follows that of Figure 4.4 (p. 74). The hatched areas denote the climatologies that are least certain and/or amended using indirect proxies (see text). Cross-hatched areas (IZA record, right panel) denote months when concomitant $[\text{CO}]$, $\delta^{13}\text{C}$ or $\delta^{18}\text{O}$ from $\Delta^{17}\text{O}$ -inclusive data indicate not representative compositions in comparison with the climatologies from the complete site observational record. Note: Because of the scant amount of data from IZA, shown $[\text{CO}]$ and $\Delta^{17}\text{O}(\text{CO})$ distributions correspond to the complete (*i.e.* not filtered) dataset.

To construct the continuous series for comparison, the uncertain or missing climatological means were further amended. Thus, the missing August and September values at ALE were substituted with those of the SPI record, reckoned to be representative owing to very similar compositions observed at these two locations (see Sect. 4.1.1 above⁴⁶). Due to the same reasoning, the May $\Delta^{17}\text{O}(\text{CO})$ value at ALE based on the single observation was replaced by the corresponding SPI average based on sufficiently larger number of samples (eight). A rather difficult case emerges with the IZA data comprising only one-third of monthly averages that can be taken as representative, according to the non- $\Delta^{17}\text{O}$ data from the climatological record. Although the maxima of $\Delta^{17}\text{O}(\text{CO})$ are likely singled out in July, it is unfeasible to infer the respective minima from the limited data. Nonetheless, the interdependence of $[\text{CO}]$, $\delta^{18}\text{O}(\text{CO})$ and $\Delta^{17}\text{O}(\text{CO})$ established in the representative points may be used for obtaining an approximate indirect estimate of the incomplete climatological means. The analysis on the timing of CO mixing ratio and isotope ratios (see previous section) concludes well-correlated oxygen isotope ratios extrema in the NH isotope CO observations. However, even if the extrema of $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ are synchronous, one cannot relate these signatures straightforwardly because their seasonal variation, in contrast to the effective sink fractionation, is unequally sensitive to the changes in the CO sources. Thus, $\delta^{18}\text{O}(\text{CO})$ extrema nearly coincide with those of $\Delta^{17}\text{O}(\text{CO})$, but the transition between maxima and minima in case of $\delta^{18}\text{O}(\text{CO})$ is additionally slowed down (in fall-winter) or sped up (in spring-summer, respectively) by the changes in source $\delta^{18}\text{O}$ signature (may reach up to 10‰, for example, see the source signature analysis for

KMW at p. 78, also Figure 4.5). In contrast, source $\Delta^{17}\text{O}$ is expected to be virtually constant and below +1‰ throughout the year (disregarding variations in the minor O_3 source). Consequently, it is expedient to use the reciprocal $[\text{CO}]$, a comparative measure of the emission/sink ratio in the atmospheric CO reservoir in the tropics (assuming transport effects negligible), as a proxy chiefly determining $\Delta^{17}\text{O}(\text{CO})$. Furthermore, all $\Delta^{17}\text{O}(\text{CO})$ data correlate best with $[\text{CO}]$ taken about one month later (see previous section, Figure 4.9, p. 87), therefore, the approximated seasonal $\Delta^{17}\text{O}(\text{CO})$ were derived using the linear regression of the representative climatological $\Delta^{17}\text{O}(\text{CO})$ values as a function of $1/[\text{CO}]$ selected from the following month in the regular climatology.⁶¹ The resulting $\Delta^{17}\text{O}(\text{CO})$ climatological series for IZA is hence represented by the four actual and eight approximated values; the latter can be identified laying in the hatched areas in Figure 4.11 (right panel). Except of few particularities, the inferred $\Delta^{17}\text{O}(\text{CO})$ seasonality at IZA fits the range of observed values well and resembles the profiles registered in the Arctic. The approximated values mostly disagree with the observations in the late fall-early winter period, of which only January compositions clearly bear an excess surface component that proportionally lowers the $\Delta^{17}\text{O}(\text{CO})$. The November and December $\Delta^{17}\text{O}(\text{CO})$ distributions are more involute and not representative (note that the statistics for IZA in Figure 4.9 is given for unfiltered data). The analysis of the air masses arriving at IZA in the corresponding months (end of 1996 and 1998) by Bräunlich^[2000] concludes their diverse origins including North America, Atlantic, Africa and Europe, with the latter two supplying biomass burning and technological sources CO-augmented air. Unfortunately, no such analysis is available for the tropical $\Delta^{17}\text{O}(\text{CO})$ sample data.

All three $\Delta^{17}\text{O}(\text{CO})$ climatologies exhibit distinct maxima in July and less pronounced minima in late February. As with the $\delta^{18}\text{O}$ signal, $\Delta^{17}\text{O}$ maxima in all series are triggered with the seasonal $[\text{OH}]$ peak, whereas minima are of likely different nature. In the NH remote data they coincide with largest $[\text{CO}]$ which points to the source effect (*e.g.* transport of variable composition from the lower latitudes), whereas minima ahead of the mixing ratio at IZA signify their photochemical origin (see previous chapter). Of all isotope signals, $\Delta^{17}\text{O}$ demonstrates the largest sensitivity to the degree of photochemical CO processing: The observed ~3‰ variation at IZA doubles at high latitudes, denoting a stronger temporal equilibrium of sources and sinks in the tropics. Conformably, the annual average $\Delta^{17}\text{O}(\text{CO})$ of +5‰ at IZA is higher when compared to the SPI/ALE value of +4.1‰ (mixing ratio-weighted climatological means). Notwithstanding, some $\Delta^{17}\text{O}(\text{CO})$ variations in the NH remote data are found uncommonly enhanced when confronted with the corresponding mixing ratio variations, as opposed to the rest of the observed data. For instance, $[\text{CO}]$ and $\Delta^{17}\text{O}$ vary uniformly around their annual averages, within $\pm 20\%$ at IZA year round and $\pm 40\%$ at SPI/ALE in fall-winter, respectively. However, high-latitude summer $\Delta^{17}\text{O}(\text{CO})$ departures are greater than +60%, accompanying otherwise regular changes in $[\text{CO}]$ of -40%. The inconsistency of such relation is that when there is sufficient oxidation of CO by OH in the atmosphere to bring about the same strong enhancements (summer $\Delta^{17}\text{O}(\text{CO})$ at SPI/ALE reach between +6.5‰ to +8.7‰), the concomitant CO concentrations become much lower than the observed 80–110 ppb. This indeed confirms a secondary, photochemical source of $\Delta^{17}\text{O}(\text{CO})$; under a few assumptions its magnitude can be directly judged using the variation surplus, as shown below.

A detailed analysis of the $\Delta^{17}\text{O}(\text{CO})$ seasonal behaviour is presented in Figure 4.12 and uses a variation of the method employed by Stein and Rudolph^[2007]. In their model study, the authors scrutinise the effect of the sink fractionation in removal of atmospheric ethane, assuming an invariable surface source composition and KIE in the sole atmospheric removal process. In the first approximation (so far neglecting the O_3 source of CO) these assumptions suit the particularities of $\Delta^{17}\text{O}(\text{CO})$, owing to nearly invariable surface sources composition of $\Delta^{17}\text{O} \sim 0\text{‰}$ and prevalent removal of CO via OH escorted with the MIF. Conformably, there are two processes that principally determine $\Delta^{17}\text{O}(\text{CO})$ in the atmosphere, namely: (1) Emission into the atmospheric reservoir, and (2) The OH sink causing MIF in leftover atmospheric CO. Let us regard (1) exemplified for an air parcel with a given background composition of mixing ratio C_{bg} and MIF at level Δ_{bg} . Upon emission into this parcel of air with C_{em} abundance of CO with a signature Δ_{em} , the resulting composition (C_{mix}, Δ_{mix}) is described by the mass-balance relation as

⁶¹ The respective approximation equation (in permil units) is $\Delta^{17}\text{O}_m^{\text{app}} = 0.399 \cdot 10^3 [\text{CO}]_{m+1}^{-1} + 0.837$, where index m denotes the month of the year. The intercept term (at $[\text{CO}]^{-1} \rightarrow 0$) signifies (in analogy with the Keeling plot approach) the approximate overall composition of the source CO, *i.e.* presumably the effective input of the O_3 to $\Delta^{17}\text{O}(\text{CO})$ at IZA. The value of +0.837‰ is at the upper limit of the estimates inferred in this study⁵⁹, however it is accurate within at least $\pm 1\text{‰}$, according to the regression analysis.

$$\Delta_{mix} = \frac{\Delta_{em}C_{em} + \Delta_{bg}C_{bg}}{C_{em} + C_{bg}} \equiv \frac{C_{bg}}{C_{mix}} \Delta_{bg}, \quad (4.1)$$

that is essentially a proportional decrease of Δ_{bg} assuming the dilution by the sources with $\Delta_{em} = 0\text{‰}$. This way, any increase of the atmospheric $[\text{CO}]$, be it a surface or in-situ source, shifts the composition of an air parcel down-right along the mixing curves in the $\Delta^{17}\text{O}(\text{CO})$ vs. $[\text{CO}]$ plot (depicted with dotted lines in Figure 4.12, panel (a)). Depending on the background mixing ratio and $\Delta^{17}\text{O}$, mixing curves are positioned higher or lower in the plot, however they never intersect at a given C_{bg} or Δ_{bg} . Observational points in Figure 4.12 usually found with lowest $\Delta^{17}\text{O}$ in a mixing-kind relationship delineate the evolution of the atmospheric reservoir during fall-winter, when it is being steadily refilled with surface CO under inhibited photochemistry conditions. The hatched area marks the range of background mixing states empirically derived for the high- and low-latitude conditions (*ibid.*, denoted with ‘LL’ and ‘HL’) hosting predominantly November to February compositions. Interestingly, the relationship (4.1) unequivocally determines the range of possible states of the background reservoir (C_{bg} , Δ_{bg}) into which an emission took place, whilst the remaining point generally positioned above the background mixing curves. Exceptional to this are the three distant points with very low $\Delta^{17}\text{O}(\text{CO})$ registered at SPI, that lie close on a mixing curve matching the background reservoir states from ~ 60 ppb of CO enriched by $+5\text{‰}$ down to $+3\text{‰}$ at 100 ppb, respectively. Notably, none of the remaining observed compositions suit as the background state that could yield such mixing result at any emission strength (disregarding, of course, negative $\Delta^{17}\text{O}$ source signatures). However, there is an alternative process, *i.e.* (2), that may hypothetically lead to these outcast compositions. Like mixing, sink fractionation process distinctly constrains the character of mutual changes to $[\text{CO}]$ and $\Delta^{17}\text{O}$, which is described by the Rayleigh function:

$$\Delta_{sink}(t) = 1 - (1 + \Delta_0) \left(\frac{C_{sink}(t)}{C_0} e^{-1} \right)^{\Delta^{17}\text{O}\eta} \quad (4.2)$$

where the composition (C_{sink} , Δ_{sink}) describes the evolution of the parcel progressively undergoing a sink from its initial state (C_0 , Δ_0), respectively. The nominal sink fractionation magnitude, $\Delta^{17}\text{O}\eta$, equals the enrichment the parcel acquires at e -folding time, that is, in case of $\text{CO} + \text{OH}$ reaction, roughly $+5\text{‰}$ (see also Sect. 3.4.4, p. 47, for details). Conformably, the decrease in $[\text{CO}]$ due to the OH sink shifts the compositions up-left along the sink fractionation curves (in Figure 4.12 they appear as solid straight lines). The abovementioned low- $\Delta^{17}\text{O}$ outcast winter points at SPI in kind could result from the continuous ageing of the parcel with initial CO content of around 200–230 ppb and 0‰ , assuming no mixing with surrounding air. The latter, however, is unlikely regarding that these compositions were sampled in November–December, *i.e.* 2–3 months after the OH and hence the CO sink seasonally cease in the NH extratropics. Neglecting possible analytical problems, the most probable scenario explicating these prominent compositions is the large late-summer CO plume followed by a moderately long-lasting sink and subsequent dilution with background CO that is low in $\Delta^{17}\text{O}$ as well.

One remarks furthermore, that starting even from the winter points highest in $[\text{CO}]$, OH sink and mixing processes cannot “shoot” the compositions higher than the respective fractionation curve, *e.g.* above April values. In other words, the observed changes in spring–summer CO follow a much steeper slope *requiring* an extra source of $\Delta^{17}\text{O}(\text{CO})$. We further demonstrate it by means of a simple exposure box-model analogous to those employed in Sect. 3.5 for the purpose of the isotope kinetic chemistry evaluation. Within the current inquiry an identical chemical mechanism and its stable isotope extension is used in three basic setups to simulate a four-month evolution CO composition in an air parcel initialised with typical winter conditions and tracer compositions (starting CO chosen at 180 ppb with $\Delta^{17}\text{O}$ of $+2.8\text{‰}$). In fact, the current model setup mimics that presented in Sect. 3.5, but with tracer emission and deposition processes excluded. The box is positioned at the surface in mid-latitudes (45°N) to achieve the average temperature and solar irradiance intensity.⁶² The objective of the simulations performed is to show the constraints of the mutual $[\text{CO}]$ and $\Delta^{17}\text{O}(\text{CO})$ evolution under three basic setups: (1) Reference setup, including *in-situ* production of CO from methane and non-methane hydrocarbons with $\Delta^{17}\text{O} \sim 0\text{‰}$ and the ozonolysis source yielding CO with the $\Delta^{17}\text{O}$ signature of $\sim +30\text{‰}$, (2) Same as the reference setup but with the O_3 composition set to $\Delta^{17}\text{O}(\text{O}_3)$ of 0‰ , and (3) Only the $\text{CH}_4 + \text{OH}$ photochemical source of CO is allowed.

⁶² See further details in Sect. 3.5.1. Typically, temperature is the key factor determining the ratio between the reaction rate coefficients of the reactions leading to the CO production, *e.g.* $\text{CH}_4 + \text{OH}$ and $\text{NMHC} + \text{OH}$, and $\text{CO} + \text{OH}$ sink reaction that is chiefly pressure-dependent. For the means of the current analysis, such setting is consistent, assuming that CO is mainly emitted in mid-latitudes and further transported to the Arctic (see also Sect. 4.1.2, p. 81).

The results of the exposure model simulations are presented in Figure 4.12 (panels (b)–(d)), with all simulations providing various fits through the observational data. Thus, setup (3) shows a clear sink-fractionation progression of $\Delta^{17}\text{O}(\text{CO})$ peaking above +7‰ enhancement owing to the low mixing ratios reached. Past the maximum, as $[\text{CO}]$ continues to drop, the simultaneous production from CH_4 takes over and dilutes atmospheric $\Delta^{17}\text{O}(\text{CO})$ by supplying CO with $\Delta^{17}\text{O}$ of air oxygen of ~ 0 ‰. Such low-CO behaviour is marked for all three setups. A similar relationship is expected at remote background locations subject to photochemistry but not surface emission (*e.g.*, Pacific), as the results of the 3D-model simulations on $\Delta^{17}\text{O}(\text{CO})$ in the current study suggest (see Sect. 6.2.8, p. 210). The setup (2) yields greater deviations from the mixing-sink relationship at the expense of larger photochemical CO production from the non-methane hydrocarbon precursors. Actually, if a surface CO emission into the parcel were to take place, it would cause an identical, mixing-like shift in the $\Delta^{17}\text{O}(\text{CO})$. However, as a trade-off, the maximum $\Delta^{17}\text{O}(\text{CO})$ that can be reached in these conditions is substantially lowered to +6.4‰ and occurs at mixing ratios lower by 30–40 ppb compared to the observed compositions. Finally, the reference setup appears to fit the observed extremes, as well as the steep $\Delta^{17}\text{O}/\text{CO}$ slope of the winter-spring transition specifically marked in the SPI data. Although the simulated hydrocarbon ozonolysis source amounts to (35–38)% of all photochemical CO production, it constitutes mere (3–4)% of the overall CO budget. Nevertheless, the estimated contribution of O_3 to the CO MIF is substantial through additional enrichments of up to +1.2‰ in $\Delta^{17}\text{O}(\text{CO})$. Conformably, a much better model fit is achieved for the concomitant $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ data. The simulated exposure model composition also fits extremely well the $\Delta^{17}\text{O}(\text{CO})$ seasonalities in the Arctic, notwithstanding that the temporal development of the observational data is around two months longer owing to the transport and mixing effects.

Summing up, the $\Delta^{17}\text{O}(\text{CO})$ observational data regarded here is comprised of the records distinguished by various level of representativeness. The records from SPI and ALE, notwithstanding less certain August–September data, grant sufficient information to create a complete seasonal $\Delta^{17}\text{O}(\text{CO})$ climatology for the remote NH locations. Conversely, only $\frac{1}{3}$ of the seasonal means can be derived from the limited data at IZA, as the cross-analysis with more complete ^{13}CO and C^{18}O records suggests. The remaining seasonal averages, fitted using the interrelation and timing of the seasonal $[\text{CO}]$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ signals, show good correspondence with representative data. Thus synthesised seasonality matches the Arctic record within the framework of our current knowledge on atmospheric $\Delta^{17}\text{O}(\text{CO})$. Not mentioned above, the analysis carried out in this section is congruent with the results of the box-model simulations presented in Sect. 3.5 as well regarding the $\Delta^{17}\text{O}(\text{CO})$ data. A more specific exposure model used to additionally explore the behaviour of the observed compositions suggests rather strong constraints on the reciprocal changes of $[\text{CO}]$ and $\Delta^{17}\text{O}(\text{CO})$ and, as a consequence, an independent evidence for the minor but not unimportant input of atmospheric O_3 to CO.

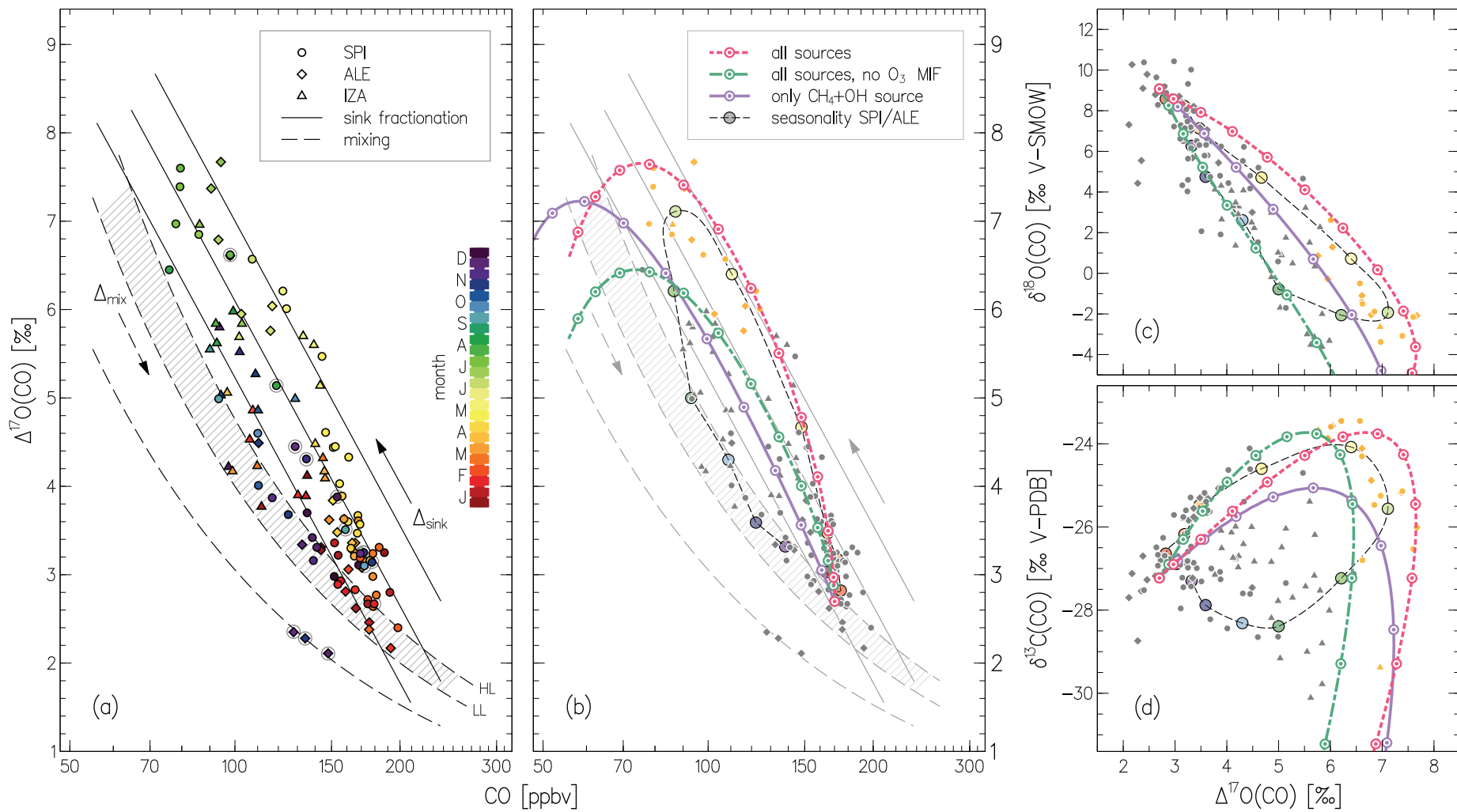


Figure 4.12 Observed surface $\Delta^{17}\text{O}(\text{CO})$ as a function of CO mixing ratio. Panel (a): Symbol colour refers to the month of the year. Dashed lines denote the mixing curves derived from Eq. (4.1) for different background mixing ratios C_{bg} and compositions Δ_{bg} , respectively. Mixing curves marked as HL and LL refer to the high- and low-latitude background profiles (taken equal to the seasonal averages at SPI and IZA in February, see text). The dashed arrow shows the course of the airborne composition change due to admixing of the surface CO with $\Delta^{17}\text{O}$ of 0‰. Solid lines present the anticipated evolution of [CO] and $\Delta^{17}\text{O}(\text{CO})$ in an isolated parcel undergoing the photochemical sink predicted by the Rayleigh fractionation process (Eq. (4.2)) for nominal sink enrichment $\Delta^{17}\text{O}_{\text{CO+OH}}$ of $\sim +5\text{‰}$ and various starting compositions (direction is exemplified by the solid arrow). Panels (b)–(d): Observed multi-isotope composition of CO overlaid with the results of the exposure model (see text). Coloured symbols denote compositions that require MIF input from O_3 to CO (see text).

4.2 Isotopic composition of CO from CARIBIC-1

Complementary to the boundary layer observations from surface stations, a comprehensive dataset on the isotopic composition of CO in the UTLS has been provided by the CARIBIC project (Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container, Brenninkmeijer *et al.*^[1999a]⁶³). Installed aboard a passenger aircraft, the CARIBIC platform comprises an airfreight container with the automated instrumentation for sampling of outboard air (by means of a dedicated air inlet system) and subsequent in-situ and posterior (*i.e.* by laboratory analysis of collected air samples) measurement of atmospheric gases and trace compounds. Data regarded here pertain to the Phase One of CARIBIC (hereafter referred to as “C1”) operated on a monthly basis from November 1997 to April 2002 onboard a Boeing 767-300 ER of LTU International Airways on long-distance flights. Overall, C1 measured tens of different trace gas species in the air sampled at the typical cruise altitudes of 10–11 km; the instrumentation allowed an on-line detection of CO and O₃ at time resolutions of 130 and 16 s corresponding the flight distances of ~32 and ~4 km, respectively (Zahn *et al.*^[2000]). For the accurate laboratory analysis of CO isotopologues (as well as the abundances of CO₂, CH₄, N₂O and other tracers including NMHCs and halocarbons), processing of larger air samples was required⁶⁴. The latter were collected in stainless steel canisters (holding ~350 litres of air STP) by the whole air sampler (WAS) of C1 with a capacity of twelve canisters. The WAS canisters were sampled within ~20 min intervals, thus representing the integral of the compositions encountered along flight segment of ~250 km length. The overall uncertainty of the measured WAS CO is reported being less than ±1% for the mixing ratio and ±0.1‰/±0.2‰ for $\delta^{13}\text{C}(\text{CO})/\delta^{18}\text{O}(\text{CO})$, respectively (Brenninkmeijer *et al.*^[2001]). An extensive overview of the C1 flights and meteorology, as well as the analysis of the CO and ozone budgets from the on-line measurements is given by Zahn *et al.*^[2002] (hereafter referred to as “Z02”). The current analysis assimilates the results of Z02, although considers exclusively the WAS data.

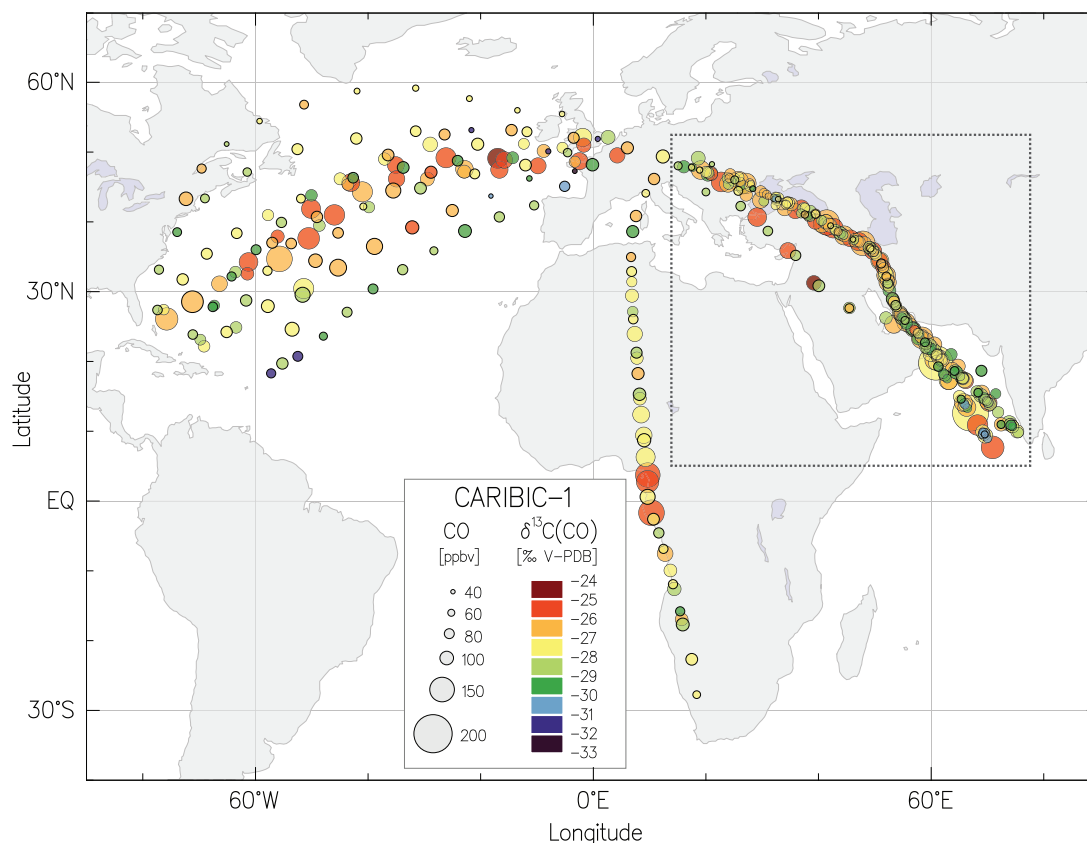


Figure 4.13 Overview of CARIBIC-1 isotope CO observations geography. Symbol sizes denote the observed CO mixing ratios; colours refer to the respective ^{13}C composition. The dashed-line rectangle denotes the Indian routes.

⁶³ See also <http://www.caribic-atmospheric.com>.

⁶⁴ However, the requirement of substantially large air samples in C1 is given by the need to collect sufficient amounts of CO that enable measurement of the ultra-trace ^{14}CO abundances (similarly to the surface station data ^{14}CO , see p. 67).

Figure 4.13 presents the geography of the WAS collection combined with the measured $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ for a total of 47 flights during the operation of C1. The flight routes are clustered in three groups, *viz.* North Atlantic (128 samples), South Africa (36 samples) and Indian Ocean (267 samples) destinations; except for a few samples, the air is collected within the 10–11 km altitude range. Notably, much different CO mixing ratios (spanning 40–190 ppb) are encountered in diverse flights, with very low abundances (compared to the typical tropical and ETNH troposphere) pertaining to stratospheric air sampled at mid- and high latitudes. To single out the stratospheric compositions, the concomitant de-trended N_2O mixing ratios were used as a proxy, following the approach by Assonov *et al.*^[2010]. At a threshold of 310 ppb, a ~15% share of the C1 samples is reckoned to contain a significant portion of stratospheric air. Figure 4.14 (p. 98) further presents the comparison of the complete C1 and station isotope CO datasets. In the left panel, the estimates of the surface CO sources' strengths and their $\delta^{13}\text{C}/\delta^{18}\text{O}$ signatures are superimposed on the observational data in the two-isotope plot. The dashed arrow indicates the tendency of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures' change upon the removal of CO from the atmosphere, as it is being escorted by the isotope fractionation (see also Sect. 6.1.4). Near the arrow's head, compositions characteristic for the equilibrium between the overall source and sink of CO are expected, so the averages of the datasets reflect the background conditions. A much more compact distribution of the C1 data, whose variability in $[\text{CO}]$ and isotope compositions merely accounts for a half of that from the surface observations, is due to the remoteness of the observational domain: Surface air, before it arrives to the UTLS, may be exposed to photochemistry and mixing for a period of days to one month.⁶⁵ Moreover, C1 sampling over ~250 km flight segments additionally homogenises WAS compositions: For instance, if a distinctly higher mixing ratio/isotope signatures characteristic for a particular source are encountered in a plume, they usually become largely attenuated by more often sampled clean background air.⁶⁶ In the “point” observations from the surface stations residing in proximity to the sources, on the contrary, the departures towards biomass burning, fossil- and biofuel sources are conspicuous on top of the elevated mixing ratios.

Like the station observational data, the C1 data underwent additional selection and processing. The selection was applied to obtain the space and time consistent observational series (*i.e.* “climatology”) for the subsequent comparison with the model results; of the complete C1 dataset only the Indian Ocean destinations offer a sufficient density of observations of 4–5 samples per degree latitude on average (see further). The processing of the data mainly concerns the samples with high (exceeding 150 ppb) ozone abundances that witness inherent artefacts in CO isotope composition on top of low CO mixing ratios. These samples (amounting to ~15% of all WAS data) are substantially enriched in ^{18}O , though do not exhibit much discernible shifts in $\delta^{13}\text{C}(\text{CO})$ (see Figure C.1, panels (c) and (d) in Appendix C, p. 247). The in-depth analysis of the affected compositions suggests that a systematic contamination of the sampled air has occurred due to the production of CO mediated by ozone, the only species that carries extremely high ^{18}O relative abundance capable of contributing with such a prominent signal. Notably, all suspicious samples bear a substantial portion of O_3 -rich stratospheric air, which is confirmed by the distinctly elevated ^{14}CO and lowered N_2O content, as well as $\delta^{13}\text{C}(\text{CO})$ values typical for stratospheric conditions (*cf.*, for example, Brenninkmeijer *et al.*^[1996]). The affected data were corrected for the contamination using the regression analysis detailed separately in Appendix C (p. 245). The correction affects the concomitant $\delta^{13}\text{C}(\text{CO})$ values subject to positive biases due to the O_3 -stemming C^{17}O , whose excess (over the typical tropospheric abundances) interferes in the laboratory ^{13}CO determination. The $\delta^{13}\text{C}$ biases are, however, small for tropospheric compositions (estimated within $+(0.2\text{--}0.5)\text{‰}$) and become noticeable (up to $+1.2\text{‰}$) only for the samples with high $[\text{O}_3]/[\text{CO}]$ abundance ratios (about 9% of all data).

⁶⁵ See, Zahn *et al.*^[2000]. By comparing with the surface observational data from NOAA-CDML, they estimate a phase shift of about 5 weeks in otherwise much similar $[\text{CO}]$ seasonalities from C1 (Indian routes) and surface CO (Israel).

⁶⁶ Excluding a few cases when the compositions of the encountered large surface emission plumes sampled an intact WAS canister.

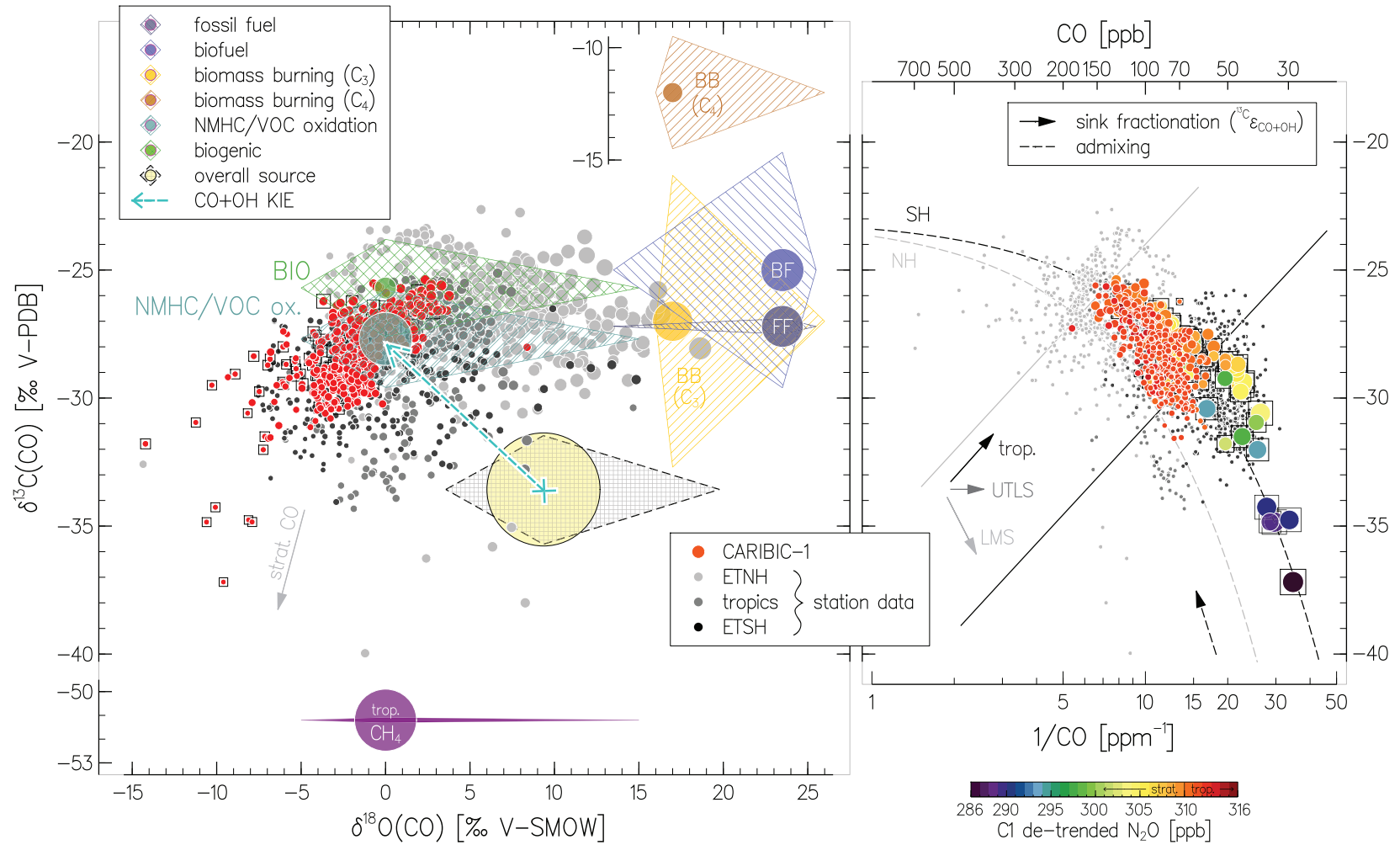


Figure 4.14 Tropospheric CO and its isotope composition observed at the surface (black and grey circles) and in the UTLS by CARIBIC (C1, red circles). Frames denote the filtered and processed data (see text). Left: Observations and principal sources of tropospheric CO in the two-isotope plot (mind the broken $\delta^{13}\text{C}$ axis). Symbol sizes indicate the variations in the mixing ratio and sources strength (not to scale). Hatched areas denote the uncertainties associated with the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signatures of a given source. The dashed arrow indicates the average magnitude of the (nominal) isotope fractionation in the tropospheric CO sink. Right: Variation of $\delta^{13}\text{C}(\text{CO})$ as a function of reciprocal $[\text{CO}]$. For the C1 observations only, the colour code denotes the concomitant N₂O mixing ratios, symbol size scales with the ^{14}C content; both characteristics are the indicators for stratospheric air. The solid and dashed lines exemplify the evolution of the compositions caused by the CO removal from and the emission into the atmospheric reservoir, respectively, reckoned for the NH and SH data (the analysis is similar to that described in Sect. 4.1.3 and Figure 4.12, p. 95). Note the three fractionation slopes (+5‰, 0‰ and -7‰) presented for the typical tropospheric, UTLS and LMS conditions, respectively.

The shape of the C1 $\delta^{13}\text{C}(\text{CO})/\delta^{18}\text{O}(\text{CO})$ distribution in Figure 4.14 differs from that of the station data, showing a higher degree of correlation between the ^{13}C and ^{18}O signals, in a similar way tropical surface CO differs from its high-latitude counterpart. The latter, as discussed above in Sect. 4.1.1 (p. 78), displays a characteristic triangular-shaped distribution (*cf.* Figure 4.5, p. 79) owing to the opposite kinetic fractionation in ^{13}CO and C^{18}O photochemical removal, whose seasonal variation is substantially large in the extratropics. Compared to the tropical surface record, UTLS CO witnesses an even higher degree of photochemical processing: The C1-observed $\delta^{18}\text{O}(\text{CO})$ never exceeds a threshold of +5‰, a very light composition acquired on account of both, large depletion due to the CO sink fractionation and, equally important, photochemical sources of $\sim 0\%$ or less in $\delta^{18}\text{O}$ (Zahn *et al.*^[2000], Brenninkmeijer and Röckmann^[1997], see also Sect. 3.4.2, p. 42). The in-situ produced CO is depleted in ^{13}C as well, however the depletion it inflicts on $\delta^{13}\text{C}(\text{CO})$ is compensated by the large effective positive ^{13}CO sink fractionation, thus the final C1 $\delta^{13}\text{C}(\text{CO})$ distribution becomes much comparable to that of the station data. The seasonal variations in the C1 $\delta^{13}\text{C}(\text{CO})$, $\delta^{18}\text{O}(\text{CO})$ and $[\text{CO}]$ are most synchronous, in contradiction to the surface compositions' timing (see Sect. 4.1.2, p. 85, also further). This suggests that the variation in the effective sink fractionation is small, whilst changes in the UTLS $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ rather reflect the seasonal shift in the overall tropical CO source apportioning.⁶⁷ Assuming an invariable sink fractionation to mass-balance the sources of ^{13}CO , the variation in C1 $\delta^{13}\text{C}(\text{CO})$ of around 2.8‰ (between the February-March and September-October averages) yields respective changes to the methane-derived CO component fraction γ_{CH_4} of $\sim 11\%$, which is significantly less than that at the surface (estimated to be within 15%–20% at tropics and high latitudes, respectively⁶⁸). The steadiness of the effective ^{13}CO sink fractionation is further enforced by the negative $^{13}\text{CO}+\text{OH}$ KIE at low pressures in the UTLS: Conjointly with the transport and mixing, it cancels out the sink fractionation effect at the pressure altitudes of ~ 100 hPa (see further Sect. 6.2.5, p. 184). The absent ^{13}C sink fractionation is seen in Figure 4.14 (right panel) as the horizontal shifts in the LMS compositions along the abscissa, when the $\delta^{13}\text{C}(\text{CO})$ values remain unaltered as the reciprocal $[\text{CO}]$ increases.

It is attainable to analyse the spatio-temporal seasonality of the tropical and mid-latitude isotope CO from C1, owing to the sufficient density of observations along the Indian Ocean routes (abbreviated “IOR” further, highlighted in Figure 4.13 above). These data typically offer two observations per calendar month, covering the 10°N – 50°N band with a dozen of samples, which is equivalent to at least six samples per degree latitude per year on average. To construct the seasonality, the data were binned in one-degree intervals on a weekly basis and further interpolated along latitude and in time. This approach is similar to that applied by Z02 for C1 ozone and CO on-line measurements, however with three key differences: (1) scrutinised is exclusively the WAS data, (2) the calendar date was used, *i.e.* multi-year observations are binned into one ‘perpetual’ year, and (3) in addition, the filtered floating average (FFA) analysis was applied to extract the inherent seasonal changes contained in the CO distributions along particular latitudes.⁶⁹ The resulting seasonalities for WAS CO data are presented in Figure 4.15, with the mixing ratio distribution being in a good agreement with that obtained by Z02 from the CO on-line instrument data (*cf. ibid.* Figure 4e), except for the tropical (south of 20°N) winter compositions. The latter in Z02 range from 130 to 230 ppb and trace back to the tropical CO plume originated from the Indonesian peat and vegetation fires in November–December 1997. This large-scale perturbation signal was conformably filtered out by the FFA, providing the average ‘background’ seasonal CO abundance at 85–95 ppb derived from the other years’ data, respectively. Besides winter 1997, Z02 note other events occurred in every year of C1 observations; these were singled out by FFA as well and are listed in Table 4.3. It is advantageous to use the isotope composition information to ascertain the potential origin of this overabundant CO. Having the seasonal averages derived for the given period and flight position, it is possible to mass-balance the compositions in question using the following relation:

$$i\delta_{\text{src}} = i\delta_e + \frac{C_s}{C_e - C_s} (i\delta_e - i\delta_s) - i\epsilon \quad (4.3)$$

⁶⁷ This inference is supported by the modelling results obtained within this study: The CO simulated by EMAC in the C1 domain carries on average the same (within $\pm 0.3\%$) effective sink fractionation, irrespective from the mixing ratio (see details in Sect. 6.2.4.2, p. 182, also Plate D.16, p. 286).

⁶⁸ See Röckmann *et al.*^[2002], also Sect. 3.5.2 and Figure 3.11 (p. 63) on the modelling of the CO budget at the surface.

⁶⁹ FFA is essentially a two-pass technique that discards the samples with values outlying the ordinary floating average by a range typically given in standard deviations; the filtering is performed along the time coordinate. For the C1 data, samples with deviations from the latitudinal averages of $[\text{CO}]$ larger than $\pm 1.64\sigma$ (equivalent to $\sim 10\%$ for the normally distributed data) are discarded, which is a weaker criterion compared to that applied to the MOP station data ($\pm 1\sigma$, see p. 76, Sect. 4.1.1).

where indices e and s denote the event and seasonal CO parameters, $i\delta$ stands for the i^{th} isotope (^{13}C or ^{18}O) composition and C for the mixing ratio, respectively. The resulting estimate of the source CO signatures $i\delta_{src}$ unequivocally depends on the effective sink fractionation magnitude $i\epsilon$, which may be approximated constant owing to a considerable age of the air masses picked at the UTLS (see above). Furthermore, the certainty associated with the derived $i\delta_{src}$ is inverse proportional to the CO excess over the seasonal value, hence larger deviations obviously yield clearer signals. Therefore, the estimates $^{13}\text{C}\delta_{src}$ of $^{18}\text{O}\delta_{src}$ presented in Table 4.3 are reckoned for the samples with the highest mixing ratios and for the average of the samples singled out by the FFA within a particular event. This also allows for probing the integrity of the source, *i.e.* whether the tendency between the peak and average $i\delta_{src}$ is in accordance to their expected evolution in a plume experiencing atmospheric mixing and/or photochemistry.

For example, for the November 1997 and April 2000 events, one remarks little or negative changes in $^{13}\text{C}\delta_{src}$ and a clear downward tendency in $^{18}\text{O}\delta_{src}$ in conjunction with a decreasing mixing ratio excess ($C_e - C_s$). Such demeanour is characteristic for the mixing and photochemistry processes introducing background and in-situ CO which is light in ^{18}O and ^{13}C ; the effect on $\delta^{13}\text{C}(\text{CO})$ is, however, attenuated by the positive sink fractionation. For the December 1997 event (alike for November 1997 it is attributed to the Indonesian fires, see Z02) one remarks very close peak and average values with low $^{18}\text{O}\delta_{src}$, suggesting an aged air mass with isotope composition much equilibrated by photochemistry but slowly diluted with the background air. Similar conclusions are drawn for the June 1998 values, however the higher $^{18}\text{O}\delta_{src}$ and comparable $^{13}\text{C}\delta_{src}$ signatures point to the surface source more enriched in ^{18}O , *i.e.* fossil- or biofuel use rather than biomass burning (this confirms the analysis of Zahn *et al.* [2000]). Notably, the timing of these events (*e.g.*, austral and boreal midlatitude summer, respectively) promotes active photochemistry conditions. At last, the March 2000 high [CO] appears to be of complex origin, as the peak value points to the biomass burning event, nonetheless the average being heavier in ^{18}O suggests other, *e.g.* anthropogenic, surface sources. It should be noted that due to the large WAS sample size (and hence large spatial integration of the compositions) the analysis shown here is rather qualitative, *i.e.* the uncertainties associated with the derived $i\delta_{src}$ are large, about a few permil.

Table 4.3 Isotope composition of source CO in the high-CO events observed in C1

Event		Composition (peaking sample / average) ^a				Source type ^c
Period	Location [°N]	C_s [ppb] ^b	$C_e - C_s$ [ppb]	$^{13}\text{C}\delta_{src}$ [‰]	$^{18}\text{O}\delta_{src}$ [‰]	
November 1997	0–20	81–86	44.8 / 20.8	–32.3 / –31.3	+17.3 / +13.7	BB ^d
December 1997	0–20	86–92	30.3 / 22.7	–27.2 / –29.1	+3.4 / +3.4	BB+PC ^d
June 1998	36–40	90–102	17.0 / 9.3	–27.9 / –24.8	+12.0 / +12.1	FF/BF+PC
March 2000	38–42	103–104	27.0 / 14.6	–27.7 / –28.5	+17.5 / +20.0	BB, FF/BF ?
April 2000	24–30	97–103	13.4 / 12.4	–26.2 / –28.3	+23.2 / +20.3	FF/BF ^d

Notes:

Abbreviations refer to: BB – biomass burning; PC – photochemistry (including sink effects); FF/BF – fossil and biofuel usage. The isotope compositions $^{13}\text{C}\delta_{src}$ and $^{18}\text{O}\delta_{src}$ are reported on the V-PDB and V-SMOW isotope standard scales, respectively (see Sect. 3.2).

^{a)} C_s and C_e denote the seasonal and event CO mixing ratios, respectively, derived using Eq. (4.3) and taking $^{13}\text{C}\epsilon = +4.5\text{‰}$, $^{18}\text{O}\epsilon = -8.5\text{‰}$ (average values diagnosed in the sensitivity simulations with EMAC, see Sect. 6.2.4.2, p. 182). See text for details.

^{b)} Span of the respective seasonal CO mixing ratios during the event.

^{c)} Discriminated according to the typical source isotope signatures listed in Table 3.7 (p. 56, Sect. 3.5.1).

^{d)} Likely to be a distinct, dominating source plume (see text).

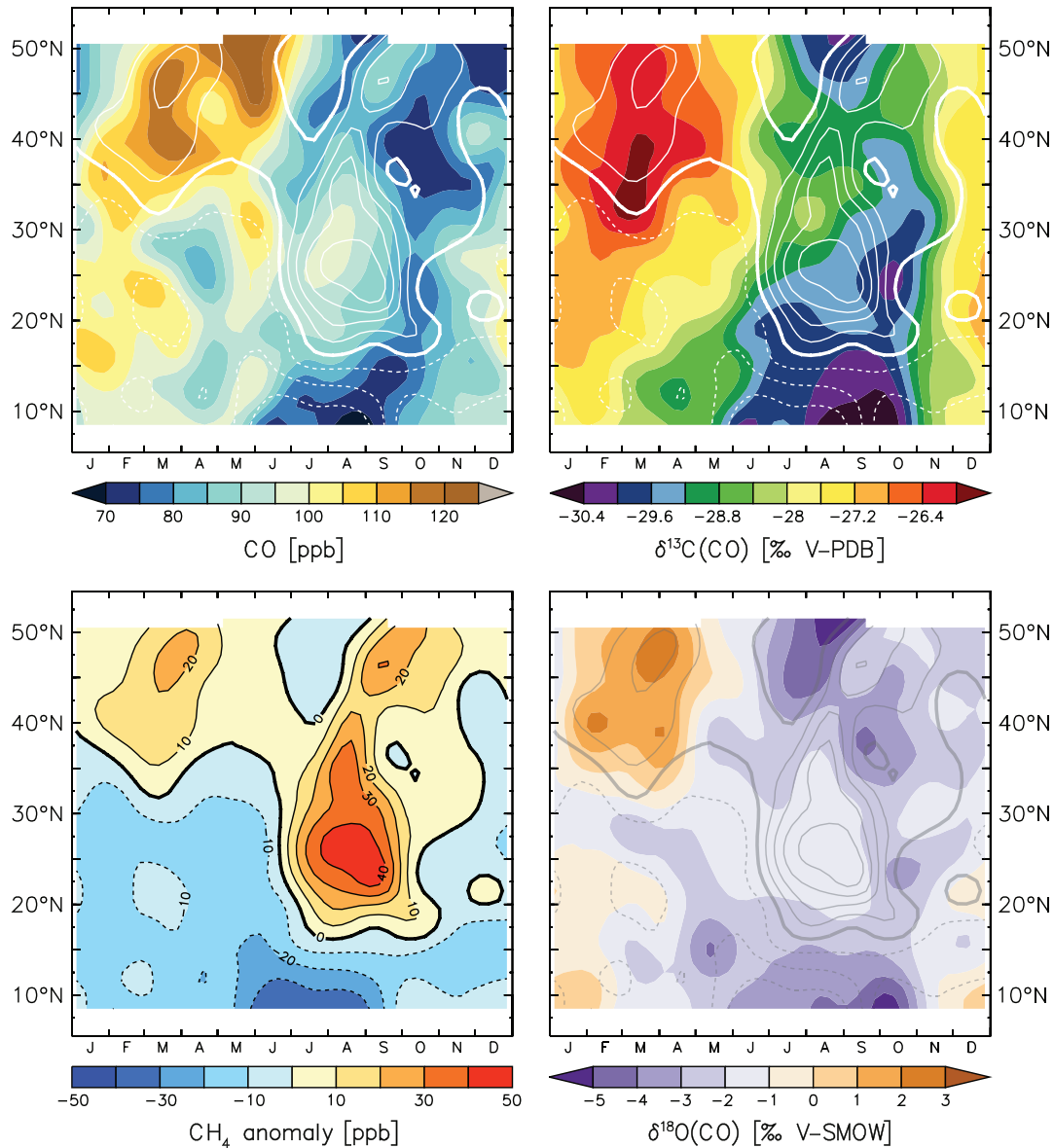


Figure 4.15 Climatology of CO mixing and isotope ratios observed by CARIBIC-1 along the Indian Ocean routes (IOR). The lower left panel presents the IOR climatology of the methane mixing ratio anomaly a_{CH_4} (with respect to the average of 1768 ppb). To aid the analysis, the contours of a_{CH_4} are superimposed on the CO distributions.

The resulting (after the large-scale CO disturbances are excluded by FFA) distributions of CO isotope and mixing ratios shown Figure 4.15 reveal distinct seasonal patterns. In particular, $\delta^{13}\text{C}(\text{CO})$ is found to vary substantially within 3‰ nearly equally over the whole range of latitudes, whereas the least temporal changes pertain to [CO] and $\delta^{18}\text{O}(\text{CO})$ between 20°N and 30°N. Similarly, clear $\delta^{13}\text{C}(\text{CO})$ variations are observed for the stations not presenting a distinct [CO] seasonality (*e.g.*, KMW, SBK and MOP, see Sect. 4.1.1), although for the UTLS CO the variation is likely a mere source effect, owing to the more steady sink fractionation. The relative timing of the C1 CO seasonal signals is obviously different from that at the surface, showing a high degree of correspondence between the mixing and isotope ratios, hence no ‘transport’ effect (*cf.* Figure 4.8 presenting surface CO timing, p. 85, also Sect. 4.1.2, p. 85 for details). The [CO], $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ extrema coincide well within the 15°–45°N latitude range, with uniform minima occurring in October. Exceptionally, the [CO] minima south of 15°N occur ~6 weeks earlier than the respective isotope minima, caused by the CO-poor but ^{13}C - and ^{18}O -rich SH air probed at this latitudes in June–October (Z02). The tropical [CO] maxima in C1 are in phase with those observed at the surface between 15°S and the equator in January–February (see Figure 4.8, p. 85), which supports the inference of Z02 that the winter compositions observed by C1 in the tropics are largely influenced by the frequent lofting of surface air to the sampling altitudes. The midlatitude seasonal C1 [CO] maxima nearly coincide with the maxima at the surface (middle-end of March), contrary to a ~5 weeks delay reckoned by Z02 from the unfiltered on-line data. Although the FFA disregards the highest WAS [CO]

encountered by C1 above 35°N in May-June and thus shifts the maxima two months back, the filtering hardly affects the timing of $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ extrema, which occur in March. The latter are better proxies for the background composition dynamics than $[\text{CO}]$, as shown for the surface station data too (see above, Sect. 4.1.1, p. 78), and corroborate the conclusion of Z02 that in the winter-spring period C1 picks well-mixed background air masses at the mid-latitudes.

The summer-fall C1 CO dynamics, however, present a more complex case: $[\text{CO}]$ minima normally expected to occur between July and August are obscured by a distinct enhancement up to 100 ppb at 20°–35°N, followed by elevated mixing ratios of up to 90 ppb above 40°N in September. This is a consequence of the seasonal switch in the transport patterns, hence of the source regions of the air masses arriving to the UTLS. The switch is mainly caused by the seasonal north-south shifts of the convection zones (*i.e.*, the Inter-Tropical Convergence Zone (ITCZ) for the C1 compositions along the IOR) and biomass burning activity, resulting in a typical semi-annual UTLS CO cycle (see, *e.g.*, Liu *et al.*^[2013] and references therein). The back-trajectory calculations and multi-tracer composition analysis for C1 by Z02 confirms that in summer the area of interest is under the influence of the southwest monsoon, *i.e.* polluted surface air from India and Southeast Asia is convectively elevated to the flight altitudes and further advected by anticyclonic transport dominating the UTLS compositions over the Arabian Sea (Park *et al.*^[2009]). The influence of the monsoon is conspicuous in the methane abundances along the IOR (Baker *et al.*^[2012]), which was concomitantly observed by C1, as shown in the lower left panel of Figure 4.15. The CH_4 mixing ratio anomaly, a_{CH_4} , exceeds +40 ppb on top of a comparable seasonal drop in the background $[\text{CH}_4]$ of –45 ppb typically registered between June and September at these latitudes elsewhere (25°N, western Pacific region, Umezawa^[2009]). The noticeably polluted air observed later in September-October at higher latitudes (>40°N), however, is attributed to the enhanced vertical transport of surface air (Z02). One notes another, earlier CH_4 enhancement in late March located around 45°–50°N, that undoubtedly pertains to the background seasonal variation in $[\text{CH}_4]$; simultaneously, the seasonal maxima in extratropical $[\text{CO}]$, $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ are observed. Methane is also a useful tracer for the SH air, identified with low June-August a_{CH_4} values surpassing –30 ppb south of 15°N.

Of the three CO characteristics, the closest correlation to a_{CH_4} is revealed for $\delta^{18}\text{O}(\text{CO})$. Thus, the negative summer a_{CH_4} above 40°N is co-located with the lowest tropospheric $\delta^{18}\text{O}(\text{CO})$, signalling the mid-latitude seasonal background minima before the monsoon-driven compositions intervene there. Elevations in $\delta^{18}\text{O}(\text{CO})$, in turn, coincide with the monsoon and mid-latitude seasonal positive a_{CH_4} and display lower (–2‰ to –1‰) and higher (+2‰ to +3‰) $\delta^{18}\text{O}$ averages, which are characteristic for the biomass burning and anthropogenic activity sources, respectively. The evolution of $\delta^{13}\text{C}(\text{CO})$, on the contrary, appears to be least dependent on the concomitant $[\text{CH}_4]$, showing a consistent seasonal drop across all latitudes until September-October and a synchronously triggered growth in November, as well as a less patchy structure than that of $[\text{CO}]$ and $\delta^{18}\text{O}(\text{CO})$. This is because $\delta^{13}\text{C}(\text{CO})$ is most sensitive to the photochemical sources, in particular to the highly ^{13}C -depleted but moderately low in ^{18}O CH_4 source. For example, a continuous drop in $\delta^{13}\text{C}(\text{CO})$ is observed throughout the monsoon enhancement, when $\delta^{18}\text{O}(\text{CO})$ remains nearly invariable around –1‰, similar to the isotope CO summer dynamics captured at the KMW station (see Sect. 4.1.1, p. 78, also Figure 4.5). Analogously, C1 observations attest a tight correlation between the CO mixing ratio and $\delta^{18}\text{O}(\text{CO})$ ensuing from the coincidental effect of the photochemical production and sink fractionation on C^{18}O , both reducing its relative abundance.

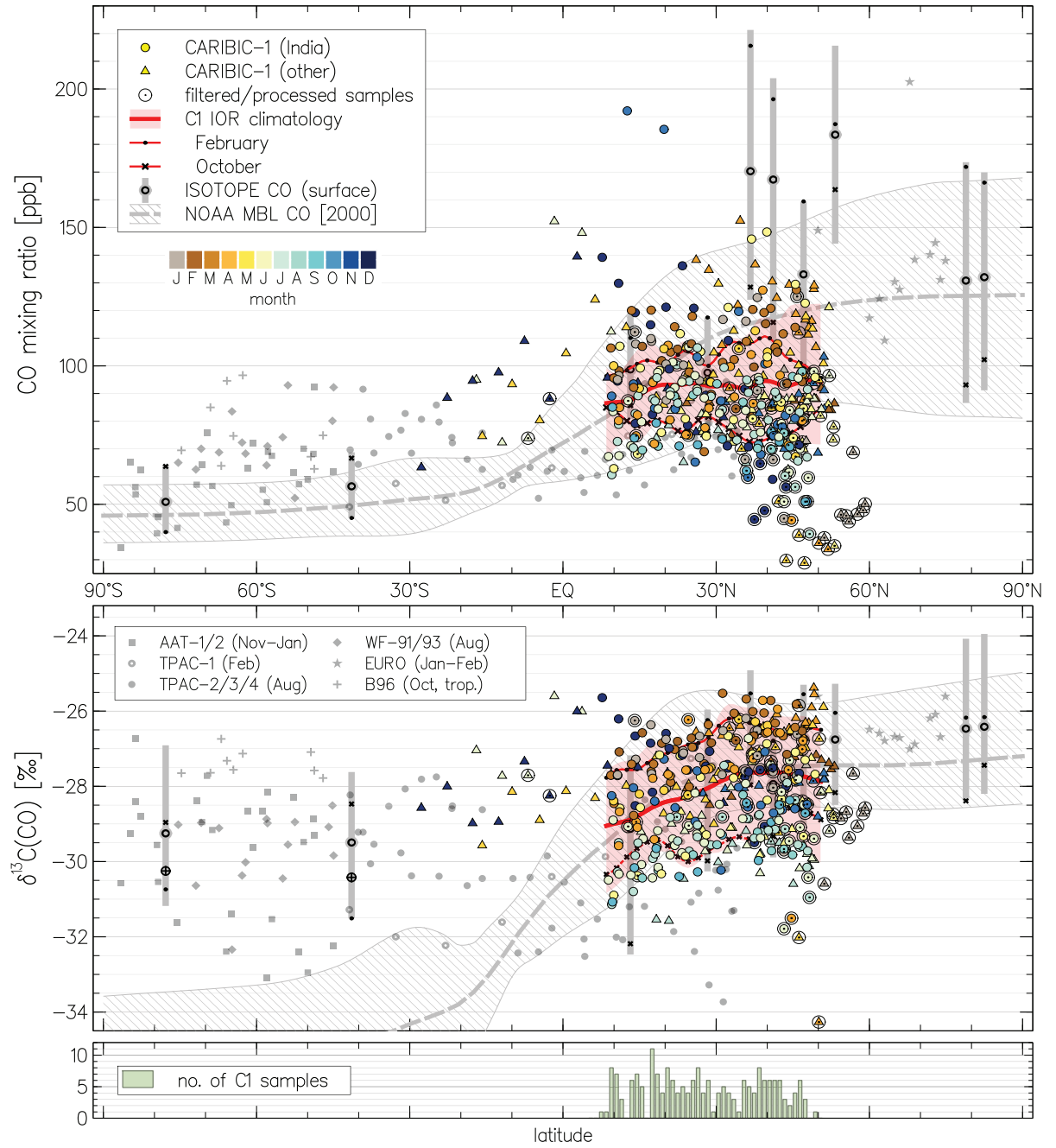


Figure 4.16 Latitudinal distribution of the CO mixing ratio (upper panel) and $\delta^{13}\text{C}$ (middle panel) observed in the UTLS and free troposphere. Coloured symbols denote the CARIBIC-1 observations, circles distinguish the samples along the Indian Ocean routes. Symbol colours refer to the season, encircled points denote the filtered/processed data (see text). Grey symbols denote the BL and free troposphere observations from various sampling trips in 1991–1993 (see Mak and Brenninkmeijer^[1998] for details), B96 refers to the UTLS observations between New Zealand and Antarctic in 1993 by Brenninkmeijer *et al.*^[1996]. Red curves denote the annual (thick line) and February/October (thin lines) averages of the C1 CO climatology along the Indian Ocean routes. The lower panel presents the overall number of the C1 samples integrated into the IOR climatology (in 1° latitude bins). Presented here for comparison, grey curves refer to the MBL CO and $\delta^{13}\text{C}(\text{CO})$ estimates from the GLOBALVIEW-CO product and derived in Sect. 4.1.2, the black symbols with grey error bars denote the isotope CO observations at the surface (see references to Figure 4.7, p. 83).

The zonal means of the derived climatologies for [CO] and $\delta^{13}\text{C}(\text{CO})$ are further included in Figure 4.16 presenting the aggregate of the C1 and other tropospheric isotope CO observations available to date. The tropical and mid-latitude IOR CO mixing ratios average out to 91 and 95 ppb, respectively, in excellent agreement with the results of Z02. Markedly, the zonal averages exhibit virtually no latitudinal gradient above 20°N, whereas the surface background mixing ratios (MBL for 2000, shown as grey curves), starting with comparable 85–95 ppb at 10°–20°N gain some additional 35 ppb by 50°N. The IOR [CO] has a non-uniform variation increasing polewards from ~30 to ~50 ppb, mostly at the expense of its upper limit, that is the winter-spring extratropical CO maxima. This result differs from Z02 who infer largest variations in tropical [CO] from the non-filtered (by FFA) on-line measurement data. The comparable mixing ratio averages derived by Z02 and here (from the WAS data) suggest, nonetheless, that the FFA-discarded outliers are little influential in determining the background abundances. The levelled latitudinal IOR [CO] annual average ensues from the counterbalancing overlap of otherwise uneven zonal distributions observed in different seasons. Clearly positive year-round below 20°N, the latitudinal gradient is indistinct within 20°–30°N, and strongly enhances further polewards, acquiring positive spring-summer and negative winter slopes up to 1 ppb per degree latitude. The concomitant $\delta^{13}\text{C}(\text{CO})$ zonal distribution appears to be an uncomplicated case and coincides well with the expected MBL averages, being as well merely a function of the average methane-derived CO component fraction, γ_{CH_4} (see the discussion on the MBL CO distribution, p. 83). The seasonal variation of $\delta^{13}\text{C}(\text{CO})$ is around $\pm 1.5\text{‰}$, or at least double the latitudinal span at any season (also seen in the rather homogeneous colour distribution for $\delta^{13}\text{C}(\text{CO})$ in Figure 4.16, as opposed to that for [CO]). Exceptionally, the tails of the IOR annual zonal average $\delta^{13}\text{C}(\text{CO})$ are bent: Upwards in the tropics, where the ^{13}C -heavy CO from the surface sources (mostly the biomass burning) is more frequently encountered in the UTLS, and downwards starting from 45°N, due to the input of the substantially low in $\delta^{13}\text{C}$ stratospheric CO diluting the tropospheric air masses. To note, a lowering of $\delta^{13}\text{C}(\text{CO})$ may also occur as a result of an integration of the stratospheric and tropospheric air portions in one large WAS sample; the latter may be still detected as tropospheric using the concomitant N_2O mixing ratios (see above, p. 97). Sampling of stratospheric air in C1 along the IOR is more frequent at higher latitudes; for example, more than 60% of the stratospheric samples (or more than 10% of the overall C1 data) were collected north of 40°N (shown as encircled points in Figure 4.16).

The remaining C1 NH compositions (mostly from the North Atlantic) are found distributed nearly identically to the IOR data, differing in larger and ^{13}C -enriched abundances at winter-spring mid-latitudes tantamount to the MBL CO levels. Of interest are also the C1 SH data collected at the African routes, with the $\delta^{13}\text{C}(\text{CO})$ values corresponding to the lower part of the mixing ratio distribution contained between -30‰ and -28‰ , which corresponds well the observations in the free troposphere by Mak and Brenninkmeijer^[1998] (hereafter referred to as “MB98”). It is difficult to infer much information from the scarce SH C1 data; nonetheless, regarding its large scatter, the Keeling plot analysis may be used to infer a rough estimate of the $\delta^{13}\text{C}$ of the tropical SH CO surface sources.⁷⁰ Thus, for all African data (13 samples collected in 3 flights in May, July and December of 2000), the analysis yields a signature of $(-25.1 \pm 2.6)\text{‰}$ ⁷¹ for the likely dominating biomass burning source. Regarding each flight separately, a reasonable (*i.e.*, within an acceptable uncertainty) and actually more definite estimate of $(-23.8 \pm 1.4)\text{‰}$ is obtained only for the data in July, the month when the biomass burning advances in the SH. This value is in a good agreement with the estimate of the SH average $\delta^{13}\text{C}(\text{CO})$ of the BB source in June–July of around -24.5‰ derived in the current study. Reckoning that a substantial fraction of the ^{13}C -enriched C_4 plant material is usually being burned in Africa, a higher average $\delta^{13}\text{C}$ of the emitted CO is expected (see Sect. 5.2.3, p. 124 for details).

Regarding the bulk of the free troposphere SH data from MB98 presented in Figure 4.16, it highlights the previously discussed (Sect. 4.1.2, p. 81) discrepancy in tropospheric SH ^{13}CO mass-balance, when the observed $\delta^{13}\text{C}(\text{CO})$ averages are distinctly elevated with respect to the values expected assuming a conventional sink fractionation magnitude of around $+5\text{‰}$ (represented by the MBL $\delta^{13}\text{C}(\text{CO})$ curve in Figure 4.16). In the analysis of their SH data, MB98 emphasise as well that this value accounts only for one half of the ETSH $\delta^{13}\text{C}(\text{CO})$ gradient observed during the AAT and WF sampling trips (see references to Figure 4.16). Notably, no poleward negative gradient of $\delta^{13}\text{C}(\text{CO})$ is apparent in the ETSH, with the annual IQR (interquartile range, see note⁴⁸, p. 76) of the data above 40°S spanning 56.2 to 70.1 ppb for [CO] and -30.6‰ to -28.9‰ for

⁷⁰ The Keeling plot analysis is only applicable here assuming invariable CO photochemical production and sink fractionation terms.

⁷¹ The uncertainties refer to the 95% confidence interval of the intercept point value (at $[\text{CO}]^{-1} \rightarrow 0$) of the linear regression through the observed $\delta^{13}\text{C}(\text{CO})$ as a function of reciprocal [CO].

$\delta^{13}\text{C}(\text{CO})$, respectively, much coherent with the observations at the surface (BHD and SCB stations, see Table 4.2, p. 72). A more direct comparison of the free troposphere and surface $\delta^{13}\text{C}(\text{CO})$ is problematic, for at least half of the SH samples exceed the MBL [CO] levels. Inspecting the part of the mixing ratio distribution that corresponds that of the MBL (below ~ 65 ppb) leaves out two clusters of samples from the AAT, TPAC and WF trips available for comparison, *viz.* those with $\delta^{13}\text{C}(\text{CO})$ above -30‰ and with some substantially lighter compositions that surpass the tropospheric (station) background minima of -31.5‰ . In the tropics, these low $\delta^{13}\text{C}(\text{CO})$ values are customary, owing to the large methane-derived CO component; in the ETSH, they likely result from the admixing of the highly depleted in ^{13}C stratospheric air.⁷² Upon disregarding the stratosphere-influenced samples, the only appropriate data left for a consistent comparison with the station record are those acquired in November–December during the AAT-1 trip. The latter display a nearly absent zonal $\delta^{13}\text{C}(\text{CO})$ gradient on top of a slight [CO] poleward decrease (-0.19‰ and -4.1 ppb per 10° latitude, respectively) and average out at $(-28.7 \pm 1.4)\text{‰}$, zonally connecting the BHD and SCB September–October seasonal averages. A good correspondence between the surface and free troposphere data is found for the aircraft observations by Brenninkmeijer *et al.*^[1996] in October, with four samples timely corresponding the seasonal surface maxima at BHD of 65 ppb in [CO] and -27.6‰ in $\delta^{13}\text{C}(\text{CO})$. No consistent comparison is possible for the observations at the latitudes around SCB, where either polluted tropospheric or distinctly stratospheric air was encountered.

Recapitulating, CARIBIC-1 offers a unique and comprehensive observational dataset on the isotopic composition of CO in the UTLS for the subsequent comparison with the model data. The analysis presented here attests the consistency of the C1 observations in view of the UTLS domain peculiarities, such as: (1) Remoteness, *i.e.* much photochemically aged and mixed air is observed, as the low average $\delta^{18}\text{O}(\text{CO})$ signatures suggest. A cross-indication of the active photochemical CO processing is the large seasonal variations in the UTLS $\delta^{13}\text{C}(\text{CO})$ loosely correlating with the concomitant CO mixing ratios. (2) The seasonally varying atmospheric transport is utterly influential in determining the compositions observed in the UTLS. The multi-year C1 observational data along the Indian Ocean routes allows to observe the climatological semi-annual [CO] and $\delta^{18}\text{O}(\text{CO})$ cycles driven by the seasonal changes in the ITCZ and the triggering of the Asian monsoon conditions. Therefore, for the consistent comparison of the C1 data with any model results, an adequate reproduction of the atmospheric transport in the model is required. By applying the FFA analysis, it becomes possible to discern the seasonal variations obscured otherwise by the large-scale perturbations in tropospheric CO observed in 1997–1998, as well as to better highlight the high-latitude UTLS CO. Disregarding the FFA, the WAS data exclusively examined here, agree very well with the concomitant on-line CO mixing ratio measurements available in CARIBIC-1 (Z02).

⁷² MB98 remark that the origin of the low $\delta^{13}\text{C}(\text{CO})$ is unclear although not stratospheric, pointing to the low concomitant ^{14}CO and O_3 abundances registered (Mak *et al.*^[1994]). The $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ of the samples in question are, however, typical for the ETSH UTLS (tropopause) region, as shown later by Brenninkmeijer *et al.*^[1996].

5

Global modelling of the CO isotope composition with EMAC – Part I

The current chapter summarises the setup of the ECHAM5/MESSy Atmospheric Chemistry (EMAC) general circulation model employed in this study for the 3D simulations of the atmospheric trace gases abundances and their isotope compositions. The chapter is comprised of the two principal parts. A brief description of the structure of EMAC, processes it implements and the isotope extension introduced are given in Sect. 5.1. The subsequent Sect. 5.2 is devoted to a novel, detailed isotope extension of the trace gas emissions inventory proposed in this study.

5.1 EMAC Model description and setup

EMAC is the comprehensive modular-structured model that aggregates numerous submodels treating the wide spectrum of the physical/chemical processes occurring in the atmosphere. The submodels operate in the domain of the base model (*e.g.* box- or 3D model), being interconnected by means of the Modular Earth Submodel System (MESSy) framework. The brief descriptions of MESSy submodels and the base 3D model (ECHAM5) are given in the following sections. The purpose of this chapter is to give a general overview of the modelling tool used, with an emphasis on the isotope specifics that arise in case of simulating the isotope-enabled configuration of EMAC.

5.1.1 Base model ECHAM5

The atmospheric general circulation model (GCM) ECHAM5 is the physical core of EMAC. It is the 5th generation of the climate GCM ECHAM developed at the Max Planck Institute (MPI) for Meteorology in Hamburg (Roeckner *et al.*^[2003]), originally derived from the weather forecast model of the European Centre for Medium-range Weather Forecasts (ECMWF). The simulations with EMAC presented here are conducted with the version 5.3.02 of ECHAM with some of the original parameterisations being replaced by the corresponding MESSy submodels (see below, Sect. 5.1.2 and Table 5.2).

ECHAM5 simulates atmospheric (thermo)dynamics, solving the primitive equations of motion for the moist atmosphere on the model grid available in a wide range of spatial resolutions (see Table 5.1, also Roeckner *et al.*^[2006]). The basic prognostic variables are vorticity, divergence, temperature, the logarithm of surface pressure and the abundance of atmospheric water in three different phases (vapour, liquid and ice). Except for water, the prognostic variables are represented (in the horizontal) as truncated series of spherical harmonics. The truncation determines the horizontal resolution of the corresponding Gaussian model grid (*i.e.* the node positions in latitude and longitude coordinates) required to maintain the spectral transformation numerically precise in every integration step. The vertical dimension is represented in a hybrid pressure σ - p coordinate system, for which the pressure coordinate is transient from terrain following (σ) for the lower layers (surface) to surfaces of constant pressure (p) for the upper layers.⁷³ The vertical resolution of typical tropospheric setups of the model comprises 19 or 31 layers with the respective top layer at 10 hPa (mid of uppermost layer). The middle-atmosphere setup (MA-ECHAM5) spans typically 39 or 90 layers up to 10^{-2} hPa, respectively. For the

⁷³ The σ - p transition is described by the following relation: $p(x,y,z,t) = a(z) \cdot p_0 + b(z) \cdot p_s(x,y,t)$, where x, y, z, t denote the spatial coordinates and time, p_0 is the model domain reference pressure and p_s is the simulated surface pressure. The parameters $a(z)$ and $b(z)$ are the constants effectively defining the vertical coordinate, specific for each given resolution (see Roeckner *et al.*^[2003], pp. 16–18).

simulations presented here, T42L31ECMWF and T42L39MA resolutions are applied, depending on the objective of the studies.

The model integration is performed with a semi-implicit two-step ‘leapfrog-scheme’ corrected with the Robert-Asselin time filter (Asselin^[1972]). The combined vertical and spectral resolutions impose constraints on the integration time step⁷⁴ (listed in Table 5.1). In order to bring the model atmosphere to the observed state (on the synoptic scale, *e.g.*, for the comparison with observational data), a simple assimilation technique, known as Newtonian relaxation, is applied (Jeuken *et al.*^[1996], Jöckel *et al.*^[2006]). That is, the prognostic variable x is relaxed in the spectral space every time step towards the corresponding observed value by adding the artificial tendency to its overall tendency:

$$\frac{dx}{dt} = F_m(x) + G_x(x_{obs} - x)$$

where F_m is the model result, G_x is the variable-specific relaxation (nudging) coefficient and x_{obs} is the “observed” value, usually derived from meteorological analysis or re-analysis products. For the simulations presented here, the ECMWF operational analysis⁷⁵ data is used. The relaxation is applied to the vorticity ξ , divergence D , temperature T and (logarithm of) surface pressure p , respectively, with varying nudging coefficients at the specific model levels. The nudging coefficients (in s^{-1} units) for the levels between 700 and 100 hPa are set to $G_\xi = 4.6296$, $G_D = 0.5787$, $G_T = 1.1574$ and $G_p = 1.1574$, respectively, whilst for the boundary layer and above 100 hPa weaker coefficients are applied.⁷⁶

The advection of the atmospheric tracers is calculated within a flux-form semi-Lagrangian scheme (Lin *et al.*^[1994], Lin and Rood^[1996]) with a correction for the mass-wind inconsistency arising from the implementation in vertical hybrid pressure coordinates (Jöckel *et al.*^[2001]). The convection and convective precipitation are calculated following the original ECHAM5 algorithms (Tiedtke^[1989], Nordeng^[1994]), however, recoded as separate submodel CONVECT (see below). Similarly, the ECHAM5 cloud microphysics parameterisation from Lohmann and Roeckner^[1996], Tompkins^[2002] has been recoded as submodel CLOUD. For the purpose of modular coupling with the other submodels, ECHAM5 has been extended to operate within the MESSy framework.

Table 5.1 ECHAM5 resolutions

Resolution	Approx. gridcell size		No. of gridpoints [lat.×lon.] ^d	Time step [s]	Top layer pressure (mid) [hPa]
	[degrees]	[km]			
T21L19 ^{a,b}	5.6×5.6	621	64×32	2400	10
T31L31ECMWF ^b	4.2×4.2	467	96×48	1800	10
T42L31ECMWF ^b				1200	10
T42L39MA ^b	2.8×2.8	311	128×64	900	0.01
T42L90MA ^c				900	0.01

^{a)} Coarse test resolution.

^{b)} Used in this study (may be only for the test simulations).

^{c)} Used in EMAC evaluation simulation (Jöckel *et al.*^[2006]), see text for details.

^{d)} Corresponding quadratic Gaussian grid.

5.1.2 MESSy interface and submodels

The Modular Earth Submodel System implies a strict modularisation and a coding standard (Jöckel *et al.*^[2005]) for the development of comprehensive Earth System Models (ESMs). The modularity pro-

⁷⁴ The constraint ensues from the so-called CFL-criterion (Courant *et al.*^[1967]) defining the maximum time step length below which the conditionally stable (*e.g.*, explicit and semi-implicit) numerical integration schemes provide a stable solution to the given set of differential equations. In essence, CFL-criterion relates the spatial and temporal resolutions of the scheme to the largest velocity of information propagation in the system, in order to assure that the scheme can retrieve the information required to form the solution. An example of the largest velocity is the speed of horizontal wave propagation (*i.e.* the speed of sound) in the case of the primitive equations of atmospheric dynamics (Jacobson^[2005], p. 181).

⁷⁵ Available at <http://www.ecmwf.int/products/data/archive/descriptions/od>.

⁷⁶ In the troposphere, weaker nudging allows avoiding inconsistencies between the boundary layer schemes of ECHAM5 and the ECMWF models. In the stratosphere, ECMWF data represent mainly the model result (as only few observations are available for analysis assimilation), thus less relaxation leads to better internal consistency of the result, *i.e.*, the stratosphere is more driven by the tropospheric wave forcing.

vides a great flexibility (*e.g.*, readily on/off ‘switching’ of a certain submodel for particular setups without the need for additional recoding) and an easy expandability (*i.e.*, introduction of new submodels) of the model. The idea behind the MESSy interface is a layered hierarchy of the structural parts of every submodel according to their functionality. A general overview of the MESSy interface is sketched in Figure 5.1. The four main layers are:

- The Base Model Layer (BML) comprises the base model (*i.e.*, ECHAM5).
- The Base Model Interface Layer (BMIL) comprises the central model infrastructure, *e.g.*, for submodel management and for data exchange.
- The Submodel Interface Layer (SMIL) comprises the submodel-specific connections to the model infrastructure, such as the main entry points, the data handling and the coupling management.
- The Submodel Core Layer (SMCL) comprises the self-consistent implementation of the submodels physical parameterisation, diagnostic calculations, *etc.*, independent from the base model.

Except for the generic MESSy submodels, the realisation of a conventional submodel comprises the two lowermost layers of the interface (SMIL and SMCL). Being coupled to ECHAM5, the submodels operate in the gridpoint space following an operator-splitting approach, *i.e.* contributing with their individual tendency to the overall tendency of a specific variable during the integration. An example of the submodel structure is sketched for the MECCA-TAG/DBL in Sect. 2.5.4 (p. 27).

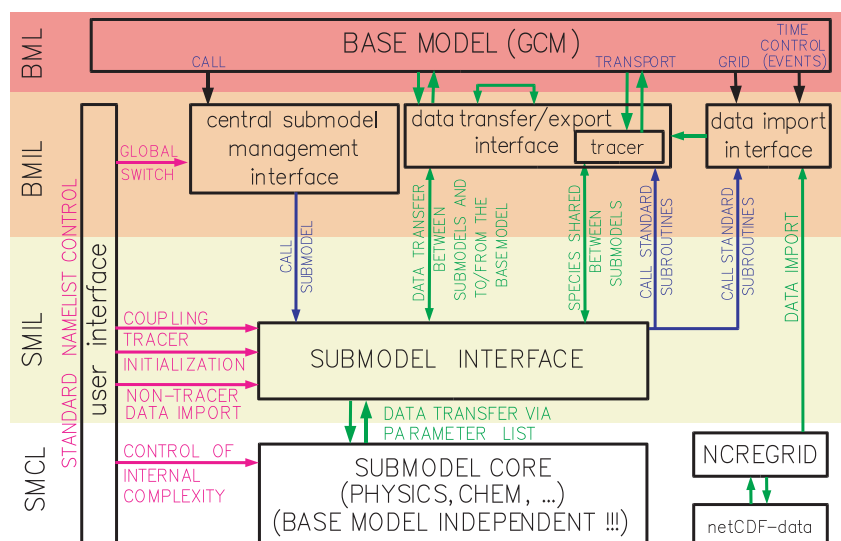


Figure 5.1 Sketch of the four-layer structure of the MESSy interface (from Jöckel *et al.*^[2005]).

The model setup used in this study is based on the setup of the re-evaluation simulation EMAC2 conducted within the Development Cycle 2 of MESSy (MESSy2, Jöckel *et al.*^[2010]), hereafter referred to as “EVAL”.⁷⁷ The chemistry calculations with the MECCA submodel have been extended by the treatment of stable isotopes in the MECCA-TAG sub-submodel, which results in a noticeable additional computational strain. Hence, coarser resolutions (T21L19 and T31L31ECMWF) for the test and selected sensitivity simulations were applied, whilst the reference simulations were performed in the T42L31ECMWF (focussing on tropospheric compositions) and T42L39MA resolutions. Not all submodels originally applied by Jöckel *et al.*^[2010] are included here, being not relevant for the present study. The employed submodels are listed in Table 5.2, for the details on each submodel and their implementation the reader is referred to the references given and in addition to the extensive descriptions provided by Kerkweg^[2005], Tost^[2006], Pozzer^[2007]. The overview on the current status of the MESSy and submodel development is available at the MESSy website⁷⁸.

⁷⁷ Amended with further modifications and extensive diagnostics, EMAC2 supersedes the precedent evaluation simulation S2 of EMAC1 (formerly ECHAM5/MESSy1, version 1.1) that has been extensively evaluated (Jöckel *et al.*^[2006], Pozzer *et al.*^[2007], Tost *et al.*^[2007]). Importantly, EMAC2 employs the improved version of MECCA for calculating the kinetic chemistry, as opposed to the MECCA1 used in EMAC1 (see details on the newly applied submodels in Jöckel *et al.*^[2010], Table 1).

⁷⁸ <http://www.messy-interface.org/>

Table 5.2 List of MESSy submodels

Submodel	Function	References ^a
CHANNEL	Memory and meta-data management and data export	Jöckel <i>et al.</i> ^[2010] b, c
CLOUD	Cloud cover calculation, cloud micro-physics including precipitation	Lohmann and Roeckner ^[1996] , Tompkins ^[2002]
CONVECT	Convective processes parameterisation	Tost <i>et al.</i> ^[2006] , Tiedtke ^[1989] , Nordeng ^[1994]
CVTRANS	Convective tracer transport	Tost ^[2006] , Lawrence and Rasch ^[2005]
DRYDEP	Dry deposition of gases and aerosols	Kerkweg <i>et al.</i> ^[2006a]
H2O	Water vapour tracer initialisation from satellite data and feedback provision	Jöckel <i>et al.</i> ^[2006]
JVAL	Calculation of the photolysis rates	Landgraf and Crutzen ^[1998] d
LNOX	Emissions of NO _x from lighting	Grewe <i>et al.</i> ^[2001] , Tost <i>et al.</i> ^[2007]
MECCA	Calculation of the gas-phase chemistry	Jöckel <i>et al.</i> ^[2010] (Sect. 7.1), Sander <i>et al.</i> ^[2011] e
MECCA-TAG	Chemistry mechanism tagging, isotopes	this work
NCREGRID	Generic grid-transformation (incl. data input)	Jöckel ^[2006] b
OFFLEM	Offline (prescribed) tracers emission	Kerkweg <i>et al.</i> ^[2006b]
ONLEM	Online (calculated) gas and aerosol emissions	Kerkweg <i>et al.</i> ^[2006b]
QBO	Assimilation of quasi-biennial oscillation zonal wind observations	Giorgetta and Bengtsson ^[1999] , Jöckel <i>et al.</i> ^[2006]
RAD4ALL	Radiation calculation and feedback on the chemistry	Tanré <i>et al.</i> ^[1984] , Nissen <i>et al.</i> ^[2007]
S4D	Sampling of the model data in four dimensions	Jöckel <i>et al.</i> ^[2010] b
SCAV	Scavenging and wet deposition of gases and aerosols	Tost <i>et al.</i> ^[2007]
SCOUT	Stationary column output	Jöckel <i>et al.</i> ^[2010] c
TNUDGE	Tracer nudging arbitrary user-defined fields	Kerkweg <i>et al.</i> ^[2006b]
TRACER	Generic management of simulated tracers	Jöckel <i>et al.</i> ^[2008] b
TROPOP	Tropopause and other diagnostics	Jöckel <i>et al.</i> ^[2006] b

Notes:

^{a)} Details on all submodels are available on the [MESSy Submodels] page at <http://www.messy-interface.org>.^{b)} Generic or diagnostic submodel.^{c)} See the supplementary material at <http://www.geosci-model-dev.net/3/717/2010>.^{d)} See additional information at <ftp://ftp.mpic.de/gromov/chb/messy/photo/photo.pdf>.^{e)} See also Sects. 3.1 (p. 29) and 3.5 (p. 55).

Several submodel interconnections and resulting model feedbacks are important: For the calculation of photolysis reactions, the kinetic chemistry submodel MECCA requires the photodissociation reaction rates. For 3D simulations, the latter are provided by the JVAL submodel for every model grid-box. The calculation is following the spectral approach by Landgraf and Crutzen^[1998], who apply the finite sum approximation of the integral photolysis rates derived from the actinic flux, the specific reagent adsorption cross section and the corresponding quantum yield. To minimise the calculation effort, the pre-calculated photolysis rates of the purely adsorbing atmosphere are used. On top of that, the total fraction of light scattering-induced modulation (due to the gas, aerosol and cloud particles) is calculated for the various spectral bands. The additional term depends on the simulated atmospheric conditions and the location and is calculated during run-time (“on-line”). Additional information about wavelength intervals and other parameters can be found in the JVAL references in Table 5.2.

The model radiation calculation is provided by the RAD4ALL submodel, which is the MESSy implementation of the original ECHAM5 routines. The feedback between the model dynamics and chemistry is established via the radiative budget accounted in RAD4ALL. This submodel requires the column abundances of the gases, the cloud cover, cloud water and ice content, and the atmospheric water vapour abundance.⁷⁹ The latter is initialised in the stratosphere and troposphere from satellite data (provided by the submodel H2O) and chemically processed in MECCA. The radiation calculation utilises the original ECHAM5 aerosol climatology (Tanré *et al.*^[1984]). The partitioning between the water vapour, liquid and ice phases is calculated by the CLOUD submodel from the cloud droplet formation processes.

EMAC utilises a set of generic submodels that provide data I/O and processing, memory management, control of the runtime execution and diagnostics (detailed in Table 5.2). For instance, the TRACER submodel

⁷⁹ The input data can be supplied either “off-line” (*i.e.* from climatologies) or “on-line” from the relevant submodels. In the current setup, RAD4ALL is on-line coupled with the submodels MECCA/TRACER (providing species abundances) and CLOUD (cloud content data).

manages the chemical tracers simulated in 3D, linked with the corresponding MECCA kinetic chemistry species. TRACER also performs necessary corrections to the tracer budgets, *e.g.* assuring their positive definiteness for the stability of the integration scheme (TRACER_PDEF).

5.1.3 Emission and removal processes

The injection of the chemical tracers into the atmospheric reservoir in EMAC is handled by the emission submodels OFFLEM, ONLEM and TNUDGE. The adequacy of the emission setup is crucial for every AC-GCM study, and the choice of the emission setup is an elaborate effort. It becomes doubled if in addition to the regular (non-isotopic) trace gas emissions the isotope ratios are required to be imposed. The detailed discussion of the selected emission setup for this study is presented in the separate Sect. 5.2 below (p. 118). In addition, the (non-chemical) removal processes are just as important as the emissions, having a significant influence on the chemical turnover of the species. This is particularly important in view of the removal of the intermediate products in the chemical reaction chains. EMAC accounts for the removal of the aerosols and trace gases in the dry and wet deposition processes.

The calculation of the wet deposition processes is handled by the submodel SCAV. It simulates large-scale and convective scavenging of trace gases and aerosols by rain, snow and ice hydrometeors, accounting for the impaction and nucleation processes. The scavenging of trace gases is formulated explicitly, *i.e.* described by a separate chemical mechanism similar to that of MECCA. It accounts for the exchange between the gas phase and hydrometeors, as well as the liquid phase chemistry within the droplets. The transfer of the gas phase tracers into the droplets is calculated from the atmospheric liquid water content and the species solubility properties. Scavenging mechanisms of various complexities can be selected, thus including the desired set of species and reactions. Within the current setup, the complex scavenging mechanism is chosen (for mechanism details see the supplement⁸⁰ to Tost *et al.*^[2007], Ch. 1). Amongst the carbonaceous species, scavenging significantly influences the turnover of methanol, formaldehyde, acetic and formic acids, which are of relevance in view of the studies on stable carbon isotopes presented here.

The dry deposition processes comprise the loss of the tracers due to the uptake at the earth's surface, mainly due to interaction with vegetation. The latter, in turn, is a complex function of the physical, chemical and biological factors. The current realisation of the dry deposition in MESSy is implemented in the submodel DRYDEP (Kerkweg *et al.*^[2006a]) and follows the parameterisation based on the big-leaf approach (Hicks *et al.*^[1987]) further adapted for GCMs by Ganzeveld and Lelieveld^[1995] and Ganzeveld *et al.*^[1998] The deposition occurs in the lowest (surface) model layer and is formulated in terms of the deposition velocity proportionally relating the deposition flux and the atmospheric abundance of the species removed. The deposition velocity is calculated on the basis of the aerodynamic, quasi-laminar boundary layer and surface resistances describing the respective specific uptake processes. The formulation of resistances accounts for the surface roughness, kinematic viscosity and the molecular diffusivity of a particular trace gas, and the various surface types. These are ocean (with a fraction of sea ice cover) and land, with the differentiation of the bare soil and vegetation fractional areas, snow cover fraction and a so-called wet-skin reservoir (humidity over the plants surface). The soil and plant leaves conductance is taken into account as well. Selected surface resistance parameters are approximated for most of the species from the relatively well-known values for ozone and sulphur dioxide. The further details on the parameterisation can be found in the respective references cited. The majority of NMHCs and VOCs experience the dry deposition, of which the effective removal of formaldehyde, methanol, formic/acetic acids, acetone and isoprene is significant. The deposition of CO is disregarded, as the EMAC sensitivity studies with the EVAL setup estimated this process insignificant (Pozzer *et al.*^[2007], see more in Sect. 6.1.4.1, p. 149).

As a characteristic kinetic process, the removal of the trace gases is expected to influence the isotopic composition of the tracers, although of a moderate magnitude, when compared with the chemical composition exchange and KIEs. The isotope fractionations escorting dry deposition and wet scavenging are discussed below in Sect. 5.1.5.

⁸⁰ <http://www.atmos-chem-phys.net/7/2733/2007/acp-7-2733-2007-supplement.pdf>

5.1.4 Isotope extension of EMAC

The presented global modelling study comprises two principal stable isotope extensions of EMAC, one for the stable $^{13}\text{C}/^{12}\text{C}$ carbon isotopes and one for the stable oxygen isotope anomaly (or mass-independent fractionation, MIF) investigations. Although the simulation of the full set of oxygen isotopes (*i.e.* $^{16}\text{O}/^{17}\text{O}/^{18}\text{O}$) is conceived in EMAC, the simulations with the box-model (Sect. 3.5, p. 55) reveal that a thorough reassessment of the emission isotope signatures in case of oxygen containing species is required. That is an excitingly interesting task not accomplished at the moment and thus is subject to future work. The MIF in atmospheric oxygen is, however, attributed solely to the chemical reactions in the atmosphere (*i.e.*, formation of O_3 and CO oxidation by OH). Therefore, for simulating oxygen isotope anomaly the problem of erroneous emission signatures can be circumvented, considering all surface emissions are non-mass dependently fractionated, *i.e.* characterised with the $\Delta^{17}\text{O}$ signature around 0‰⁸¹. The specific task of the modelling study is then reduced to the mere simulation of the tracers' anomalous enrichment in the chemical mechanism and accounting for the emission from the surface sources that attenuate the atmospheric MIF signal. Another convenience in simulating anomalous enrichments is that $\Delta^{17}\text{O}$, as opposed to $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, is insignificantly altered by any of the numerous mass-dependent isotope effects of the physical origin (*e.g.* during the phase change or diffusion).

Subsequently, the chemical mechanism simulated by MECCA in EMAC was extended with the stable carbon and oxygen isotope chemistry by using the tagging technique implemented in MECCA-TAG sub-model and applying the respective carbon and oxygen isotope *tagging configurations* (detailed in the previous chapter, see also Sect. 2.5.4, p. 27). The regular chemistry mechanism is based on the mechanism incorporated in the EVAL setup, however, with reduction of the iodine chemistry, in order to reduce the amount of reactions to be simulated, but still representing in sufficient detail the CO isotope composition. The employed mechanism and tagging configurations are summarised in Table 5.3 (p. 114). Conformably, the carbon and oxygen kinetic isotope effects and isotope composition transfer are included as described in Sects. 3.3 and 3.4. Noteworthy, the isotopologues of all three stable isotopes are simulated in the oxygen tagging configuration, although ultimately only the resulting $\Delta^{17}\text{O}$ is analysed, disregarding the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values determining it.⁸² Simulating both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, however, is preferable in order to account for the slightly negative $\Delta^{17}\text{O}$ values ensuing from the small, but non-zero effects of the chemical and non-chemical mass-dependent KIEs (see Sects. 3.4.2, 3.2) and slightly negative $\Delta^{17}\text{O}$ composition of atmospheric oxygen (ensues from the unified $\Delta^{17}\text{O}$ formulation introduced in this study, see Sect. 5.2.8). Importantly, negative $\Delta^{17}\text{O}$ values cannot be represented by the frequently used “mass-balance” approaches operating with exclusively positive MIF (see, for example, Morin *et al.*^[2011] and references therein).

Similarly to the tagging performed for isotopologues in MECCA-TAG/DBL (see Sects. 2.3, 2.5), additional isotope tracers are introduced in EMAC to represent the individual isotopologues of the regular tracers. Except of the apparent mass differences, the isotopologue tracers inherit the main properties of the regular tracers (tracer meta-information, Jöckel *et al.*^[2008]), *e.g.* the respective medium (gas phase), participation in advection, convection, vertical diffusion, dry deposition and wet scavenging processes. Following the concept of the tagging technique, the tagging tracers (isotopologues) from different (isotope) tagging configurations are processed by the relevant submodels analogously to the regular tracers. They take part in the same chemical/physical transformations, but without interfering with the regular tracers. Moreover, since the submodels account for the individual isotopologues in calculations, they inherently introduce isotope effects, for example mass-dependent fractionations in the calculation of processes involving tracers' mass.⁸³ Multiple (isotope) tagging configurations can be included in the same model setup. This is exploited here in the simulations of the stable carbon isotopes, when the contributions of the various in-situ sources of CO are assessed by means of additional diagnostic tagging configurations (see below). Analogously with the tagging approach applied to

⁸¹ This definition essentially follows that by Weston^[2006]. See also Sects. 5.2.8, 3.2 and 3.5.1 for details.

⁸² Changes to $\Delta^{17}\text{O}$ are nearly insensitive to the choice of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ signatures that may vary in wide range of values yielding, however, similar $\Delta^{17}\text{O}$. Moreover, despite potentially erroneous $\delta^{18}\text{O}$ signatures of the emission sources, the effect of a certain factor on resulting $\delta^{18}\text{O}$ can be adequately differentiated in a sensitivity study (as it is done, for example, for the assessment of the influence of the O_3 isotope composition to $\delta^{18}\text{O}(\text{CO})$, see Sects. 3.5 and 6.2.8).

⁸³ Exceptionally, the isotope effects are disregarded in the processes involving physical transformation of the atmospheric water (*i.e.*, precipitation and phase changes) in the hydrological cycle of EMAC (and therefore ECHAM5), which is an elaborate task beyond the scope of this work. Nonetheless, atmospheric kinetic transport and equilibrium effects introduce changes to $\Delta^{17}\text{O}(\text{H}_2\text{O})$ on the order of tens *per meg* (Angert *et al.*^[2004], Luz and Barkan^[2010]) which is negligible compared to the $\Delta^{17}\text{O}$ variations in the sources' composition (see Sect. 5.2.8) or those introduced by the chemical KIEs (see Sect. 3.4.2).

MECCA, isotope extension of EMAC tracers is purely diagnostic, *e.g.* model feedback (for instance, via species' abundances required for the radiation in RAD4ALL, see above) is calculated on the basis of the regular tracers, whereas any coupling with their isotope counterparts is avoided.

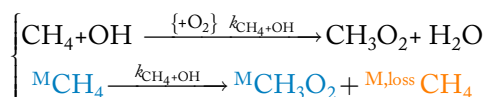
5.1.4.1 Diagnostic tagging configurations

In addition to the stable isotope configurations, the subsidiary tagging configurations are introduced in EMAC for estimating the relative contribution of the key in-situ source species to the final product, *i.e.*, for budgeting. For example, the CO isotopic signature is largely influenced by the ^{13}C -depleted methane carbon (see Sect. 5.2.6, p. 133). Because a much detailed chemical mechanism is employed in EMAC, it becomes difficult to estimate the end-product CO stemming from CH_4 : Before ending up in CO, carbon in the methane oxidation chain passes through various reaction pathways involving different intermediates (see Figure 3.2, p. 35). Ordinarily, to estimate the CO produced from methane, one should count the molecules entering the chain (*i.e.* reacted in the CH_4 oxidation steps) and those CO molecules exiting it (*i.e.* in HCHO oxidation or photolysis reactions). When some of the intermediates experience a removal from the chain (*e.g.* deposition or reacting to other products), it decreases the overall yield of CO from CH_4 . To complicate the matter, in the chemical mechanism of MECCA some of the intermediates of the CH_4 -initiated chain are shared with other CO production chains, *e.g.* isoprene-initiated. This involves complications in calculating yields, since one has to distinguish those intermediates produced from methane and non-methane sources, for instance, methane- and isoprene-derived HCHO.

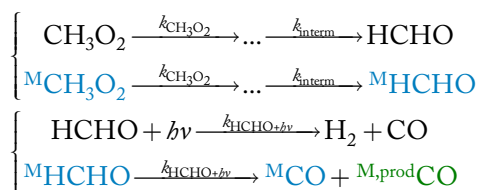
The tagging approach suites this problem well. Indeed, one can select the set of species in the methane chain and tag them into two classes, namely “M” (methane) and “N” (non-methane). In addition, all molecules of CH_4 should be assigned to the class “M”, whilst the other species' molecules are initialised to the “N” class. Reacting methane fills the class “M” of the intermediates and eventually ends up in CO. As a result, the value

$$\gamma_{\text{CH}_4}(\text{CO}) = [\text{MCO}] / ([\text{MCO}] + [\text{NCO}]) \equiv [\text{MCO}] / [\text{CO}]$$

gives the momentary fraction of CO carbon originating from methane. In fact, the number of tagging classes for this kind of tagging can be reduced to merely one “methane”-class. The abundances of the classes for each species are additive to the regular abundance, *i.e.* $[\text{X}] = [\text{M}\text{X}] + [\text{N}\text{X}]$, and the reaction rates are proportional to the share of the respective class only (see Sect. 2.3). Hence, it is sufficient to simulate only the “methane-class” of tagged species relating their abundances to those of the regular species. An example of methane tagging is given in the following. The chain-initiating reaction and its tagging equivalent are



with the imposed equal mixing ratios of $[\text{MCH}_4] \equiv [\text{CH}_4]$. The intermediate and end-chain reactions are tagged similarly:



Here, for conciseness, only the sequence of intermediates and one of the end-chain reactions producing CO during the photolysis of HCHO are shown. In addition to the tagged species, the loss and production terms $\text{M}_{\text{loss}}\text{CH}_4$ and $\text{M}_{\text{prod}}\text{CO}$ are added respectively to the chain-initiating and any of subsequent reactions, thus counting the total number of those methane-derived molecules that participated in the following CO formation. The resulting fraction γ_{CH_4} of “methane-carbon” in the CO and the yield from methane λ_{CH_4} are calculated using the regular mixing ratio and production terms as

$$\begin{aligned} \gamma_{\text{CH}_4}(\text{CO}) &= \frac{[\text{MCO}]}{[\text{CO}]} \\ \lambda_{\text{CH}_4}(\text{CO}) &= \frac{[\text{M}_{\text{prod}}\text{CO}]}{[\text{M}_{\text{loss}}\text{CH}_4]} \end{aligned}$$

It is noteworthy, that the yield values diagnosed this way should be considered carefully. If, for instance, some of the intermediates are effectively transported to the regions where the calculated loss term is significantly less, one may end up with the local (grid-box) yield values greater than those expected from the mass balance. In that case, the respective production and loss terms should be integrated over the whole transport domain to give the reasonable overall value of λ . When investigating the carbon exchanges in the system, the maximum yield value is proportional to the ratio of the carbon atoms in the source and produced species, *e.g.*, for CO derived from isoprene (C_5H_8) the maximum possible yield value is 5.

In addition to the methane-derived carbon, the analogous NMHC-carbon tagging of the chemical mechanism is applied for budgeting of CO and other tracers in EMAC in the current study. Alike in the methane carbon tagging, NMHC tagging imposes mixing ratios from the regular mechanism on the tagged “source” carbon species (*i.e.*, not produced photochemically in the mechanism, but directly emitted). The compounds mediating the exchange between CO, CH_4 and NMHCs comprise approximately one-third of all carbonaceous species simulated in the mechanism in approximately half of the reactions mediating carbon exchange. The diagnostic tagging configurations employed and their quantitative indices are summarised in Table 5.3. It reads, for instance, that the transfer of carbon from CH_4 to CO in the employed chemical mechanism proceeds via 15 various species in some 98 reactions.

Table 5.3 Tagging configurations employed in the EMAC simulations

	Number of (tagged)		
	Species	Reactions	Classes
Regular mechanism ^a	140	352	–
Tagging configurations ^b			
Isotopic carbon (IC)	71	268	2
Isotopic (anomalous) oxygen (AO)	84	314	3
Methane/NMHCs/Isoprene carbon fraction (FM/FN/FI) ^c	17/42/22	98/129/101	1

Notes:

^a) This mechanism is larger than that employed in the box-model studies described in Sects. 2.5 and 3.5 (the latter is detailed in Appendix A), owing to the inclusion of the bromine/mercury gas-phase and heterogeneous chemistry compounds and reactions. The mechanism is obtained by selecting the reactions subset identified with the expression “(((Tr && (G || Het) && !)) || St))” in the setup routines to MECCA. Thus the 3D (box-model) setup mechanisms contain 252(167) gas-phase, 80(55) photolysis and 20(–) heterogeneous reactions, respectively.

^b) Quoted are numbers of tagged species (thus added tracers) and reactions they participate in.

^c) The NMHCs carbon fraction tagging (FN) includes all source hydrocarbons except isoprene (C_5H_8). These are ethane (C_2H_6), ethene (C_2H_4), propane (C_3H_8), propene (C_3H_6) and n-butane (representative for higher alkanes, C_4H_{10}). Since this tagging includes multiple source species, the yields of species are calculated per carbon basis, *i.e.* as the ratio of produced to reacted carbon atoms, not molecules.

5.1.5 Non-chemical isotope effects in EMAC

Aside of the chemical effects (*i.e.*, composition exchange and KIEs), the isotopic ratios are altered in the physical processes, in the first place owing to the isotopologue mass differences. Considering Earth’s troposphere and lowermost stratosphere (hence effects like gravitational separation or thermal diffusion are out of scrutiny), the relevant isotope effects are those connected with thermodynamics. Regarding the gaseous tracers studied here, the fractionations are to appear merely due to the changes in diffusivities of the isotopically substituted molecules and owing to the phase transitions. The latter are of importance exclusively for atmospheric water. The enrichments associated with the vertical diffusion of the tracers are largely dampened by the photochemistry and eddy diffusion, and become significant only in the middle atmosphere (Kaye^[1987]), thus are not discussed here.

5.1.5.1 KIEs in dry deposition removal

The diffusional fractionations, nevertheless, ought to appear in the dry deposition processes, due to the processes accompanying the uptake of the tracers by soil and vegetation. To assess the origin and magnitude of the effects simulated in EMAC, the dry deposition parameterisation implemented in the submodel DRYDEP (Kerkweg *et al.*^[2006a]) is briefly examined here. The intensity of the tracer’s removal is expressed in terms of the deposition velocity v_d , which is a proportionality factor between the deposition flux density F_d and the atmospheric concentration C of the species x :

$$F_d(x) = v_d(x) \cdot C(x) \quad (5.1)$$

The deposition velocity is formulated in terms of aerodynamic (R_a), quasi-laminar boundary layer (R_q) and surface (R_s) resistances from

$$v_d(x) = (R_a + R_q(x) + R_s(x))^{-1} \quad (5.2)$$

with the first term describing the resistance between the specific height and the surface being common to all gases. The boundary layer resistance R_q importantly depends on the molecular diffusion, thus on the isotope substitution (identical terms for the isotopologues of the same species are omitted):

$$R_q(x) \propto \left(\frac{Sc}{Pr}\right)^{2/3} \propto D_x^{-2/3} \propto \left(\frac{\mu_x + \mu_{air}}{\mu_x \mu_{air}}\right)^{-1/3} \quad (5.3)$$

where Pr is the Prandtl number (assumed equal for every species) and Sc is the Schmidt number that constitute D_x , the ratio of kinematic viscosity of air to the molecular diffusivity of a trace gas. For the diffusion of the tracers through the air molecules, the respective D_x terms can be further reduced to the square root of the reduced mass of the molecular weights of the diffusing molecule μ_x and air μ_{air} , respectively, when looking at the differences in R_q caused by the isotope substitution (Craig^[1954]).

The dependence of the bulk surface resistance R_s on the diffusive properties of the tracer is somewhat more complex, as this term describes the net influence of the diffusion through the soil and leaves, with the latter accounting for the diffusion through leaf stomata. Approximations from Wesely^[1989] applied in the DRYDEP parameterisation relate R_s to the combination of specific “parallel” resistances of each of the contributing processes, including the stomatal resistance r_{sx} which accounts for the diffusivity of the tracer and the water vapour D_{H_2O} :

$$R_s(x) = \left(\sum_p 1/r_p + 1/r_{sx} \right)^{-1} \quad (5.4)$$

$$r_{sx} = r_s \cdot D_{H_2O}/D_x \propto \sqrt{\frac{\mu_x}{\mu_{H_2O}}}$$

Here r_p stands for the low-level canopy, wet-skin reservoir, sea-surface, soil, mesophyll and cuticular resistances; r_s is the total canopy (stomatal) resistance, a function of solar irradiation and surface air temperature. The diffusivities ratio is computed as a square root of the ratio of the relative molar masses of water and given tracer. The remaining surface resistances accounted in r_p selectively depend on the solubility of the tracer, air relative humidity, soil pH, *etc.* and do not contribute to the isotope fractionation. Conclusively, changes to the minor isotopologue resistances $^{min,i}R$ with regard to the major isotopologue resistances ^{maj}R upon the isotopic substitution are

$$^{min,i}R_q(x) = \left(\frac{^{min,i}\mu_x + \mu_{air}}{^{maj}\mu_x + \mu_{air}} \frac{^{maj}\mu_x}{^{min,i}\mu_x} \right)^{-1/3} \cdot ^{maj}R_q(x) \quad (5.5)$$

$$^{min,i}R_s(x) = \left(\sum_p 1/r_p + \sqrt{\frac{^{maj}\mu_x}{^{min,i}\mu_x}} / r_{sx} \right)^{-1} \left(\sum_p 1/r_p + 1/r_{sx} \right) \cdot ^{maj}R_s(x)$$

Taking the formaldehyde as an example ($^{12}C\mu_{HCHO} = 30.015$ and $^{13}C\mu_{HCHO} = 31.019$ g/mol), the relative changes upon the ^{13}C isotope substitution amount to +5.3‰ in R_q and +16.5‰ in stomatal resistance r_{sx} , respectively.⁸⁴ The increase in resistances signifies that the uptake of ^{12}C is favoured, thus the species in atmospheric reservoir become enriched in ^{13}C .

For the different surface types (ocean, bare soil or vegetation covered land) and conditions (*e.g.* fraction of the canopy over the soil, plant water content or snow cover of the grid-box), contributions to (5.2) are calculated from the set of predefined resistances. The final deposition velocity v for each tracer is a complex function

⁸⁴ Changes to R_q can be regarded as the KIE associated with the boundary layer resistance, $^{min,i}\eta_{R_q}$. The value of $^{min,i}\eta_{R_q}$ is approximated using (in permil units) $^{min,+1u}\eta_{R_q} = 5.9 \cdot (\mu_x/\mu_{air})^{-1.4} - 0.3$ and $^{min,+2u}\eta_{R_q} = 11.4 \cdot (\mu_x/\mu_{air})^{-1.4} - 0.5$ for the minor isotopologues of the relative molar mass differences of +1 u and +2 u compared to the major isotopologue, respectively. This empirical approximation is accurate within $\pm 0.1\%$ for molar weights μ_x above 20 and below 160.

of numerous parameters varying spatially and temporally. Due to the resistance-based formulation, estimating the overall magnitude of the isotope fractionation requires the other resistances r_p to be known. Therefore, it is more practical to derive the overall dry deposition KIE magnitude η_{drydep} from the simulated deposition velocities for the minor and major isotopologues:

$${}^i\eta(x)_{\text{drydep}} = \left(\frac{{}^iR(x)_d}{{}^iR(x)_a} - 1 \right) = \frac{{}^i\kappa_v(x) - 1}{(q-1) {}^i\kappa_v(x) \cdot \min, {}^iC(x) / \max, {}^iC(x) + 1}, \quad (5.6)$$

$${}^i\kappa_v(x) = \min, {}^i v_d(x) / \max, {}^i v_d(x)$$

where ${}^iR(x)_d$ and ${}^iR(x)_a$ stand for the isotopic ratios of the molecules being deposited in the flux and residing in the atmosphere, respectively, and ${}^i\kappa_v(x)$ denotes the ratio of the corresponding deposition velocities for the i^{th} minor and major isotopologues of the species x . The correction for the amount q of atoms of the selected isotope in the molecule is required; omitting it, for example, for isoprene (by setting $q = 1$ instead of $q = 5$ when calculating the fractionation for carbon) will result in an overestimation of η of about 20% due to the neglected abundant isotopes in the minor isotopologue.

The resulting overall fractionation magnitudes ${}^{13}\text{C}\eta_{\text{drydep}}$ diagnosed in the reference simulation for the carbonaceous tracers are listed in Table 5.4 in three categories integrating the dry deposition KIE over the vegetation-covered land, ocean/desert surfaces (the latter includes also any surface devoid of vegetation) and their average. The respective values of ${}^{13}\text{C}\eta_{\text{drydep}}$ are always positive, denoting that lighter isotopologues are being preferentially removed, *i.e.* species in the atmospheric reservoir become enriched in ${}^{13}\text{C}$. The removal fractionations are typically large for the deposition over the land owing to larger surface resistances R_s , whilst the contribution of the quasi-laminar boundary layer resistance R_q is sufficiently low (<1‰) and is dominant for the deposition over the ocean and desert surfaces. Figure 5.2 additionally depicts the variation of the removal KIE resulting from various combinations of specific resistances r_{sx} determining R_s (see Eq. (5.5)). DRYDEP calculates significant fractionations escorting dry deposition for formaldehyde, methanol, formic/acetic acids, ketones (MEK, MVK) and isoprene (hydro)peroxides (represented by ISOOH). All these species contribute to CO either directly or indirectly (mainly through HCHO), so an additional ${}^{13}\text{C}$ enrichment in precursors due to their dry deposition removal is expected to affect the final ${}^{13}\text{C}$ signature of the photochemically produced CO.

5.1.5.2 KIEs in wet scavenging processes

In contrast to the dry deposition, the isotope effects related to the solubility of the species are neglected in the current setup. The solubility isotope effects (SIE) for others than hydrogen isotope substitutions are found to be small (van Hook and Rebelo^[2007], Jancsó^[2002]). SIE is a particular case of the vapour pressure isotope effect; theoretical studies employing quantum-mechanical theory and thermodynamics calculations (for example, Bacsik *et al.*^[2002]) semi-quantitatively predict small effects as well, however for the majority of the species of interest here no such estimates are available. A few studies suggest that the SIEs for hydrocarbons are usually inverse, *i.e.* heavier isotopologues dissolve easier and deplete the atmospheric gas-phase compartment. Harting *et al.*^[1976] measured the change in solubility of ${}^{13}\text{CH}_4$ with respect to ${}^{12}\text{CH}_4$ at +0.62‰ to +0.33‰ within the 20–80°C range. In a subsequent study regarding ethane isotopologues, Abou El-Nour *et al.*^[1977] estimated comparable but much less temperature-sensitive changes in solubility for ${}^{13}\text{C}^{12}\text{CH}_6$ of +0.48‰ to +0.40‰ within the 13–80°C range. Dias and Freeman^[1997] report no significant fractionation for the solution of organic acids (measured magnitudes were below or equal +0.5‰) and selected hydrocarbons (up to +0.4‰, respectively).⁸⁵ For the majority of lower NMHCs and VOCs (*i.e.* with five carbon atoms and less) no estimates of SIEs are presently available, however. Above all, the simulated wet scavenging in EMAC is generally a minor removal process for carbonaceous tracers as opposed to the dry deposition (*cf.* Table 5.4). Therefore, even large isotope effects are not expected to significantly alter atmospheric compositions, being dominated by the fractionations in the dry deposition whose intensity is at least one order of magnitude larger.

⁸⁵ Studied hydrocarbon compounds were toluene, methylcyclohexane, hexanol; organic acids were acetic, propionic and valeric.

Table 5.4 Carbonaceous tracers' budget and associated isotope fractionations

Species	$^{13}\text{C}\eta_{\text{drydep}} [\text{‰}]^a$			Effective enrichment $^{13}\text{C}\varepsilon_{\text{drydep}} [\text{‰}]^d$	Yearly averaged burden $[\text{TgC}]^e$	Deposition $[\text{TgC/yr}]^e$	
	land ^b	ocean ^c	overall			Dry	Wet
CO	—	—	—	—	137.8	—	—
CH ₃ OH	+9.1	+0.2	+7.9	+2.5	0.86	32.20	0.04
HCHO	+9.2	+0.7	+4.1	+1.2	0.42	14.40	0.25
CH ₃ OOH	+5.8	+0.2	+1.1	+0.3	0.66	6.88	0.01
HCOOH	+3.4	+0.7	+2.6	+1.1	0.11	4.03	0.03
CH ₃ COOH	+4.4	+0.4	+2.4	+0.6	0.15	4.92	0.09
CH ₃ CHO	+6.0	+0.02	+5.5	+1.4	0.08	1.73	<10 ⁻³
CH ₃ COCHO	+3.8	+0.4	+3.1	+0.8	0.02	2.10	—
PAN	+2.0	+0.006	+1.8	+0.4	0.47	1.74	<10 ⁻³
MVK	+3.9	+0.03	+3.9	+1.0	0.05	9.70	—
MEK	+3.2	+0.02	+2.7	+0.6	0.10	3.74	—
C ₃ H ₈	+0.3	+0.005	+0.3	+0.0	0.01	4.76	—
C ₃ H ₈ OH	+1.2	+0.3	+1.2	+0.4	0.01	3.01	—
DMSO	+2.9	+0.4	+2.5	+0.7	<10 ⁻³	<10 ⁻³	—

^{a)} Averages of the flux-weighted values of deposition velocity over the respective surfaces calculated in the reference simulation.

^{b)} Represents vegetation covered surfaces.

^{c)} Includes deserts and surfaces devoid of vegetation.

^{d)} The expected effective enrichment of the airborne tracer fraction due to removal fractionation and emissions.

^{e)} Values are diagnosed in the reference simulation.

5.1.5.3 Effective enrichment in non-chemical processes

To summarise, excluding chemical interaction, significant alterations to the isotope compositions of the tropospheric species are expected in EMAC from the dry deposition and tracer transport/mixing processes. The actual (or *effective*) enrichments brought by the removal of the tracers from the atmospheric reservoir are usually lower than the respective fractionation magnitudes, being dampened by the mixing and emission processes (except for the cases when the amount of removed molecules becomes comparable to the tracer abundance). An approximate estimate of thus effective enrichment can be inferred using the deposition velocity itself in a simplified model of Rayleigh fractionation adapted to account for continuous removal processes (Cann^[1982]). The change to the isotopic composition $^iR(x)_a$ of the compartment undergoing gradual fractionating loss of the fraction f_d characterised by the isotopic ratio $^iR(x)_d$, with the remaining long-term equilibrated fraction f_a residing in the atmosphere, can be described as

$$d^iR(x)_a = \frac{f_d(x)}{f_d(x) + f_a(x)} (^iR(x)_d - ^iR(x)_a) , \quad (5.7)$$

assuming the steady state conditions and absence of other than dry deposition fractionations. Eq. (5.7) can be further reformulated in terms of fractionations: Dividing it by the standard isotope ratio $^iR_{\text{st}}$ converts the term in parentheses on the RHS into the overall dry deposition fractionation η_{drydep} . Likewise, the LHS becomes reformulated in the δ -terms, according to Eq. (5.14) (p. 134). Reducing the fractional terms f in Eq. (5.7) by f_a yields an equivalent expression using the deposition velocity $v_d(x)$. The final effective dry deposition fractionation ε is then

$$^i\varepsilon(x)_{\text{drydep}} = \frac{v_d(x)}{v_d(x) + 1} ^i\eta(x)_{\text{drydep}} . \quad (5.8)$$

The effective fractionation has a typical Rayleigh-process dependence on the deposition velocity. For typical values of v_d of $1 \text{ cm}\cdot\text{s}^{-1}$, the effective depletion of the atmospheric composition is only one half of those induced by the nominal deposition KIE; at an extreme $v_d = 4 \text{ cm}\cdot\text{s}^{-1}$, $\varepsilon_{\text{drydep}}$ reaches ~ 0.8 of η_{drydep} . The unity (in $[\text{cm}\cdot\text{s}^{-1}]$ units) arising in Eq. (5.8) signifies that we consider the whole compartment equilibrated with the emission and removal processes. The typical average deposition velocities calculated in DRYDEP for the carbonaceous tracers range from 0.07 (isoprene) to 0.76 (formic acid) which corresponds to factors of 0.07–0.43 in (5.8). The largest effective fractionations are diagnosed for methanol, formaldehyde, formic acid, acetaldehyde and ketones, with magnitudes of more than +1‰. The precursors' enrichments are expected to propagate to the in-situ produced CO; an assessment of the net effect of the dry deposition and mixing/transport processes on $\delta^{13}\text{C}(\text{CO})$ and other tracers in a sensitivity simulation is presented in Sect. 6.2.4.2 (p. 182).

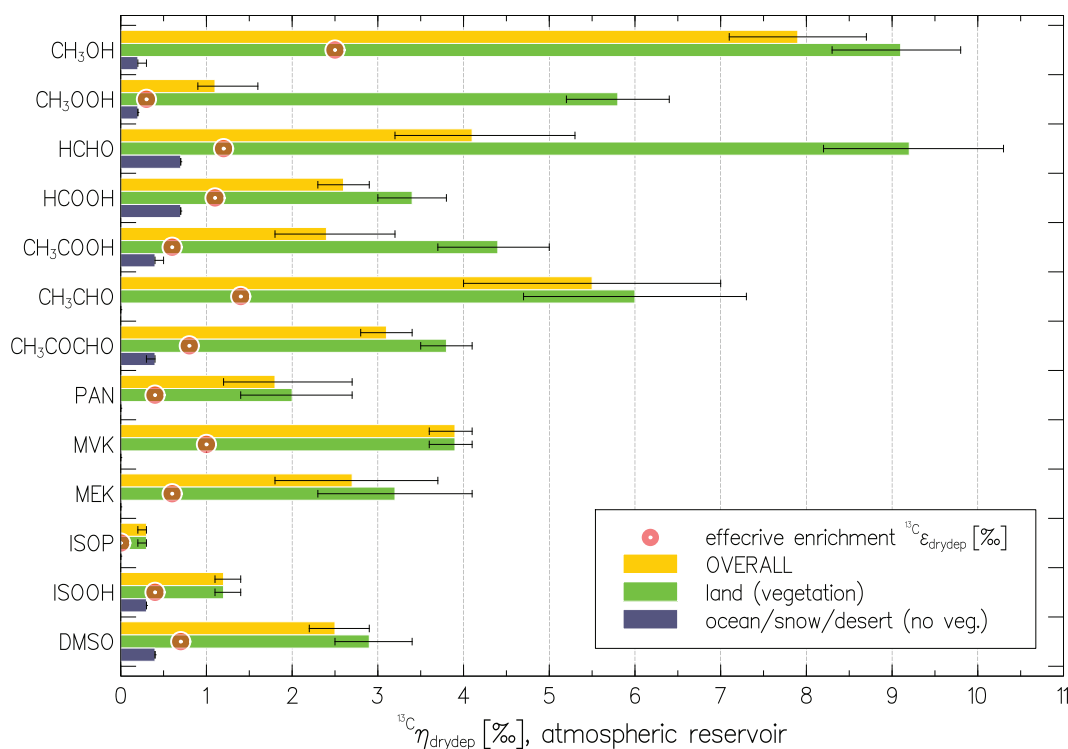


Figure 5.2 (accompanies Table 5.4) Stable carbon fractionations induced by the dry deposition processes simulated in EMAC. The horizontal lines on the top of the bars represent the variation due to the various deposition surface types and conditions.

5.2 Preparation of the isotope emission data

The realistic reproduction of the trace gases abundances in an AC-GCM vitally depends on the choice of the boundary conditions imposed on the mixing ratios of the chemical species, in particular the emission setup. The latter, in case of isotope modelling studies, has to be extended with the relevant isotope ratio information. As a part of the work described here, a set of pre-processing tools for preparing the isotopic emission data in EMAC was created. These tools are flexible to operate with any given isotope extension and are easily applicable to various datasets used in the model. This study embodies the emission setup following that of the EVAL simulation (see Sect. 5.1.2), with the isotope information superimposed. Adopting the evaluated setup avoids the potential pitfall of choosing a modified but untested setup, and brings at the same time new diagnostic information provided by means of the isotope ratios. The emission of trace gases in EMAC is treated by the submodels OFFLEM, ONLEM and TNUDGE, which embody off-line and on-line emission processes, and a pseudo-emission approach (tracer nudging), respectively. The conventional way of accounting for emissions applied in EMAC is realised by adjusting the tendencies of a given tracer, or by modifying its vertical diffusive flux boundary conditions at the lowest model layer (Kerkweg *et al.*^[2006b]).

The off-line emission process is a prescribed tracer flux into the atmospheric reservoir at the surface layer(s) or, for instance, for the emission from the air transportation, at respective altitudes. This type of emission does not require a parameterisation dependent on the model parameters. The current setup employs emissions from datasets comprising the following categories:

- anthropogenic emissions, based on the EDGAR emission inventory,
- biomass burning emissions (GFED project database, 2nd version) and
- biogenic emissions based on the OLSEN/GEIA databases⁸⁶.

⁸⁶ <http://www.geiacenter.org>

Various key assumptions determine the emission isotopic signatures. Depending on the specificity of the emission category, each of the datasets requires separate pre-processing for the isotopic extension. These are described in sections 5.2.2–5.2.4, respectively.

The on-line emissions, in contrast, are calculated during the runtime and require some of the model variables (*e.g.* surface temperature or precipitation) for calculating the resulting emission flux at the given model time step. For example, online emission suits for parameterisation of the trace gas emissions related to the biosphere-atmosphere interaction processes. The current setup includes the online emissions of VOCs (isoprene/monoterpenes) from plants and soil-biogenic NO. The latter is based on the implementation of the algorithm proposed by (Yienger and Levy^[1995]) using soil temperature and moisture, precipitation, fertiliser application and the inferred biomass properties; it is modified to its present version as described by (Ganzeveld *et al.*^[2002]). Alike in the EVAL simulation setup, on-line emissions were scaled with a factor of 0.6 to achieve the net yearly emissions of 305–340 Tg(C) of isoprene and 6.7–7.0 Tg(N) of NO_x, respectively (see Pozzer *et al.*^[2007], supplemental material). With this adjustment of the parameterisations (see details in Kerkweg *et al.*^[2006b]), realistic mixing ratios of isoprene in the boundary layer are achieved, conjointly with a soil-biogenic NO emission flux corresponding to the estimates. Another on-line source of NO_x in the model setup is the *in-situ* production due to lightning. This is calculated by the LNOX submodel from the global lightning flash frequency data and parameterised vertical distribution of produced NO_x (Price and Rind^[1992], Pickering *et al.*^[1998]). The global production of NO_x from lightning in the model amounts to approx. 2 Tg(N) yr⁻¹ (Jöckel *et al.*^[2006]).

At last, the pseudo-emission approach (TNUDGE) is a technique performing the relaxation (nudging) of the mixing ratios of sufficiently long-lived tracers towards prescribed (in space/time) fields. These can be, for example, the zonally-averaged tracer gradients compiled from ground observations). Referring to the EVAL setup, in this study the mixing ratios of H₂, N₂O, CH₄, chlorinated carbons (CH₃CCl₃, CCl₄, CH₃Cl), SF₆, and CO₂ are prescribed as the lower boundary conditions using the observed mixing ratios. The isotopic separation of the pseudo-emission fields for carbonaceous species is described below in Sect. 5.2.6.

The details of the emission processes implementation in EMAC and the corresponding model parameterisations are described in (Kerkweg *et al.*^[2006b]). The next sections describe substantially the choice of the emission signatures for the model setups including the stable carbon isotope configuration. For setups including the anomalous isotope oxygen composition configuration, all surface sources are considered to be mass-dependent, *i.e.* Δ¹⁷O ~ 0‰ for every emitted oxygenated species. A few necessary details on emission Δ¹⁷O signatures are given in Sect. 5.2.8.

5.2.1 Isotopic separation of the fluxes

The isotopic extension procedure consists of the separation of the regular species fluxes into the individual isotopologues fluxes accounting for the given isotopic ratio and thus the isotope content of a given species. Additionally, the consistency between the regular flux and the sum of isotopically separated fluxes is verified. The minor isotopologues fluxes are calculated by weighting the regular species flux with the minor fractions ${}^{\text{min},i}f$ according to:

$${}^{\text{min},i}f = \frac{{}^{\text{min},i}R \cdot q}{1 + (1 - q) \cdot \sum_j {}^{\text{min},j}R}, \quad {}^iR = (\delta^i + 1) \cdot {}^iR_{\text{st}} \quad (5.9)$$

where q is the number of atoms of the selected isotope in a given species' molecule, iR is the isotopic ratio of a particular isotope i in the flux, R_{st} is the reference standard ratio. When accounting for multiple rare isotopes, all ratios are required for the correct calculation of the resulting fraction of each of the isotopologues. The major isotopologue flux fraction, in turn, is calculated from:

$${}^{\text{maj}}f = 1 - \sum_j {}^{\text{min},j}f \quad (5.10)$$

thus assuring that the sum of isotopically separated fluxes of the major and minor isotopologues equals the regular flux value. The resulting fluxes of the regular species and its isotopologues are:

$$\begin{cases} \text{maj}F = F \cdot \text{maj}f \\ \text{min},iF = F \cdot \text{min},if \\ F \equiv \text{maj}F + \sum_j \text{min},jF \end{cases} \quad (5.11)$$

For the sake of clarity, the molecular fractions f above are calculated plainly from the atomic content q and the isotopic ratios. The isotopic compositions of the emission fluxes, nevertheless, are usually (and within this study) reported using delta values δ^i , which relate the isotope ratio iR and the standard ratio $^iR_{\text{st}}$ in (5.9). The standard ratios used here are reported in Sect. 3.2 (p. 30).

During the isotopic extension of the emission data, the preparation tools import the input data files (usually provided in netCDF⁸⁷ format, with the fluxes values in units of molecules/m²/s), process the fluxes according to the given isotopic signatures and output data files containing the individual isotopologues fluxes. These are subsequently fed to the model data import interface in a conventional way and utilised by the emission submodels (*e.g.* OFFLEM). Depending on the source data used, the spatial resolution of the emission datasets varies. The input fields are adjusted during the model initialisation to the particular model resolution with the help of the NCREGRID submodel (Jöckel^[2006]).

5.2.2 Anthropogenic emissions

The anthropogenic emissions setup is based on the EDGAR database (version 3.2 “fast-track”⁸⁸, van Aardenne *et al.*^[2005]) as described by Pozzer *et al.*^[2007]. The inventory was compiled for the year 2000, thus the anthropogenic emissions are expected to be most consistent for this period. It is noteworthy, that despite its complex structure (the emission is distributed to tens of various classes), the database has no seasonality, *i.e.* spatially distributed emission fluxes composing the emission are constant throughout the year. The inventory comprises approximately 40 source types referring to the different anthropogenic emissions (summarised in Table 5.5), which enables to assign characteristic isotopic signatures individually to each emission source. The influx is distributed to the surface and multiple near-surface model layers, depending on the emitted species and the emission source. This serves to account for specific sources that deliver the pollutants to the various effective altitudes. The majority of the sources (except for power generation, industrial fuel usage and waste treatment) are located at the surface and adjacent layers representing 45 m and 140 m heights. The remaining sources, lofted with the various plume updrafts, are distributed to the higher layers (spanning from 240 m to 800 m above the ground). The detailed anthropogenic emission setup and levelling of the emission sources is described by Pozzer *et al.*^[2009].

Table 5.5 lists the carbon isotopic signatures for CO and emitted compounds assigned to the particular emission category for anthropogenic emissions. Unfortunately, to date the information in the literature on the measured isotopic compositions of the different emitted compounds is scarce, particularly for non-methane hydrocarbons (NMHCs) and other volatile organic compounds (VOCs). Therefore, here the choice for the unknown signatures will follow the EDGAR classification, assuming the emission source material (*e.g.* crops, bio- or fossil fuels) and its characteristic processing (generally either biomass burning or high-temperature combustion) to determine the resulting isotopic ratio of the emitted tracer.

The least uncertain signature is those referring to the fossil fuel usage, to a large extent due to the transportation sector. It is associated with an average characteristic composition of -27.5‰ in $\delta^{13}\text{C}$, as reported for the world average engine exhaust by Stevens *et al.*^[1972] and used as a proxy value for CO and other NMHCs/VOCs. Although quite diverse emitted CO isotope signatures were measured for various engine/fuel types (Kato *et al.*^[1999]), any better assessment based on this signatures is not feasible because the inventory does not provide the related information. For transportation-related sources, a slight variability in emission ratios for selected NMHCs is reported (Rudolph *et al.*^[2002]), but for the majority of species within less than 2‰ deviation from the abovementioned value, and representing the chosen signature within the measurement uncertainty. The exception of substantial enrichment was found for ethyne, which is not represented in the MECCA chemistry mechanism and may potentially constitute an enriched moderate source (see, for example, Ho *et al.*^[2009]). It is also consistent with the biomass burning emissions, as ^{13}C enrichment accompanying ethyne formation during

⁸⁷ <http://www.unidata.ucar.edu/software/netcdf>

⁸⁸ <http://www.mnp.nl/edgar/model/v32ft2000edgar>

the burning process was found (Czapiewski *et al.*^[2002]). In other respects, it is generally recognised that the fossil-related sources reflect the average isotopic ratios of the precursor crude oils. The aircraft emissions are associated with this source as well. However, the corresponding EDGAR emission (class F57) is replaced by the inventory compiled by Schmitt and Brunner^[1997].

In analogy to the fuel combustion category (classes “F”), the same isotopic signature (−27.5‰) is used for the industrial category sources (classes “I”). It is expedient to assume that those sources represent dominantly the fossil nature of the precursor carbon, as the emission is mainly associated with the combustion of fuels in the majority of the industrial processes. An example in case is iron and steel production (class I10), where CO is emitted concomitantly during the thermal processing of the product in the furnaces (IISI^[2004]). On the other hand, the influence of industrial sources on the resulting emission signature is minor, taking into account their small share in the overall anthropogenic emission. The comparison of the contributions of each EDGAR source class to the total emission of CO is presented in Figure 5.3. Notably, the largest emissions are associated with classes B40 (biofuel consumption in the residential/commercial sector) and F51 (non-CO₂ combustion emissions from road transport), thus the relative mixture of these two sources is decisive for the average isotopic composition of the emission. The total emission associated with industry amounts to 34.5 Tg(CO) per year, that comprises approximately 6.3% of the total anthropogenic emission.

The most uncertain isotope signatures are associated, in turn, with the biofuel category (classes “B”), because of the high uncertainties associated with estimates of the biofuel source itself (Olivier *et al.*^[2002]). No detailed information is available about the biofuel production and use, particularly for the period the EDGAR inventory was compiled for. Likewise, there are no specific measurements of the isotopic signatures of CO and other NMHCs/VOCs from biofuel sources reported yet (Goldstein and Shaw^[2003]). These mainly comprise the use (primarily by combustion) of vegetable oil- and biomass-derived fuels, of which biodiesel and ethanol constitute the major parts (Demirbas^[2008]). To eliminate a potentially wrong association with the biofuel category, the woodfuel and waste/residue crops sources used primarily for heating and cooking in Asian and African regions (Yevich and Logan^[2003]) are accounted in the inventory under the biomass burning category as discussed further. The proportion of ethanol/biodiesel fuel sources is not reflected in the inventory, nor the origin of precursor biogenic material. Thus only a rough estimate of the isotopic signature is feasible, assuming a certain average composition of the biomass and negligible isotope effects accompanying the emission. On average, plant material is enriched in ¹³C with respect to fossil fuels and can be considered as a composite of the carbon originating from two cardinal kinds of plant species, namely C₃ and C₄ plants (explained in detail in the following sections). Tersely, the isotopic compositions of those differ conspicuously owing to the differences in the plant photosynthesis mechanisms, yielding average (median) compositions of −27‰ for C₃ species and −12‰ for C₄, respectively (Dawson *et al.*^[2002]). The expected composition of the mixture is hence constrained by these values. Within the reference setup of this study the value of −25‰ following Emmons *et al.*^[2004] is adopted, which corresponds to an approximate 4:1 ratio of C₃ to C₄ plant material. There are, however, estimates (O'Connor^[2009]) that report a significant fraction of C₄ plants being used in global biofuel production, with the source plants contributions quoted for ethanol and biodiesel. Whilst the latter is mainly produced from C₃ species like soy, rapeseed, canola and oil palm tree, ethanol is dominantly manufactured from corn and sugarcane, which are C₄ crops. Projecting this partitioning on the gross production rates for the year 2000 (Demirbas^[2009]) of 156·10⁸ and 9.7·10⁸ litres for ethanol and biodiesel, respectively, will yield a rather high value for the average emission signature of −12.9‰. Here, the fractionation associated with the fermentation process during the ethanol production is assumed to be negligible too, although a few studies (Vallet *et al.*^[1998], Zhang *et al.*^[2003]) indicate that the biogenic ethanol may be even slightly enriched with respect to the source material. A substitution of the reference biofuel δ¹³C signature of −25‰ with the above derived value of −12.9‰ will result in approximately +2.8‰ increase of the overall surface CO emission δ¹³C compared to the reference emission setup (see Table 5.9). The sensitivity of the model results to the selection of the isotopic signature of the biofuel emission is discussed in Sect. 6.2.3.2 (p. 179).

Table 5.5 Description of EDGAR FT32 emission sources and associated isotopic signatures

Category	Source classes	Emission activity	$\delta^{13}\text{C}$ [‰]
Biofuel combustion	B10, B20, B30, B40, B51	industry, power generation, charcoal production, RCO*, road transport	-25.0 ^g
Fuel combustion, production and transmission	F10, F20, F30, F40, F51, F54, F58, F60 ^d , F80, F90 ^c	industry, power generation, conversion, RCO*, road/non-road transport, international shipping, gas production	-27.5
	F57 ^a	air traffic	-27.5 ^f
Industrial	I10, I20 ^c	iron and steel, non-ferrous metals	-27.5 ^f
	I30 ^c , I60 ^c , I70 ^c , I90 ^c , I50 ^b	chemicals, food/beverages/tobacco, solvents, misc. industry, pulp and paper	-27.5 ^f
Land use ^b	L41, L42, L44, L47	(in)direct deforestation, savannah burning, vegetation fires	- ^a
	L43	agric. waste burning	-22.2 ^{c,g}
Waste ^b	W40, W50 ^c	waste incineration, misc. waste handling	-24.0 ^{f,g}

Notes:

^a) Excluded from the setup (or treated separately).^b) Assumed a biomass burning-related emission source.^c) Only CO emission (no VOCs).^d) Only VOCs emission (no CO).^e) For CO, a different signature of -21.3‰ is used (see text).^f) Fossil source assumed.^g) Reflects the relative contribution of C₃ and C₄ plant material.

* (Residential, Commercial and Other)

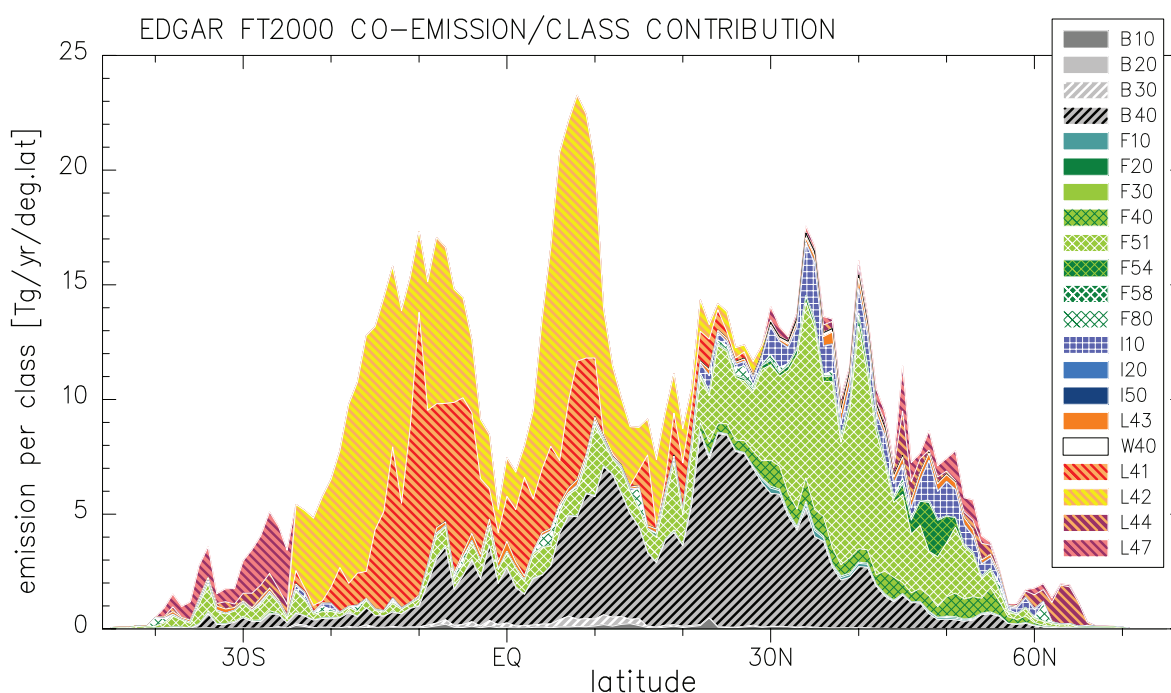


Figure 5.3 Relative contributions of EDGAR emission source classes to the overall anthropogenic emission of CO. Values are given in [Tg/yr] per degree latitude. Note: original EDGAR biomass-burning classes L41, L42, L44 and L47 are being substituted by the GFED inventory and presented here for the comparison only.

The original biomass burning emission inventory of the EDGAR (referring to land use, classes “L”) in the current setup is substituted by the more comprehensive GFED inventory described in the following section. Exceptionally, the agricultural waste burning class (L43), which is not included in GFED is kept. The emission $\delta^{13}\text{C}$ signature of -22.2‰ is assigned to this source using the average composition of the burnt material estimated for 2000 by Randerson *et al.*^[2005]. They use the C₃/C₄ ratio of the burned vegetation inferred with the help of a vegetation-inclusive inversion-adjusted model and comparison with observed CO₂ ratios. A different signature of -21.3‰ for CO is used, following the estimation similarly based on plant distribution, fuel loads and neglecting concomitant fractionations by Conny^[1998]. The estimates of burned plant composition by Randerson *et al.*^[2005] do not consider the potential kinetic isotope effects that may escort biomass burning emission for various tracers. Czapiewski *et al.*^[2002] and later Komatsu *et al.*^[2005] and Nara *et al.*^[2006] report that $\delta^{13}\text{C}$ of the major NMHCs emitted from biomass burning generally follows that of the fuel burnt, and the measure-

ments did not reveal significant additional fractionations associated with the formation processes. Consequently, here (and further for GFED data) the KIEs for biomass burning is assumed to be negligible. Nonetheless, the combustion conditions play a key role in CO formation during the biomass burning: Normal (+0.5‰ to +3.6‰) and inverse (−2.1‰ to −6.8‰) KIEs were found to escort flaming and smouldering burning stages, respectively, with a further complex dependency on the burnt plant type (Kato *et al.*^[1999]). The average composition of CO is rather expected to be depleted with respect to the source fuel, since CO emission is expected to be favoured in the smouldering phase (Yokelson *et al.*^[1997]). Unfortunately, the representation of the combustion stages in the emission data is limited; hence one can provide only a qualitative estimate of the isotope effect (depletion). The quantitative estimates of the contributions from various stages (like, for instance, in the modelling study by Soja *et al.*^[2004]) could be improved with the use of the isotopic composition in this case. Conclusively, in contrast to the primary biomass burning sources, the emissions from the class L34 induce a minor influence on the average CO emission signature, accounting for a total of 16.3 Tg(CO) per year (less than 3% of the total anthropogenic emission). In an analogous way, the waste treatment-related sources (classes “W”) are assigned to a slightly enriched (compared to the average fossil fuel carbon) composition of −24‰ using the ratio of the biological to fossil carbon for waste incineration from Johnke^[2000]. It is assumed that the waste treatment category refers to the waste incineration processes mainly.

Table 5.6 Anthropogenic emission sources strengths and their isotopic signatures

Species	Source [Tg(gas) yr ^{−1}]			Totals	
	Biofuel	Fossils	Waste ^a	Emission ^b	δ ¹³ C (‰)
CO	250.42	280.41	16.35	547.18 / 234.63	−26.15
CH ₃ OH	6.58	3.13	0.43	10.14 / 3.80	−25.70
HCHO	3.50	0.98	0.23	4.71 / 1.88	−25.45
HCOOH	3.56	–	0.23	3.79 / 0.99	−24.94
C ₂ H ₄	5.11	3.54	0.34	8.99 / 7.70	−25.97
C ₂ H ₆	2.91	6.11	0.19	9.21 / 7.36	−26.58
C ₃ H ₆	2.28	1.49	0.15	3.92 / 3.36	−26.05
C ₃ H ₈	0.91	9.45	0.06	10.42 / 8.51	−27.18
C ₄ H ₁₀	1.16	70.67	0.08	71.91 / 59.44	−27.36
CH ₃ CHO	2.04	–	0.13	2.17 / 1.18	−24.94
CH ₃ COOH	6.52	–	0.43	6.95 / 2.78	−24.94
CH ₃ COCH ₃	1.89	3.18	0.12	5.19 / 3.16	−26.44
MEK	4.42	4.22	0.29	8.93 / 5.95	−26.10

Notes:

^a) Refers to the EDGAR category L43.

^b) Values are in [Tg(gas) yr^{−1}] and [Tg(C) yr^{−1}] units, respectively.

Table 5.6 lists the anthropogenic emissions and the compositions for the EDGAR database. The emissions for CO sum up to almost 550 Tg/yr, while the overall influx for the other trace gases amounts to approximately 150 Tg/yr. The mixing of the compositions of the main CO contributors (bio- and fossil fuel) in proportion of ~250:280, respectively, yields the average composition of −26.15‰. This value is apparently sensitive to the assumed biofuel δ¹³C signature. The influence of the biofuel sources is dominating for methanol, formaldehyde, formic acid, acetaldehyde and acetic acid, with values close to −25‰. Alkanes and alkenes emissions are enriched similarly to CO, with an increasing influence of the fossil fuel input towards the higher hydrocarbons. The spatial distribution of the δ¹³C of anthropogenically emitted CO is depicted in Figure 5.4, with the panels referring to the specific emission altitudes as described above. The two lowermost layers subsume the majority of the emission classes, including the shipping and biofuel-related sources (equally distributed to the layers) and fossil fuel sources (falling mainly in the surface layer). The emission signatures reflect the dominant biofuel emissions in Africa, eastern Asia and Oceania (panel a). In the second emission layer (panel b) the agricultural waste burning and waste incineration sources are reflected together with the biofuel emission. The superincumbent layers include the mixture of industrial and power generation sources, with the latter prevailing in the top two layers.

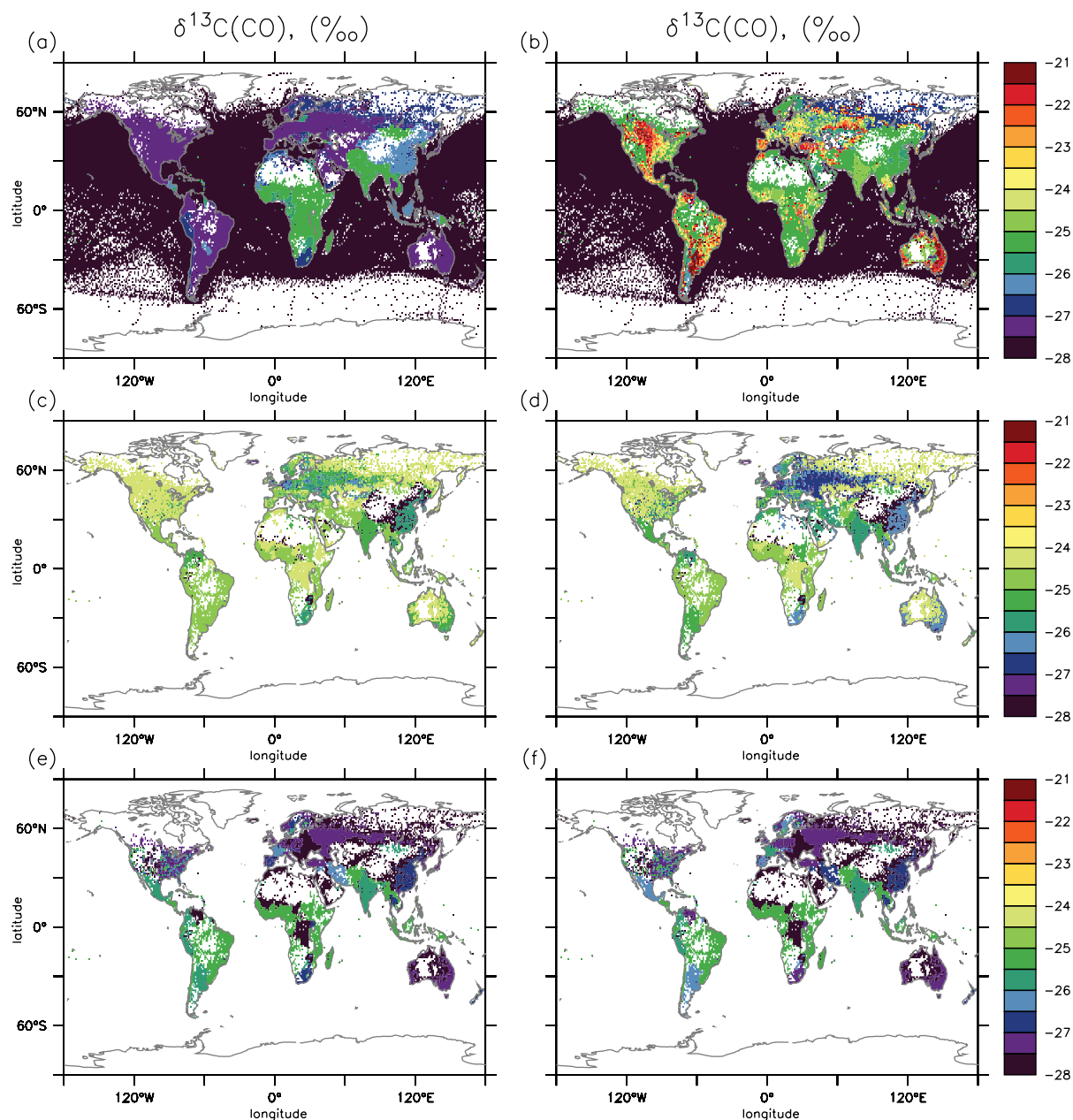


Figure 5.4 Stable carbon isotope composition of CO emitted from anthropogenic sources compiled on the basis of the EDGAR FT2000 inventory. Panels (a)–(f) refer to the specific emission heights of 45, 140, 240, 400, 600 and 800 m, respectively (see text for details).

5.2.3 Biomass burning emissions

The biomass burning emission data is prepared from the ORNL DAAC Global Fire Emission Database (GFED), version 2.1 inventory⁸⁹ (Randerson *et al.*^[2007]), an updated and extended version of the initial GFED version 1 release (van der Werf *et al.*^[2006]) used in the EVAL setup (Pozzer *et al.*^[2009]). In the current setup, monthly mean emission fields covering the period from 1997 to 2005 are used. The inventory includes emission fluxes for CO, NMHCs, nitrogen oxides (NO_x) and other species; in addition, the estimation of the C_4 plant carbon fraction of the burnt material is provided (Randerson *et al.*^[2005]). The latter is used to assign the isotopic signatures to the emission fluxes, assuming negligible isotopic fractionation during the burning, as discussed above. The resulting isotopologues fluxes are calculated as:

⁸⁹ http://daac.ornl.gov/VEGETATION/guides/global_fire_emissions_v2.1.html

$$\begin{cases} \frac{{}^{13}\text{C}F}{F} = (1 - f_{C_4}) \frac{q \cdot R_{C_3}}{R_{C_3} + 1} + f_{C_4} \frac{q \cdot R_{C_4}}{R_{C_4} + 1} \\ \frac{{}^{12}\text{C}F}{F} = (1 - f_{C_4}) \frac{(1 - q) \cdot R_{C_3} + 1}{R_{C_3} + 1} + f_{C_4} \frac{(1 - q) \cdot R_{C_4} + 1}{R_{C_4} + 1} \end{cases} \quad (5.12)$$

The notation follows that from (5.9) and f_{C_4} denotes the C_4 fraction of the burnt plant material, F is the total emission flux. Ratios R_{C_3} and R_{C_4} refer to the ${}^{13}\text{C}$ isotope content associated with C_3 and C_4 plants, respectively; the corresponding isotopic signatures are discussed above. The emission is released into the second emission layer corresponding to 140m height (see Sect. 5.2.2).

For the application in the sensitivity simulations, an averaged (ensemble mean) yearly biomass burning “climatology” was derived, referring to the 2000–2005 period of the original data. The “climatological” yearly average spatial distribution of a burnt C_4 biomass fraction and its translation into $\delta^{13}\text{C}$ values of the emission are presented in Figure 5.5. The heaviest (*i.e.*, most enriched in ${}^{13}\text{C}$) composition of the emission is associated with the grassland and savannah burning regions, where the C_4 crops are superior.

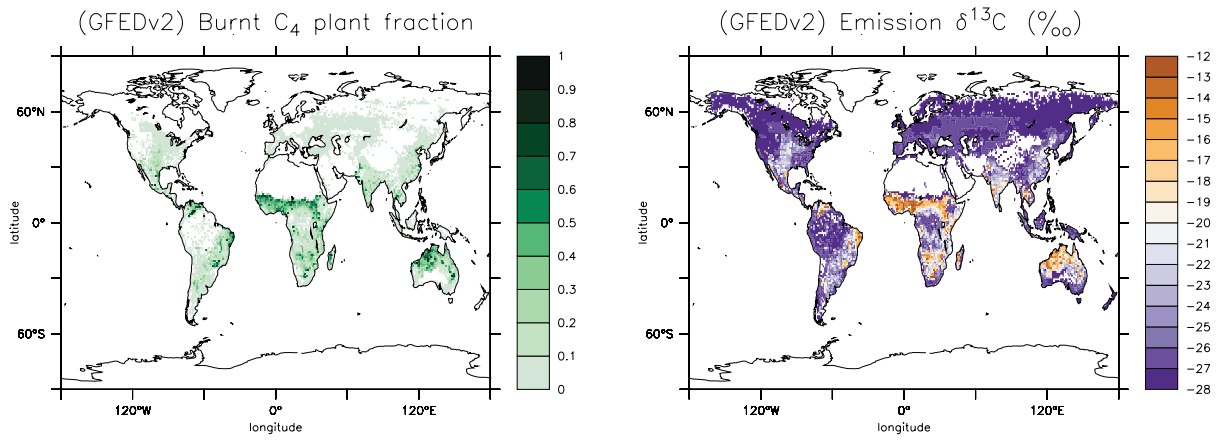


Figure 5.5 Burnt biomass C_4 plant fraction (left) and corresponding isotopic signature of the emitted carbon (right) from GFEDv2.1 data-base. Fields are “climatological” yearly averages (see text).

In Figure 5.6 the temporal evolution of the hemisphere-integrated CO emission from biomass burning is presented. The markedly intensified emission rates in 1997–1998 are attributed to the increased wildfires due to the dry conditions and droughts induced by the enhanced atmospheric southern oscillation and El-Niño climate pattern (ENSO, Dube^[2009]). This event is also notable (although less pronounced) for the years 2002–2003. Interestingly, ENSO activity is virtually not reflected in the isotopic composition of the emission. However, the influence of the biomass source, especially important for its ${}^{13}\text{C}$ enriched composition in the tropics and southern hemisphere, without doubt increases during El-Niño years. The variation of the flux $\delta^{13}\text{C}$ is twice as large in the northern hemisphere (NH) compared to that in the southern hemisphere. Such a difference arises from the large C_3 plant extent at the northern high latitudes and the pronounced seasonal fire cycle. The summer/fall extratropical fires in the NH occur predominantly in C_3 plant communities, mainly forests of an average -27‰ composition. In the winter time the (sub)tropical sources take over enriching the emission to the maximum of -19‰ due to the large C_4 plant fraction burnt in Africa and Asia. In the southern hemisphere, the spatial diversity of C_3/C_4 ratio is smaller over the smaller land extent, and the average signature varies around -24‰ within $\pm 1\text{‰}$ only.

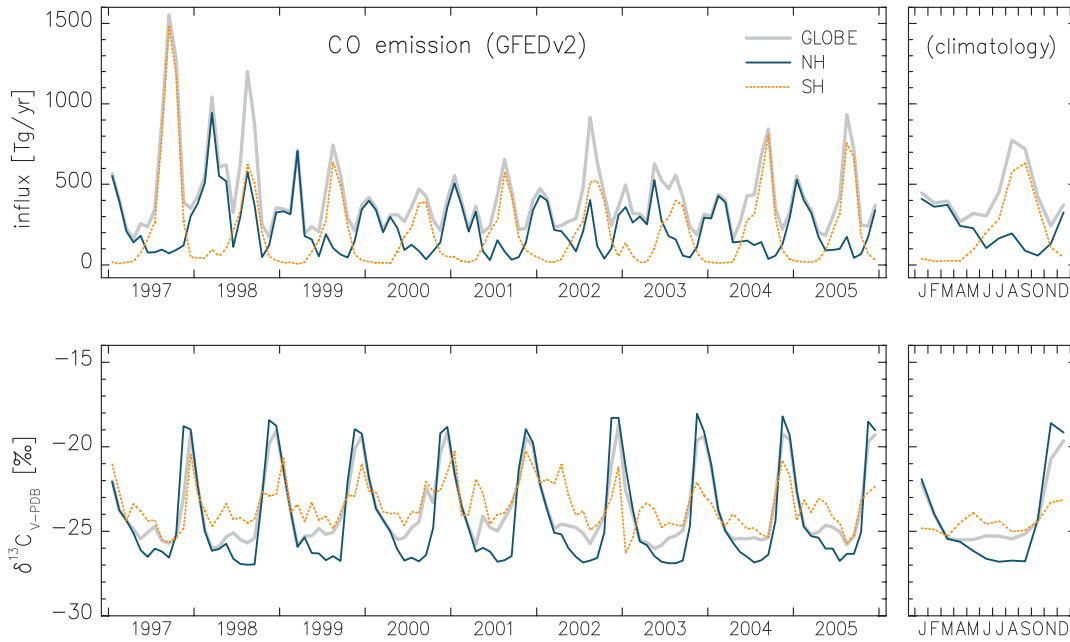


Figure 5.6 Emission of CO from biomass burning sources based on the GFED v2.1 data. Upper: CO integrated flux in the northern (NH), southern hemispheres (SH) and globally. Lower: The carbon isotope composition of the respective fluxes. The right panels depict the “climatology” ensemble averages used for sensitivity simulations.

Table 5.7 Biomass burning emission sources strengths and their isotopic signatures

Species	Source [Tg/yr]			Average $\delta^{13}\text{C}$ [‰]	
	NH	SH	Total ^a	NH	SH
CO	223.18	202.75	425.93 / 182.64	-24.0	-24.4
CH ₃ OH	3.17	2.98	6.15 / 2.31		
HCHO	1.69	1.58	3.27 / 1.31		
HCOOH	1.73	1.62	3.35 / 0.87		
C ₂ H ₄	2.47	2.32	4.79 / 4.10		
C ₂ H ₆	1.41	1.32	2.73 / 2.18		
C ₃ H ₆	1.11	1.04	2.15 / 1.84		
C ₃ H ₈	0.44	0.41	0.85 / 0.69	-24.3	-24.7
C ₄ H ₁₀	0.56	0.52	1.08 / 0.89		
CH ₃ CHO	0.99	0.93	1.92 / 1.05		
CH ₃ COOH	3.16	2.97	6.13 / 2.45		
CH ₃ COCH ₃	0.91	0.86	1.77 / 1.08		
MEK	2.14	2.00	4.14 / 2.76		

Notes:

^a Values are in [Tg(gas)/yr] and [Tg(C)/yr units], respectively.

The annual average BB emission rates for CO and NMHCs/VOCs are listed in Table 5.7. All NMHCs/VOCs emitted possess an equal isotopic composition, since the fluxes for carbonaceous species are principally derived from the same burned carbon emission proxy (van der Werf *et al.*^[2006]). In order to obtain the individual tracer emission, the proxy is scaled with the corresponding emission factor (conventions and values from Andreae and Merlet^[2001] are used), but the spatial distribution of the emission, hence C₃/C₄ carbon ratio, is the same. The hemispheric difference in $\delta^{13}\text{C}$ averages amounts to 0.4‰ with the heavier emission in the SH. For CO, a different proxy was used in GFED, which for the same burnt C₄ plant fraction results in a slightly heavier (+0.3‰ in $\delta^{13}\text{C}$) average composition. Notably, the GFED v2.1 inventory provides the combustion completeness parameter, the estimate of the fraction of the actual fuel load combusted which might to a certain degree reflect the burning stage conditions (*i.e.* flaming or smouldering phases). Unfortunately, the correspondence between these two parameters is not assessed to date; future applications of combustion completeness for accounting for the kinetic isotope effects escorting biomass burning would be of great benefit.

5.2.4 Biogenic emissions

The biogenic emissions comprise the discharge of organic species into the atmosphere associated with the biosphere activity, particularly oceanic and plant emissions. The current biogenic emission setup follows Guenther *et al.*^[1995] as described by Kerkweg *et al.*^[2006b], and comprises two parts for offline and online emissions, respectively (see the introduction in Sect. 5.1.3). The offline part is reassessed by Pozzer *et al.*^[2007] and prescribes the emission for the major set of NMHCs/VOCs, excluding isoprene/monoterpenes emission which are calculated online. The data have a temporal resolution of one month, thus approximating the emission seasonal variation with no interannual variability. The emission is performed into the lowermost model layer. The CO emission comprises in-place oxidation of some (non-industrial) hydrocarbons not accounted for in the applied MECCA chemistry (*i.e.* higher alkenes ($C>3$), terpene products other than acetone, higher aldehydes, and some direct CO emissions by vegetation and decaying plant matter. The oceanic CO emission strengths (monthly zonal distribution) are taken from Bates *et al.*^[1995]. No biogenic emissions for formaldehyde (HCHO), acetaldehyde (CH_3CHO) and higher ketones (represented by MEK species) are included. The total annual emission strengths for CO and NMHCs/VOCs with the corresponding average compositions are listed in Table 5.8.

For the majority of the species, plant activity is the dominating emission. For a few species, namely acetic acid (CH_3COOH), formic acid ($HCOOH$) and ethene (C_2H_4), the emission from the soils is estimated to be of comparable magnitude to the plants source (Kesselmeier and Staudt^[1999]). Unfortunately, hardly any measurements or estimates of the isotopic composition of the soil-emitted carbon of these VOCs are available. The soil organic matter composition is also not well known (Boutton^[1991]). Regarding the example of methane, whose microbial production in soils is associated with large fractionations (Bréas *et al.*^[2001]), soil emitted VOCs may constitute the source with the most uncertain signature. On the other hand, the aggregate of soil emissions is negligibly small compared to the overall CO turnover; even a radical change in its signature will be hardly reflected in the average $\delta^{13}C(CO)$.

A similar case arises with the oceanic emissions for which the strengths are debatable, and no isotopic signatures were measured for NMHCs. Rudolph^[1997] suggests the photochemical processing of dissolved organic carbon (DOC) to be the origin of the ocean-emitted NMHCs. Within the current setup an a priori signature of -20.5‰ representing the marine isotopic carbon content (Avery Jr *et al.*^[2006], lower limit) is assigned. This value is somewhat higher than -22‰ used for oceanic emission by (Stein and Rudolph^[2007]) in their modelling study on ethane isotopes. For CO, heavier oceanic emissions of -13.5‰ are assumed, according to Manning *et al.*^[1997]. This value is based on the inverse modelling study and observations in the SH, where ocean input on CO is evidently significant. Quite contrary to this value, Nakagawa *et al.*^[2004] estimate the ocean emitted CO to possess a rather depleted composition of -40‰ . This value appears to be still questionable, as the composition of the seawater-extracted CO was measured, the assumed precursor DOC composition was depleted (of average -31‰) and the sampling was done in a single, fairly non-remote location in waters with high microbial activity (thus escorted with the significant KIE during the production). Finally, Bergamaschi *et al.*^[2000] estimate the composition of CO emitted from the oceans to be as high as $+5.1\text{‰}$ (scenario S2). Similarly to biofuel-related sources, the oceanic CO is associated with a very uncertain isotopic composition. The change of this source signature from -13.5‰ to -40‰ will result in the decrease of the average biogenic emission signature by 3‰ with a corresponding 0.3‰ decrease in the overall CO surface emission composition.

5.2.4.1 Plant emissions

For the plant biogenic emissions, a novel approach referring to the plant physiological properties is proposed here. In most previous (modelling) studies, the isotopic composition of the biogenically emitted tracers is based on the average global isotopic signature derived from the limited, often not consistent set of observations available. CO is a case in point here: the majority of the CO isotope modelling studies assume a $\delta^{13}C$ of CO emitted due the plant activity to be as low as -32.2‰ , referring to the particular single estimate by Conny^[1998]. The latter was retrospectively derived from the observations at a rural US site (Stevens and Wagner^[1989]), tolerating some important approximations, in particular (1) a two-component mixing model of the background and NMHC-only sources, (2) constancy of the background composition throughout June to October, and (3) neglecting the variable effect of kinetic isotope effects in CO. If (1) is fairly applicable to the observations at a rural site, (2) and (3) rely on the five months constant background composition and neglect the variable input from the $CO+OH$ KIE. This is a too rough approximation, considering the intensive chemistry in

the summer and characteristic CO lifetime shorter than a month. Indeed, the isotopic composition of CO undergoes significant changes from spring to fall, and the competition of the CO+OH reaction KIE and the varying in-situ contribution from methane are the two non-negligible effects.⁹⁰

Besides the temporal variation, the global average value does not represent the biogenic sources' variable spatial distribution, which is important, since biogenic CO is mainly a product of the rapid oxidation of NMHCs. The latter, in turn, are expected to acquire specific isotopic ratios being emitted from various plant species in different environmental conditions. The most studied compound in this respect is the isoprene (C₅H₈), one of the major biogenically released VOCs. Sharkey *et al.*^[1991] measured the carbon isotopic composition of the emitted isoprene and found it dependent on the composition of the recently fixed carbon, *i.e.* those from the air CO₂ incorporated in the plant material during the initial step of the photosynthetic cycle. The isotope effects related with the plant activity and plant-CO₂ exchanges are extensively studied (see, for instance, Dawson *et al.*^[2002]). These usually operate with the isotope discrimination Δ , a representative parameter describing the fractionation of the plant tissue relative to the atmospheric reservoir (Farquhar *et al.*^[1989]):

$$\Delta = \frac{\delta_a - \delta_p}{1 + \delta_p}, \quad (5.13)$$

where δ_a and δ_p refer to the isotopic composition of the air CO₂ and plant tissues, respectively. In the form of Eq. (5.13), discrimination expresses the superposed effect of the various biological factors. The contribution of each of them, *e.g.* various plant metabolism pathways (C₃ or C₄), water availability for the plants (response to droughts), solar irradiance or various stress factors ought to be parameterised separately (Lloyd and Farquhar^[1994]), hence it is a complex parameter. The largest effect on Δ is induced by the differences in the plant metabolism, the characteristic fixation mechanism of air CO₂ for the subsequent photosynthesis. The majority of the terrestrial plants incorporate the C₃ metabolism, when the fixation is escorted by the fractionation induced by RuBisCO (the specific enzyme used for the fixation in the so-called photosynthetic Calvin cycle). Accounting additionally for the other fractionations (*e.g.* diffusion of air CO₂ through the stomata, *etc.*), typical Δ values for C₃ plants span from 15‰ to 25‰. Note, that discrimination is expressed on the positive scale. Assuming a certain δ_a (approximately -8‰ for air CO₂) and using Eq. (5.13), one derives the C₃ plant composition within the range of -32‰ to -23‰ in $\delta^{13}\text{C}$. C₄ plants employ other than RuBisCO enzymes; their efficiency is associated with lower Δ values of 2.5‰ to 5‰, corresponding to a -10‰ to -13‰ range of plant material $\delta^{13}\text{C}$. In addition to C₃ and C₄ plants⁹¹, a minor fraction of terrestrial CAM (crassulacean acid metabolism) plants exists. CAM can be regarded as a temporal coupling of C₃ and C₄ metabolisms employed by the plant for optimised adaptation to arid conditions. Therefore, CAM plants are characterised with the wide range of discriminations from 2‰ to 22‰ (Griffiths^[1992]), or -10‰ to -30‰ expressed in $\delta^{13}\text{C}$ of the plant tissue carbon. The specified plant biomass compositions result from the permanent isotopic equilibration with the atmospheric pool (*i.e.* CO₂) escorted by discrimination, thus the use of Eq. (5.13) is rational when the long-term value of Δ is considered.

In view of the correlation between the emitted species isotopic composition and the plant isotope discrimination, the latter is assumed here as a proxy for biogenic emission signatures in the current emission setup, rather than the global average signature. This approach, however, premises upon the following key assumptions:

- Few studies indicate that a moderate part (9% to 28%, Schnitzler *et al.*^[2004], Karl *et al.*^[2002]) of the emitted isoprene may be issued from a separate carbon source of the plant. Its composition may differ from that expected from Δ , the photosynthetically fixed carbon. Moreover, neither the isotopic composition of the suggested alternative sources was deduced, nor the fractionations associated with their incorporation in the emission product. Affek and Yakir^[2003] overcame this issue showing that the long-term value of Δ may be used as a proxy for the average bulk leaf biomass, thus concluding the depletion of the emitted isoprene in relation to it. It is important to note that the contribution of alternative sources becomes larger as the plant is put under stress (*e.g.*, experiments of Schnitzler *et al.*^[2004] were partly carried in CO₂-free air). For natural conditions, the proportion of the non-photosynthetically fixed carbon is likely to be smaller.

⁹⁰ See the detailed observational data analysis touching upon the applicability of the mixing model approach to CO isotope composition in view of its background variations in Sect. 4.1.1 (p. 78).

⁹¹ Indices 3 and 4 indicate the number of carbons in the initial fixation product molecule.

- The abovementioned studies have analysed exclusively isoprene; no comparable measurements were performed regarding the other species. Nevertheless, there are isotopic compositions of biogenically emitted NMHCs/VOCs reported being relative to the plant bulk leaf composition (Rudolph *et al.*^[2003], Sharkey *et al.*^[1991] Conny and Currie^[1996]), as well as few measurements of the plant-emitted VOCs whose $\delta^{13}\text{C}$ is found comparable to that of the expected bulk composition (Giebel *et al.*^[2010]). Thus it is practicable to derive the emission signatures from the measured depletions of the trace gas composition relative to that of the plant leaf. It is tolerable under the assumption that the latter is determined by the long-term value of Δ yielding from the specific plant metabolism and diffusion/equilibrium effects of the CO_2 photosynthetic fixation and respiration.

For constructing the emission signatures, the estimated global distribution of the leaf discrimination is taken from Scholze *et al.*^[2008]. They use a dynamic global vegetation model extended with the terrestrial isotopic carbon module. The parameterisation of the leaf carbon discrimination is based on the framework by Lloyd and Farquhar^[1994] neglecting poorly understood fractionations in several processes involved in the photorespiration. The vegetation dynamics model accounts for the plant and soil carbon reservoirs and a numerous set of parameters including the vegetation composition, its productivity, fire disturbance, water availability and land use schemes, as well as climate forcing (monthly temperature, precipitation and cloud cover fields). For the detailed model description, the reader is referred to Scholze *et al.*^[2003] and the abovementioned references. The simulated leaf discrimination for the year 1995 from the ISOLUCP experiment (depicted in Figure 5.7, left panel) is adopted here. The characteristic variability of the global leaf discrimination magnitude is on the order of decades, thus the data referring to 1995 is reckoned to be consistent for the studied year 2000. The bulk leaf composition δ_p is calculated straight from the isotope discrimination defined in Eq. (5.13), for which the isotopic composition of CO_2 , namely δ_a , is required. For the period of 1997–2005 (corresponding biomass burning data in the current setup), the estimate of the surface CO_2 isotopic composition from the GLOBALVIEW project (GLOBALVIEW-CO2C13^[2009]) is taken. These data comprise latitudinal weekly averages (shown in Figure 5.7, right panel), thus the latitudinal mean of the $\delta^{13}\text{C}(\text{CO}_2)$ went into the calculations. Except for isoprene, the fractionations accompanying species emission are considered to be negligibly small, as no significant deviation (within measurement SD of 1‰) from the source plant material for the selected NMHCs was reported (Conny and Currie^[1996], Guo *et al.*^[2009]). For the fractionation escorting isoprene emission, the lower limit of 4‰ depletion relative to the bulk leaf composition from Affek and Yakir^[2003] is taken.

The biogenic emission strengths and resulting isotopic signatures (average values for the year 2000) are listed in Table 5.8. The largest offline emissions pertain to CO and methanol; note the increased emission for the latter compared to the EVAL setup. The final signatures reflect the proportion of the land (average –25.7‰) and oceanic sources. The average composition of the CO emission of –24.2‰, compared to the previously assumed –32.2‰ (Conny^[1998]), results in an effective increase of +0.8‰ in the overall surface emission $\delta^{13}\text{C}$. The major part of the emissions is placed in the tropics, with the summer-triggered large emission in the NH. An example for CO is sketched in Figure 5.8. The largest influx is associated with the areas of rather depleted sources. The land sources are weaker than the oceanic sources in NH winter, which is markedly reflected in the isotopic composition of CO emissions. Based on the same proxy, the emission signature dynamics is similar for the other species.

The isoprene emission, in turn, is calculated on-line, utilising model parameters obtained during the calculation. The emission parameterisation is described by Ganzeveld *et al.*^[2002] and implemented for EMAC in the ONLEM sub-model (Kerkweg *et al.*^[2006b]). The key variables for the isoprene emission are the temperature and radiative balance over the canopy (both are provided by the base model) and the vegetation foliar density (prescribed). The isoprene influx is calculated every model time step from the abovementioned variables. To account for the isotopic isoprene emission, the necessary extension to ONLEM was implemented. The influxes of the $^{12}\text{C}/^{13}\text{C}$ isotopologues are calculated from the original isoprene emission flux and either simulated or prescribed average CO_2 isotopic composition. The leaf discrimination distribution is imported as a parameter (similarly to the other prescribed data fields). The overall emission amounts to approximately 350–380 Tg/yr with the corresponding average ^{13}C signature within the range of –28.6‰ to –27.2‰ depending on the proportional contributions from the source regions. As indirect (in-situ oxidation) source of CO, isoprene dominates over the sum of all remaining VOCs accounted for in the setup.

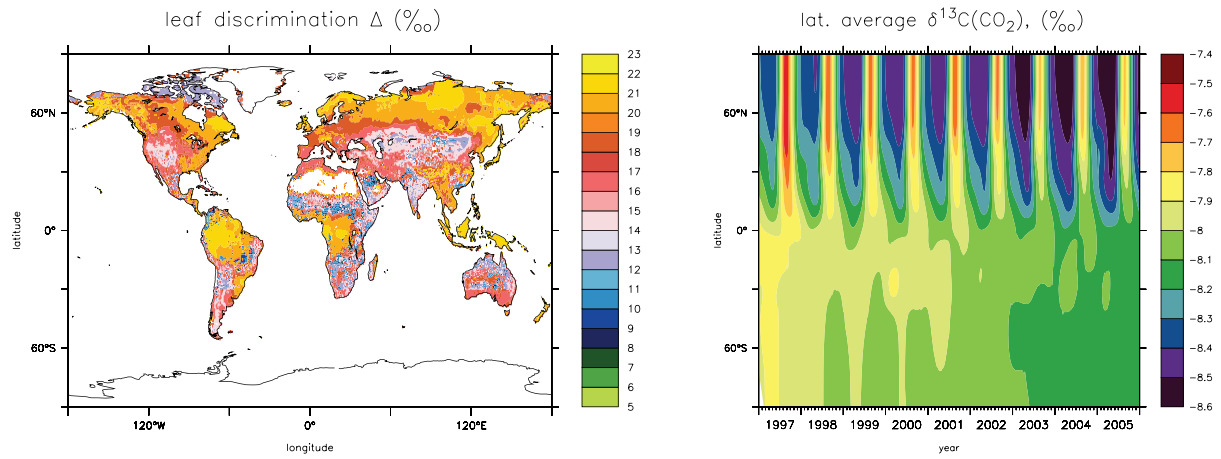


Figure 5.7 Left: Global mean leaf discrimination distribution (ISOLUCP experiment) from (Scholze *et al.*^[2008]). The distribution generally reflects the proportion of the C_3/C_4 metabolism and characteristic carbon photorespiratory fractionation in the various ecosystems, land use regimes and climate zones. Right: Time series of the latitudinal average surface isotopic composition of CO_2 from the GLOBALVIEW-CO2C13^[2009] data.

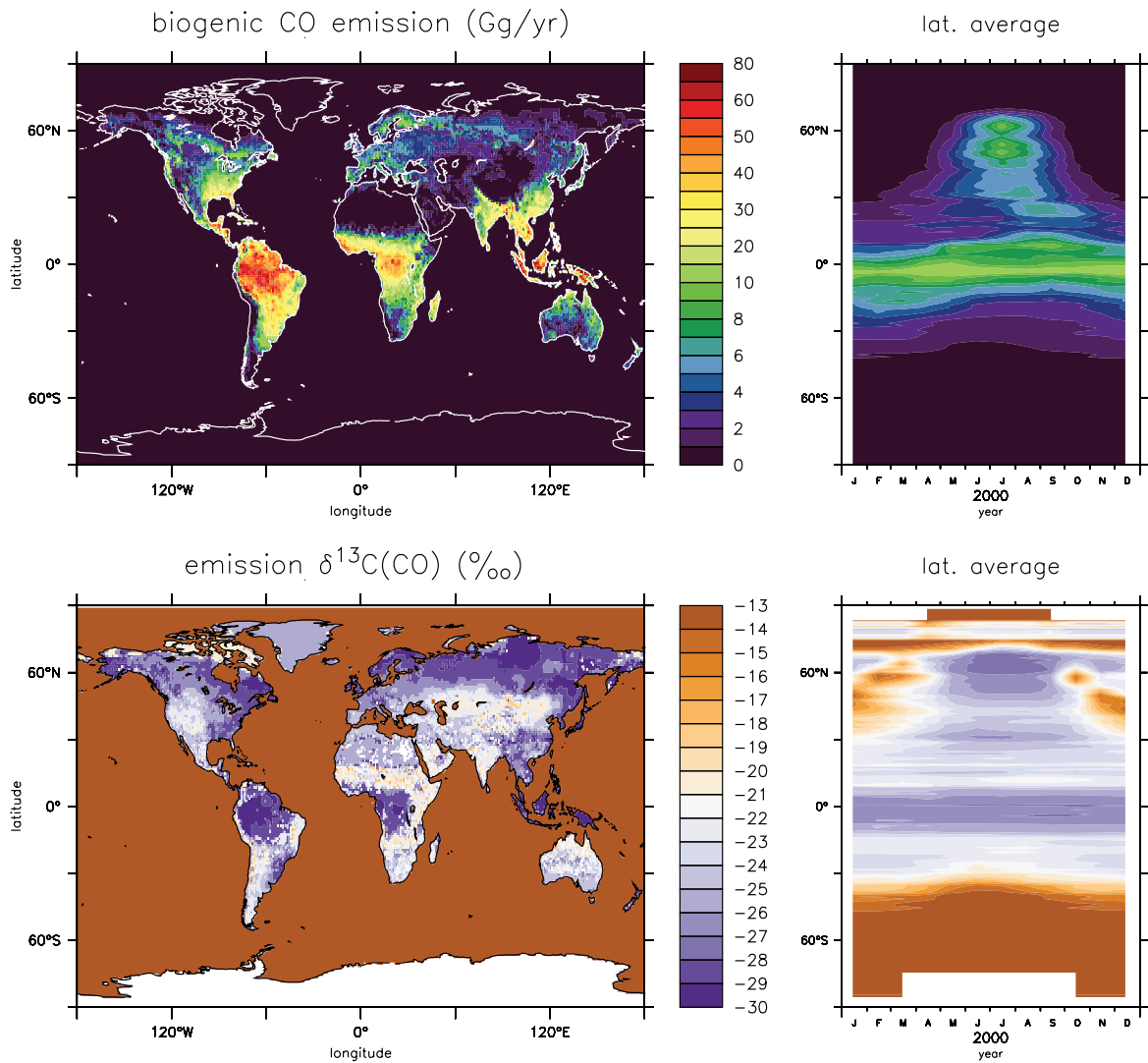


Figure 5.8 Left: CO emission from the biogenic sources (upper panel) and corresponding isotopic signature (lower panel). Right: Corresponding time series of latitudinal averages for the year 2000 emission with identical colour scales.

Table 5.8 Biogenic emission sources strengths and their isotopic signatures

Species	Sources [Tg/yr]		Totals	
	Land (Soils)	Ocean	Emission ^a	$\delta^{13}\text{C}$ [‰]
CO	100.0	12.7	112.7 / 48.3	-24.2
CH ₃ OH	151.0 ^b	–	151.0 / 56.6	-25.8
HCOOH	5.58 (1.65)	–	5.58 / 1.46	-25.4 ^c
C ₂ H ₄	10.0 (3.0)	0.91	12.13 / 5.19	-23.4
C ₂ H ₆	–	0.54	0.54 / 0.22	-20.5
C ₃ H ₆	2.15	1.27	3.41 / 2.92	-23.8
C ₃ H ₈	–	0.35	0.35 / 0.29	-20.5
C ₄ H ₁₀	–	0.40	0.40 / 0.33	-20.5
CH ₃ COOH	3.39 (1.44)	–	3.39 / 1.36	-25.7
CH ₃ COCH ₃	40.57	–	40.57 / 24.74	-25.7
DMS	0.91	–	0.91 / 0.35	-25.7
Isoprene ^d	346.03–385.35	–	346.03–385.35 / 305.07–339.73	-28.6 to -27.2

Notes:

^a Values are in [Tg(gas)/yr] and [Tg(C)/yr] units, respectively.^b Recommended updated value from (Pozzer *et al.*^[2007]).^c Corrected for emission from formicine ants (0.22 Tg/yr) of -19‰ (Johnson and Dawson^[1993]).^d Calculated online.

5.2.5 Final composition of the surface sources

Table 5.9 lists the annually integrated trace gases emissions from the surface in the reference emission setup of this study. For the carbonaceous species, stable carbon isotopic compositions resulting from the superposition of the various emission types are given; values refer to the year 2000. The inter-annual variability for 1997–2005 of the average $\delta^{13}\text{C}$ signature of emitted CO is less than 0.5‰ yr⁻¹ resulting from the variability of $\pm 0.6\text{‰ yr}^{-1}$ in the biomass burned carbon and a negative trend in the CO₂ composition in last decades (-0.02‰ to -0.03‰ yr^{-1} due to the input of fossil fuel-derived carbon into the atmosphere, Yakir^[2011]) propagating into the biogenic emissions.

Table 5.9 Surface emission sources in the reference emission setup

Species	Source [Tg/yr]			Totals	
	Anthropogenic (Biofuel)	Biomass burning	Biogenic	Emission [Tg/yr] ^a	$\delta^{13}\text{C}$ [‰]
CO	547.18 (250.42)	425.93	112.70	1085.81 / 465.60	-25.2
CH ₃ OH	10.14 (6.58)	6.15	151.00	167.29 / 62.71	-25.7
HCHO	4.71 (3.50)	3.27	–	7.98 / 3.19	-25.1
HCOOH	3.79 (3.56)	3.35	5.58	12.72 / 3.32	-25.0
C ₂ H ₄	8.99 (5.11)	4.79	10.91	24.69 / 21.14	-24.5
C ₂ H ₆	9.21 (2.91)	2.73	0.54	12.48 / 9.97	-25.9
C ₃ H ₆	3.92 (2.28)	2.15	3.42	9.49 / 8.13	-24.9
C ₃ H ₈	10.42 (0.91)	0.85	0.35	11.62 / 9.50	-26.8
C ₄ H ₁₀	71.91 (1.16)	1.08	0.40	73.39 / 60.66	-27.3
CH ₃ CHO	2.17 (2.04)	1.92	–	4.09 / 2.23	-24.7
CH ₃ COOH	6.95 (6.52)	6.13	3.39	16.47 / 6.59	-24.9
CH ₃ COCH ₃	5.19 (1.89)	1.77	40.57	47.53 / 28.98	-25.7
MEK	8.93 (4.42)	4.14	–	13.07 / 8.71	-25.6
DMS	–	–	1.82	1.82 / 0.70	-25.7
Isoprene	–	–	365.69	365.69 / 322.40	-29.4
SO ₂	149.6 (3.09)	2.60	–	152.19 / –	–
NH ₃	–	–	67.21	67.21 / –	–
NO _x ^b	33.87 (2.48)	9.28	6.77–7.00	49.92–50.15 / –	–

Notes:

^a Values are in Tg(gas)/yr and Tg(C)/yr units, respectively.^b Values are in Tg(N)/yr units.

The spatial distribution and annual dynamics of the surface CO emission is presented in Figure 5.9. The largest emission is situated in the tropics, particularly in Africa and Asia and attributed to the biomass burning season in July-September in the SH, African fires in December and high-latitude fires in Eurasia and Northern America from May to September. A comparable emission proportion is made up by the anthropogenic sources, which have no distinct seasonality and are present in the NH high latitudes; these are mostly transportation and industry (*i.e.*, fossil fuel related sources). The relative dynamics of the isotopic composition is weaker than that of the corresponding flux magnitudes, indicating that the dominant sources are close to the average -25‰ to -27‰ of terrestrial carbon, with the exception of the North African and Australian fires, when a significant proportion of C_4 plants is being burnt. The largest portion of ^{13}C -enriched CO enters the atmosphere from December to March from the African equatorial fires. Interestingly, mixing of the fossil fuel-derived CO from ships and the heavier oceanic CO emissions highlights the most navigated ship tracks in the $\delta^{13}\text{C}(\text{CO})$ map, where the strengths of these sources become comparable.

The average compositions of the majority of NMHCs/VOCs fall in the range of -26‰ to -24‰ with the exception of isoprene, propane and butane (Figure 5.10). For the latter two, the major emission is coming from anthropogenic sources, which are close to -27‰ . The isoprene composition reflects an assumed 4‰ depletion from the average terrestrial carbon composition. The annual emission dynamics for NMHCs/VOCs basically reflects the proportion of the sources, *e.g.* for CH_3OH and CH_3COCH_3 the dynamics is mainly driven by the biogenic emission. The particular source dynamics for various NMHCs/VOCs resemble each other being derived from the same proxies (*e.g.* burnt carbon in GFED). The uncertainties associated with emissions and corresponding signatures are discussed in Section 5.2.7.

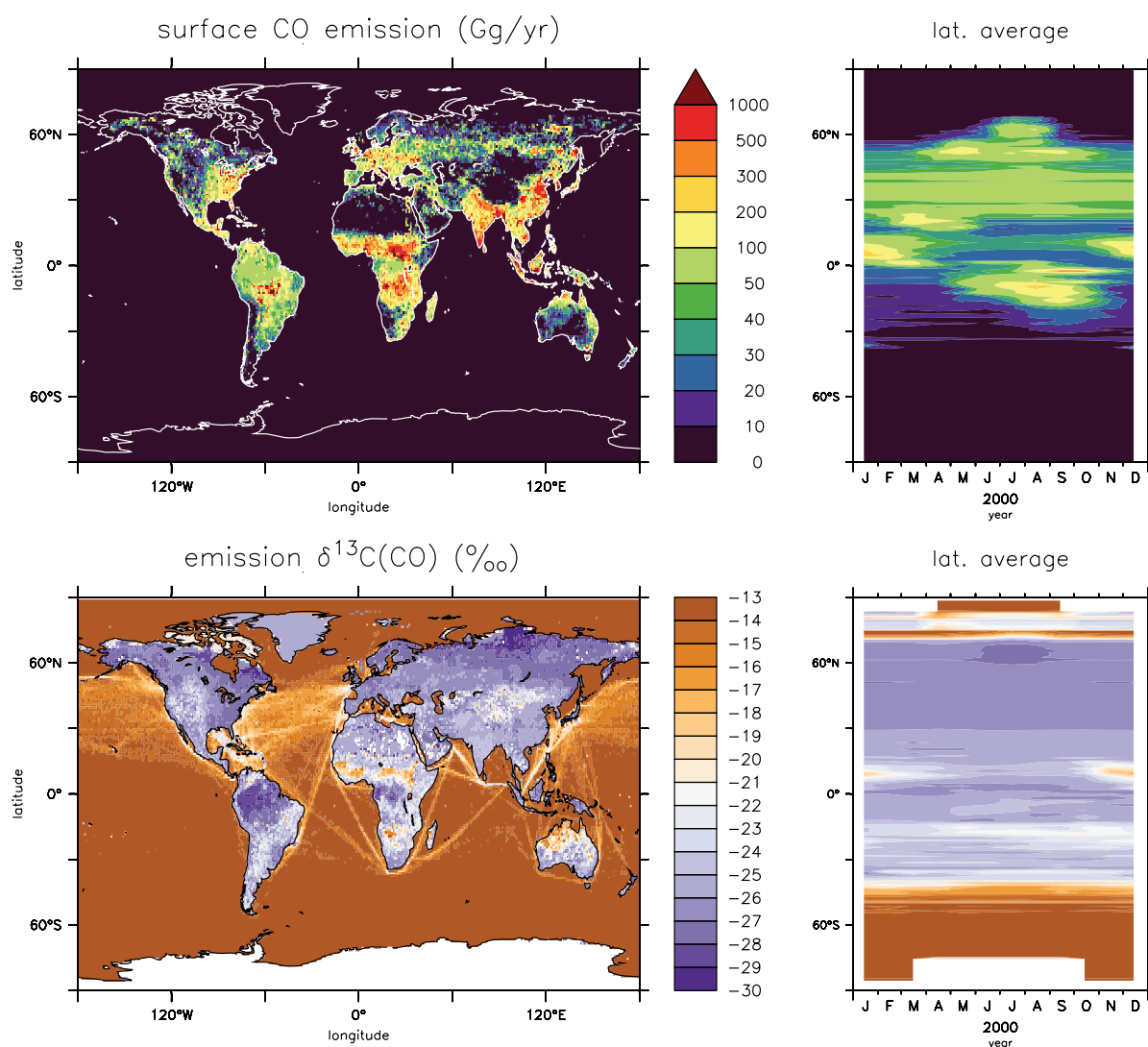


Figure 5.9 Left: Annual CO emission from the surface sources (upper panel) and corresponding carbon isotopic composition (lower panel). Right: Respective time series of zonal averages for the year 2000 emission with identical colour scale.

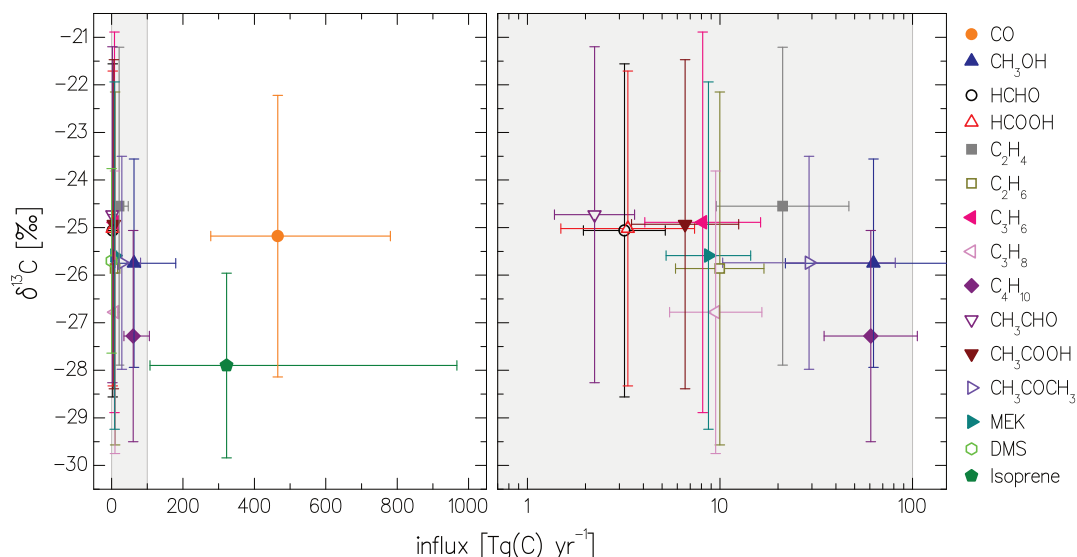


Figure 5.10 Left: Overall annual surface emission isotopic compositions of the carbonaceous compounds. Right: Expanded shaded area in the left panel for the NMHCs/VOCs. The uncertainties are plotted referring to the uncertainty factors from Table 5.9 and discussed in Sect. 5.2.7.

5.2.6 Pseudo-emission data

For the few long-lived tracers in the current setup the pseudo-emission approach is applied by performing the relaxation of the species mixing ratios towards the lower boundary conditions. The relaxation is handled by the TNUDGE submodel (Kerkweg *et al.*^[2006b]) and applied at every model time step with typical relaxation times of 3 h, for all species. The nudging fields are based on the observed mixing ratios from the AGAGE database (Prinn *et al.*^[2000]). Amongst the tracers undergoing nudging, CH₄, CH₃CCl₃, CCl₄, CH₃Cl, and CO₂ are isotopically separated. For CO₂, the time series of the zonally averaged composition from the GLOBALVIEW-CO2C13 database (described above, see Figure 5.7) was superimposed on the regular CO₂ nudging fields from the EVAL setup.

Methane is an important trace gas, being the only source of atmospheric CO with a very distinct carbon isotope signature. Tropospheric CH₄ possesses a markedly ¹³C-depleted composition, particularly due to the large contribution of the sources associated with the biogenic activity that prefers emitting isotopically light methane (Bréas *et al.*^[2001]). The average tropospheric δ¹³C(CH₄) value of −47.3‰ ensues from the composition of the surface sources (estimated equilibrated average of −51.2‰) and atmospheric oxidation KIEs, of which the reaction with OH (+3.9‰) is the dominant in the troposphere (Saueressig *et al.*^[2001], see also Sect. 3.4.1.1, p. 39). Since methane is largely abundant and long-lived, its signature shows a low variability on top of a weak long term trend of around +0.3‰ per decade (Lassey *et al.*^[2000]) due to the input of the industrial fossil carbon, and little spatial and temporal variability. Quay *et al.*^[1999] estimated the hemispheric gradient (averages of −47.2‰ versus −47.4‰ for the SH and NH, respectively) and the monthly variation of δ¹³C(CH₄) to be both on the order of ±0.2‰. That is negligible in view of ~3–5‰ variations in δ¹³C(CO) and its large surface sources. Therefore, the constant value of −47.2‰ is applied to isotopically separate the original nudging fields of CH₄ in the current setup.

Among the chlorinated carbons, the only source of isotopic carbon accounted for in the employed chemical mechanism of MECCA is the photolysis of chloromethane (decomposing to CH₃O₂). The remaining chlorinated carbons contribute only as the in-situ sources of chlorine, thus their composition is omitted here. The main sources of chloromethane in the atmosphere are to date not clearly identified (Keppler *et al.*^[2005]), the estimate of the average global isotopic atmospheric composition is δ¹³C(CH₃Cl) = −32.6‰ (Thompson *et al.*^[2002]). This value is used for the pseudo-emission of chloromethane. The contribution of this source to the carbon pool in the atmosphere is low. The estimates of the major CH₃Cl sink through the reaction with OH give a global average of 3.37 Tg(CH₃Cl)/yr equivalent to 0.8 Tg(C)/yr in the oxidised products (methyl peroxy radical).

5.2.7 Emission uncertainties analysis

It is desirable to estimate the uncertainties associated with the emission signatures for the subsequent analysis of the modelling results, particularly in view of comparison with observational data. However, deriving the isotope composition uncertainties for composites of the various different sources with superposed individual isotopic ratios is an intricate task. First, it should be clearly comprehensible how the uncertainties of the isotopic ratios are related, particularly in view of summing of separate compartments (*e.g.* emission fluxes) of various isotope mixtures, all given with their individual uncertainties for the abundance and isotope composition. Second, the uncertainties associated with the *amounts* being summed are expected to influence the combined uncertainty of the *ratio* of the final aggregate, as a consequence of the law of error propagation in action. To give an example, even if the isotopic signature of each share (*i.e.* particular emission type) is determined (ideally) absolutely precisely, the non-zero uncertainties associated with the amounts of each share (*i.e.*, emission fluxes) impose a non-zero uncertainty on the final isotopic signature of the total (emission). The practical approaches to calculate combined emission and its isotope composition uncertainties are meagrely referred in the literature, thus they are derived below. The following analysis is based on the common practical fundament of uncertainties (see, for instance, Dros^g^[2009], Criss^[1999]).

Foremost, it is expedient to switch from the relative isotope composition reporting to the equivalent ratio, *i.e.* from δ^i to iR . The use of delta variables will introduce impermeable complexities in further calculation, because in contrast to ratios, it is much more difficult to relate delta-values with extensive quantities, *e.g.*, fluxes. The relation of the uncertainty $\langle\delta^i\rangle$ reported for the delta value δ^i to the uncertainty $\langle^iR\rangle$ of the corresponding ratio iR is

$$\langle^iR\rangle = \left(\frac{d\delta^i}{d^iR}\right)\Delta\delta^i = ^iR_{st} \cdot \langle\delta^i\rangle \quad (5.14)$$

Here and further the notation from Eq. (5.9) is applied.⁹² The delta-value uncertainty is linearly proportional to the ratio uncertainty with the reference standard ratio being the proportionality factor. Further, the ratio iR can approximate the relation of the i^{th} minor isotopologue influx $^{\text{min},i}F$ to the total emission flux F as

$$^iR = \frac{^{\text{min},i}F}{^{\text{maj}}F + \frac{q-1}{q} \sum_j ^{\text{min},j}F} \simeq \frac{^{\text{min},i}F}{F} \quad (5.15)$$

assuming that the fraction of the rare isotopologues is negligibly small in the total flux, which is valid for the isotopes of the light elements (*e.g.* C, N, O). This is the only approximation that affects the further analysis. Neglecting the abundant isotopes in the rare isotopologues introduces errors in the estimate of F on the order of $q\%$ for carbonaceous species, assuming an average fraction of ^{13}C carbon of 1% in the total flux. Thus the resulting approximation of the flux

$$^{\text{min},i}F \simeq ^iR \cdot F \quad (5.16)$$

is approximately 1% inaccurate for CO and 5% for isoprene, *i.e.* depending on the number of carbon atoms incorporated in the species molecule. Compared to the typically large errors for the emission fluxes (see below), this inaccuracy is an order of magnitude smaller.

The total emission flux F_e is a composition (sum) of the particular emission source fluxes F_s . Employing the same notation, the total regular and rare isotopologue emission fluxes are

$$\begin{aligned} F_e &= \sum_s F_s, \\ ^{\text{min},i}F_e &= \sum_s ^{\text{min},i}F_s = \sum_s ^iR_s \cdot F_s = ^iR_e \cdot F_e \end{aligned} \quad (5.17)$$

The summation in Eq. (5.17) is performed over the emission sources using index s . Clearly then, the resulting total flux isotopic ratio iR_e is

$$^iR_e = \varphi \sum_s ^iR_s \cdot F_s, \quad \varphi \equiv \left(\sum_s F_s \right)^{-1} \quad (5.18)$$

⁹² Also, alike in Sect. 3.2, for clarity the angle brackets $\langle \rangle$ are introduced in place of conventional “ Δ ” to denote the uncertainty values.

Here φ is introduced for the sake of notation simplification. Noteworthy, in Eq. (5.18) the source fluxes F_s have to be used, but not the total flux F_e , since every F_s contributes to the total uncertainty with the individual uncertainty $\langle F_s \rangle$. It is important for the applied method to differentiate that the uncertainties associated with the emission fluxes magnitudes and the emission ratios are *uncorrelated*, *i.e.*, the various given estimates are independent of each other. Of course, the uncertainty of the guesses (*e.g.*, if the biofuel emission comes dominantly from C_3 or C_4 plant material) cannot be accounted for. The combined uncertainty integrating the error propagation is calculated with the total differential of the function describing the product. Thus, the combined emission uncertainty $\langle F_e \rangle$ of the total emission F_e in Eq. (5.17) expressed through the independent uncertainty components $\langle F_s \rangle$ characterising individual sources F_s is

$$\langle F_e \rangle = \sum_s \left| \frac{\partial F_e}{\partial F_s} \right| \cdot \langle F_s \rangle = \sum_s \langle F_s \rangle \quad (5.19)$$

i.e., a simple addition of the individual uncertainties. Analogously, the combined uncertainty $\langle R_e \rangle$ for the resulting total emission ratio R_e is calculated from both, flux components ($F_s \pm \langle F_s \rangle$) and ratio components ($R_s \pm \langle R_s \rangle$) as follows (index n varies similarly to s , enumerating the sources):

$$\begin{aligned} \langle R_e \rangle &= \sum_s \left(\left| \frac{\partial R_e}{\partial F_s} \right| \cdot \langle F_s \rangle + \left| \frac{\partial R_e}{\partial R_s} \right| \cdot \langle R_s \rangle \right) = \\ &= \sum_s \left(\varphi^2 \cdot \sum_n F_n (R_s - R_n) \cdot \langle F_s \rangle + |\varphi \cdot F_s| \cdot \langle R_s \rangle \right) \end{aligned} \quad (5.20)$$

The first term of the final sum in Eq. (5.20) describes the uncertainty in the ratio arising purely from the uncertainty in emission strengths modified by the difference in the isotopic ratios between each pair of sources. The second term adds the sources' isotope ratio uncertainties weighted by the corresponding emission flux. The formulations (5.19) and (5.20) in their general form can be employed for the uncertainty estimation of any given combination of isotopic compartments, referring only to their abundances and isotopic ratios. Thus it is not necessary to account for the ratios of the other rare isotopes (*cf.* isotopologue fraction calculation in (5.9)). Often one utilises a different (quadrature) form of (5.19) and (5.20) implying that the uncertainties are reported for the values that have the normal distribution about their mean values (*i.e.*, standard deviations). That is not the case for emission estimates, however.

To calculate the overall emission uncertainties in this study, every emission source characterised by a particular signature was accounted for. The emission magnitudes and uncertainties were expressed in equivalent carbon units to avoid improper counting when isotopic ratios are considered. Table 5.10 lists the uncertainties associated with every emission category. For the fluxes so-called uncertainty factors (UF) are quoted, which are commonly practised in emission estimates. For example, the uncertainty factor of 2 implies that the range of uncertainty spans from $F/2$ to $2 \cdot F$, or, in percent, from $-50\% F$ to $+100\% F$. Exceptionally, the UFs reported for the EDGAR inventory (see Olivier *et al.*^[1999], Table 8) suggest the equivalent span range derived from the largest (*i.e.* upper end) value, that is for the above example would be $\pm 50\% F$. Such treatment is used for the analysis here too, that is, selecting the largest (forward) uncertainty ΔF from

$$\frac{\langle F \rangle}{F} = (u_F - 1)$$

where u_F is the uncertainty factor. Diversely, signatures' uncertainties are reported plainly in δ -units, as the isotopic ratios do not depend on the flux magnitudes.

The uncertainties for some of the signatures have to be derived additionally, referring to the assumptions they are based on. For the composites of the different plant material, the uncertainties of C_3 and C_4 signatures contribute to the final uncertainty, similarly using (5.20) and substituting for $\langle F_s \rangle$ the respective fractions. The uncertainties of C_3 and C_4 signatures itself are inferred as two standard deviations of the signature distributions (assumed normal) based on the histogram data of the measured terrestrial compositions (Cerling *et al.*^[1999] and Tipple and Pagani^[2007]). The isotopic composition variability in C_3 plants is much larger than that of C_4 , which is reflected in the resulting uncertainties of $\langle \delta^{13}C(C_3) \rangle = 5.7\text{‰}$ and $\langle \delta^{13}C(C_4) \rangle = 2.5\text{‰}$, respectively. This means that if, for instance, the plant is considered to be of the C_4 kind, its composition is likely to be found within the range of $\delta^{13}C(C_4) = (12 \pm 2.5)\text{‰}$. From the "emission guess" point of view, the uncertainty defines the degree of error introduced by assuming all C_4 plants to have the composition of the C_4 distribution mode of 12‰ . The errors associated with the plant compositions are the largest in this setup and they

propagate to the final uncertainty mainly via the biofuel category. Interestingly, if one assumes that biofuel plant material comes dominantly from C₄ plants (see Sect. 5.2.3), it significantly decreases the overall uncertainty estimate.

Table 5.10 Uncertainties associated with emission sources and isotopic signatures

Category	Source	Emission (signature) uncertainty ^a		
		CO	NMHCs/VOCs	Other ^b
Anthropogenic	Biofuel ^c	2 (4.6‰)	2 (4‰)	–
	Fossil fuel	1.5 (0.3‰) ^d	1.5–2.0 (2‰) ^e	–
	Waste ^c	2 (4‰)	2 (4‰)	–
Biogenic	Land (plants ^f)	3 (1.94‰)	3 (1.94‰)	3 (1.94‰)
	Ocean	2 (3.6‰) ^g	2 (2‰) ^h	–
Biomass burning		1.27 (2‰)	1.17 (2‰)	–
Pseudo-emission ⁱ	CH ₄	–	–	0.04% (0.05‰) ^j
	CO ₂	–	–	0.03% (0.02‰)
	CH ₃ Cl	–	–	0.15% (0.3‰) ^k

Notes:

^a Given is the emission uncertainty factor (see text) and isotopic signature uncertainty (δ_p) (in parentheses).

^b Values assumed for biogenic isoprene, terrestrial DMS (plant emitted), and respective pseudo-emitted species.

^c C₃/C₄ plant composite, based on $\langle \delta^{13}\text{C}(\text{C}_3) \rangle = 5.7\text{‰}$ and $\langle \delta^{13}\text{C}(\text{C}_4) \rangle = 2.5\text{‰}$ (see text).

^d From Stevens *et al.*^[1972].

^e Varies for each species due to the proportion of the fossil fuel (1.5) and industry (2.0) uncertainty factors contribution (Olivier *et al.*^[1999]).

^f Derived from $\langle \delta^{13}\text{C}(\text{CO}_2) \rangle = 0.02\text{‰}$ and leaf discrimination uncertainty of $\langle \Delta \rangle = 2\text{‰}$.

^g Manning *et al.*^[1997].

^h Based on variability in $\delta^{13}\text{C}$ of the marine carbon content from Avery Jr *et al.*^[2006].

ⁱ Quoted are mixing ratio uncertainties (not uncertainty factors).

^j Assigned from the upper limit of the atmospheric variation.

^k Error of the mean from Thompson *et al.*^[2002].

An additional calculation is required for those biogenic emissions originating from plants, whose signatures are derived from the leaf discrimination Δ and air CO₂ composition (see Eq. (5.13)). The uncertainty of the latter is on the order of 0.01‰ according to the GLOBALVIEW-CO2C13 dataset⁹³ (here the double of that value is assumed). The errors in Δ are as large as 2‰, taking one standard deviation of the comparison of the simulated and measured characteristic discriminations for various plant functional types (Scholze *et al.*^[2008]). The resulting weighted uncertainty amounts to $\langle \delta_p \rangle = 1.94\text{‰}$ (at the average global discrimination of $\Delta = 17\text{‰}$ and $\delta^{13}\text{C}(\text{CO}_2) = -8\text{‰}$) and accounts for all plant emissions, whose UFs of the magnitude of 3 are the largest (Guenther *et al.*^[1995]). The biomass burning signatures uncertainties are set to 2‰ referring to the upper limit of errors in atmospheric $\delta^{13}\text{C}$ used to validate the C₃/C₄ burnt vegetation distribution incorporated in the GFED v2.1 inventory (Still *et al.*^[2003]). The UFs for biomass burning emissions are derived from the standard deviations for CO and carbon (proxy for NMHC/VOC emissions) for the year 2000 GFED data (van der Werf *et al.*^[2006]).

The resulting estimated overall uncertainties are listed in Table 5.11. Essentially high uncertainties are associated with isoprene and plant-dominated emissions of methanol (CH₃OH), acetone (CH₃COCH₃), dimethyl sulphide (DMS) and formic acid (HCOOH). The errors are lower (uncertainty factors of 1.5–2.0) for the species dominantly emitted from the fossil anthropogenic sources. On average, final uncertainties associated with the isotopic signatures are larger than 3‰. The biofuel source error has a large contribution of +0.8‰ to +1.2‰ to the final values. The terrestrial emissions are least uncertain resulting from the lower error in leaf carbon discrimination compared to the uncertainties from C₃/C₄ plant composites.

Despite the large biofuel input, the uncertainty of the CO $\delta^{13}\text{C}$ signature is around 3‰ due to the compensating large input from the fossil fuel source with a signature of a higher certainty (0.3‰). The final emission strength is defined within $\pm 70\%$, which is a rather high value. Reckoning the surface sources of $\sim 1100 \text{ Tg/yr}$ in the global turnover of CO of $\sim 2600 \text{ Tg/yr}$ (see the estimates in Sect. 6.1.5, p. 157), the emission uncertainties are expected to propagate in the model result errors with approximately $\pm 30\%$ in CO mixing ratios

⁹³ See http://www.esrl.noaa.gov/gmd/ccgg/globalview/gv_integration.html and references therein.

and $\pm 1.3\text{‰}$ in $\delta^{13}\text{C}(\text{CO})$. To estimate the uncertainties associated with the in-situ produced CO, the emission uncertainties of the respective NMHCs/VOCs sources should be used as the proxies. The uncertainties of CO mixing ratio and isotope composition simulated with EMAC are discussed in Sect. 6.2.2 (p. 167).

Table 5.11 Surface emission sources and their uncertainties in the reference setup

Species	Total emission [Tg(C)/yr]	Aggregate uncertainty factor	Final $\delta^{13}\text{C}$ [‰]
CO	465.6 $\pm$ 315.0	1.7	-25.2 $\pm$ 3.0
CH ₃ OH	62.7 $\pm$ 117.1	2.9	-25.7 $\pm$ 2.2
HCHO	3.2 $\pm$ 2.0	1.6	-25.1 $\pm$ 3.5
HCOOH	3.3 $\pm$ 4.1	2.2	-25.0 $\pm$ 3.3
C ₂ H ₄	21.1 $\pm$ 25.6	2.2	-24.5 $\pm$ 3.3
C ₂ H ₆	10.0 $\pm$ 6.9	1.7	-25.9 $\pm$ 3.7
C ₃ H ₆	8.1 $\pm$ 8.1	2.0	-24.9 $\pm$ 4.0
C ₃ H ₈	9.5 $\pm$ 7.0	1.7	-26.8 $\pm$ 3.0
C ₄ H ₁₀	60.7 $\pm$ 45.3	1.7	-27.3 $\pm$ 2.2
CH ₃ CHO	2.2 $\pm$ 1.4	1.6	-24.7 $\pm$ 3.5
CH ₃ COOH	6.6 $\pm$ 5.9	1.9	-24.9 $\pm$ 3.5
CH ₃ COCH ₃	29.0 $\pm$ 52.3	2.8	-25.7 $\pm$ 2.2
MEK	8.7 $\pm$ 5.7	1.7	-25.6 $\pm$ 3.7
DMS	0.4 $\pm$ 0.7	3.0	-25.7 $\pm$ 1.9
Isoprene	322.4 $\pm$ 644.8	3.0	-27.9 $\pm$ 1.9

5.2.8 Oxygen isotope composition of emissions

As it is discussed above (in Sects. 5.1.4 and 5.2), oxygen isotope compositions of the surface emissions are assumed mass-dependently fractionated (MDF), *i.e.* the $\Delta^{17}\text{O}$ signature of the emitted compounds is $\sim 0\text{‰}$. To be precise, main terrestrial oxygen reservoirs, one way or another contributing with their O to the atmospheric tracers, possess the MDF isotope compositions which exhibit slight variations in $\Delta^{17}\text{O}$ (see Table 5.12). The reason for that is the natural variation in the $^{17}\text{O}/^{18}\text{O}$ enrichment slopes β for all mass-dependent terrestrial processes (Luz and Barkan^[2000], see also Sect. 3.2, p. 30, for definitions). These tiny variations in $\Delta^{17}\text{O}$ are commonly disregarded in the studies involving the chemistry-driven mass-independent fractionations (MIF), duly resorting to the fact that these are at least an order of magnitude larger (see, for instance, Morin *et al.*^[2007]). Similar reasoning is valid for the current study regarding two appreciable MIF KIE in the O₃ formation and CO+OH reactions, with a few important peculiarities that intervene regarding the $\Delta^{17}\text{O}$ in CO, as discussed below.

At first, Table 5.12 highlights two “distinct” $\Delta^{17}\text{O}$ signatures of the main terrestrial (tropospheric) oxygen reservoirs, *viz.* all waters, whose $\Delta^{17}\text{O}$ varies within tens of permeg around 0‰, and atmospheric oxygen of $\Delta^{17}\text{O}(\text{O}_2) = -0.455\text{‰}$ substantially depleted with respect to them. The negative tropospheric $\Delta^{17}\text{O}$ of O₂ (derived from the respective $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ reported *vs.* V-SMOW) virtually ensues from the unified definitions for isotopes accepted in this study (see Sect. 3.2, p. 30), being recalculated with the universal slope coefficient β of 0.5281 observed for meteoric waters, and the logarithmic definition for $\Delta^{17}\text{O}$ (*ibid.*, Eq. (3.5)). Similarly, the exemplified MDF CO of $\delta^{18}\text{O} = 10\text{‰}$ in the definitions used by Röckmann *et al.*^[1998b] is represented in the current study by a non-zero, slightly negative $\Delta^{17}\text{O}$. Secondly, oxygen in most of atmospheric tracers generally derives from water or air oxygen, depending on the tracer formation process. For instance, species produced in processes involving oxidation by O₂ (*e.g.* biomass burning or reaction of CH₄ with OH⁹⁴) typically acquire a slightly negative $\Delta^{17}\text{O}$ from the atmospheric O₂. The alternative sources, namely H₂O reservoirs with 0‰, commonly donate O in the biosphere-related processes, such as plant VOCs emission. As a result, the final $\Delta^{17}\text{O}$ of the emitted tracers is constrained by these signatures and defined by the proportion of the respective sources’ strengths. Subsequently, alike with the carbon isotope emissions, the ratios of the emitted oxygen isotopologues in EMAC were assigned according to the emission categories and their respective signatures listed in Table 5.12. Furthermore, oxygen isotope compositions of tropospheric O₂, H₂O and CO₂ were constrained in

⁹⁴ The carbonaceous product of this reaction, CH₃O₂, is formed from the air O₂ (see Sects. 2.4.3 or 3.3.2.3).

the simulations (in a similar way to the pseudo-emission approach described in Sect. 5.2.6) to assure that the photochemically produced species receive appropriate compositions.

Table 5.12 Isotope signatures of the main oxygen reservoirs and associated emission categories

Reservoir/source	Isotope composition [‰] ^a			MDF slope β ^c	Associated sources
	$\Delta^{17}\text{O}$ ^b	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$		
Seawater	-0.005 ± 0.015 ^{LB10}			0.528	biogenic (plant VOCs, soil NO)
Meteoritic waters	$+0.037 \pm 0.025$ ^{LB10}				
Leaf water	-0.010 ± 0.020 ^{L06}			0.511–0.520	
	$+0.015 \pm 0.020$ ^{U10}				
Tropospheric water vapour	$+0.040 \pm 0.025$ ^{L11}			0.528	photochemistry
	$+0.076 \pm 0.080$ ^{L07 d}				
	0.0 ^e	0.0 ^e	0.0 ^e		
Tropospheric O ₂ ^e	-0.455 ^{BL05}	+32.88	+12.08	–	anthropogenic (bio- and fossil fuel), biomass burning, lightning NO _x
Tropospheric CO ₂ (MDF) ^e	-0.1 ^{A11}	+42.78	+22.27	0.516	
Example MDF CO ^f	-0.068	+10.0	+5.2	0.520	
Tropospheric CO (MIF) ^f	$+4.11$ ^{R98}			0.520	
Surface emitted CO (MDF) ^g	-0.408				
Total MDF CO source ^h	~ -0.330				

References:

LB10 – Luz and Barkan^[2010]; L06 – Landais *et al.*^[2006]; U10 – Uemura *et al.*^[2010]; L11 – Landais *et al.*^[2012]; L07 – Lin^[2007]; BL05 – Barkan and Luz^[2005]; A11 – S. Assonov (pers. comm., 2011); R98 – Röckmann *et al.*^[1998b].

Notes:

- ^{a)} $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are given vs. V-SMOW standard (see Sect. 3.2, p. 30).
- $\Delta^{17}\text{O}$ values are recalculated using the conventions on $\Delta^{17}\text{O}$ used in the current study (see text).
- ^{b)} Observed (estimated) bulk average and variability (when given).
- ^{c)} Slope of the MDF-line inferred (or assumed) for the given reservoir/species.
- ^{d)} These compositions observed in the Arctic are identified to carry a non-negligible portion of MIF from the stratospheric H₂O.
- ^{e)} Values used to constrain the tropospheric composition in EMAC.
- ^{f)} Recalculated from the reported linear $\Delta^{17}\text{O}$ formulation (*ibid.*, Eq. (3.6)) with $\beta = 0.52$.
- ^{g)} Calculated from the data in Table 5.9 (p. 131) assuming biogenic sources with $\Delta^{17}\text{O} = 0\text{‰}$.
- ^{h)} Calculated from the data in Table 6.3 (p. 158) assuming O₂-derived CH₄ and H₂O-derived NMHC oxidation sources.

Regarding carbon monoxide emissions, the resulting overall $\Delta^{17}\text{O}$ of the surface CO amounts to -0.408‰ that reflects a ~1:9 ratio of the biogenic to other sources' contributions. Projected onto the overall CO turnover estimated within this study (see Sect. 6.1.5, p. 157), the average $\Delta^{17}\text{O}$ of the CO injected into the atmosphere amounts to approximately -0.33‰ , thus attenuating the MIF signal in atmospheric $\Delta^{17}\text{O}(\text{CO})$. Importantly, the effect introduced into $\Delta^{17}\text{O}(\text{CO})$ by the slightly “depleted” in $\Delta^{17}\text{O}$ air O₂ is comparable to that of the O₃ MIF input of up to $+1\text{‰}$ (upper limit of the estimates given in Sects. 3.5, 4.1.3 and 6.2.8.1) and undoubtedly important when the observational data are scrutinised. That is, when the observed $\Delta^{17}\text{O}(\text{CO})$ is around 0‰ , it denotes a small but non-negligible MIF signal, whereas $\Delta^{17}\text{O}$ of -0.33‰ or lower points to the likely MDF composition. To note, this discrepancy virtually does not depend on the formulation and slope β used to define the $\Delta^{17}\text{O}$ characteristic.

6

Global modelling of the CO isotope composition with EMAC – Part II

Within the scope of this final chapter, the results of the numerical simulations of the carbon and oxygen isotope compositions of the atmospheric tracers with the AC-GCM EMAC are presented and discussed. The concluding Sect. 6.2 focusses on the EMAC-synthesised global isotope composition of tracers, particularly CO, with a comparison of the latter with the available observational data. The sensitivity of the modelled CO isotopic composition to the key factors, namely the chosen emission setup and tracer removal effects, as well as to selection of the CO+OH KIE parameterisation, is investigated. Prior to that, the overview of the previous modelling studies on atmospheric CO isotopes is given in Sect. 6.1.

6.1 Overview of the previous and current modelling studies

The inclusion of stable isotope information in modelling studies of atmospheric carbon monoxide lingered awhile due to a large ambiguity about the isotope ratios of the major sources of CO and the isotope effects in its removal by OH. At an early stage, Stevens *et al.*^[1972] provided an extensive analysis of the ^{13}C and ^{18}O content of atmospheric CO based on a large set of observational data from urban and rural areas. Their analysis revealed the large seasonal and spatial variability in CO isotope ratios, indicating the mixture of the multiple sources with distinct compositions. In particular, heavy ^{13}CO from fossil fuel combustion was identified; however, the contributions from other potential sources (despite the fact that CH_4 was foreseen as the source of light ^{13}CO), especially the terrestrial ones, could not be singled out. The information on KIEs escorting in-situ production and scavenging of CO (the latter was expected as the major contributor to the seasonal variations of the isotope ratios) was missing as well. This, for example, in part led to erroneous results of the early instructive model on the global ^{13}C and ^{18}O composition of CO used in a subsequent study by Weinstock and Chang^[1974]. Applying a steady-state assumption for $\text{CH}_4 \rightarrow \text{CO} \rightarrow \text{CO}_2$ conversion, and compelled to compare their results only with scarce theoretical calculations, they derived largely unrealistic positive KIEs for heavy C and O isotopologues of CH_4 and CO in reactions with OH.⁹⁵ The laboratory studies later revealed smaller but significant effects in these reactions (described in Sect. 3.4.4), allowing a better constraining of the CH_4 source signature. Concerning the CO+OH reaction, its complex kinetics feature unconventional KIEs associated with various isotopologues, with a pressure-dependent and furthermore mass-independent behaviour. Whilst the positive KIE in CO+OH removal was confirmed for the ^{13}CO isotopologue, the effect turned out to be negative for C^{18}O , thus OH-driven removal of ^{12}CO and C^{18}O is favoured in the troposphere.

Because of the relatively short atmospheric lifetime of CO, a substantially detailed estimate of the seasonal and spatial variability of its sources was required. The identification of the major sources of atmospheric carbon monoxide (*e.g.*, Logan *et al.*^[1981], Graedel *et al.*^[1993], Badr and Probert^[1994] and references therein) was subsequently supplemented by improved estimates of their carbon and oxygen isotope ratios. The new laboratory and observational data and analysis (Cantrell *et al.*^[1990], Brenninkmeijer^[1993], Brenninkmeijer *et al.*^[1995], Lassey *et al.*^[1993], Lowe *et al.*^[1994], Conny and Currie^[1996]) and re-analysis of the previous estimates (Stevens and Wagner^[1989], hereafter referred to as “SW89”) had eventually enabled Manning *et al.*^[1997] (“M97”) to conduct the

⁹⁵ The crucial faux pas of this study was, however, to assume methane to be the only source of the atmospheric CO, which is an apparent misjudgement of the previously presented ^{13}CO data and analysis of Stevens *et al.*^[1972]. However, whilst the carbon isotope composition of atmospheric methane is today the most certain term amongst the CO sources, the oxygen isotope ratios of the CH_4 -derived products remain debatable (see Sect. 3.4.2, p. 42).

first consistent modelling study on global CO including ^{13}C isotope ratios. They used a global two-dimensional (zonally averaged) chemistry transport model (CTM) incorporating tracers for CO and ^{13}CO and their surface sources (including those approximating the oxidation of NMHCs) with a prescribed latitudinal distribution and soil sink. The simplified chemistry scheme included only CH_4 -initiated production and OH removal terms for CO, calculated using the climatologically averaged OH fields. These model results represent therefore the climatological averages of the longitudinally homogeneous compositions susceptible to latitudinal transport. The results were compared against the extensive multi-year observational data on CO isotopes collected at Baring Head, New Zealand, 41°S (Brenninkmeijer *et al.*^[1992]) representing the background CO composition in the Extratropical Southern Hemisphere (ETSH). Importantly, *a priori* source strengths (including the methane source) were improved by fitting both, simulated CO concentrations and isotope ratios, into the observations by means of an inversion technique. Despite the reduced model detail and a limited series of observations available from a single station only, M97 provided the largest possible insight into the global isotope CO turnover.⁹⁶ The ^{13}C mass-balance of the latter yielded a principally different partitioning of the CO sources, in particular, a smaller CH_4 input compared to the previous, non-isotope studies. M97 found, however, a significant ambiguity of the result and its crucial dependence on model parameters whose values had to be *assumed* owing to the limitations of the modelling approach, largely due to using a considerably reduced chemistry scheme. In effect, the discord in subsequent estimates of the methane-derived CO between the ^{13}C -inclusive and non-isotope studies exists to date, despite the availability of extended observational data and improved models. Moreover, studies employing inversions of both, emission fluxes and their isotopic signatures, may not provide an unequivocal answer whether the source partitioning is correct, suggesting *a posteriori* derived compositions outside of the sensible uncertainties of the respective *a priori* estimates. The aim of the present study is to resolve the remaining ambiguities about the isotopic content of atmospheric CO by thoroughly revisiting the key aspects determining it within a more detailed modelling approach. Therefore, the essential factors determining the ^{13}C content of atmospheric CO, the corresponding model parameters and results from the available preceding studies are first summarised below. The reader is referred to Table 6.3 (page 158) for the aggregate comparison of the model studies, including the two estimates from the current work pertaining to the reference (base case) and revised model setups considered.⁹⁷

6.1.1 Methane source of CO and related parameters

Principally, the isotopic composition of atmospheric CO is determined by the cumulative composition of the main sources characterised by different isotope ratios, modified by the combination of the isotope fractionation effects escorting the removal of CO and its precursors, in case they serve as intermediates in the CO photochemical production chains. Importantly, if the photochemical conversion in the chain is complete, *e.g.* that all carbon atoms passed via the intermediates eventually end up in CO, the kinetic isotope effects in reactions of any intermediate do not affect the isotopic composition of the final CO produced. On the contrary, any irreversible removal of the intermediates from the chain (by either scavenging from the atmosphere or reacting to other compounds), modifies the effective strength of the sources and, if escorted by KIEs, additionally alters the composition of their contribution. The conceptual representation of the aforesaid for CO in the atmosphere is schematically depicted in Figure 6.1, along with the ^{13}C isotope compositions of the main sources and magnitudes of the fractionation effects.

⁹⁶ This term, in contrast to “budget”, implies here the aggregate estimate of the sources, transformations and sinks, both direct (*i.e.* to/from the surface) and of photochemical origin, that determine the atmospheric burden and isotopic composition of CO.

⁹⁷ For the details on the reference setup and sensitivity experiments of the current study, see Sect. 6.2 (p. 164).

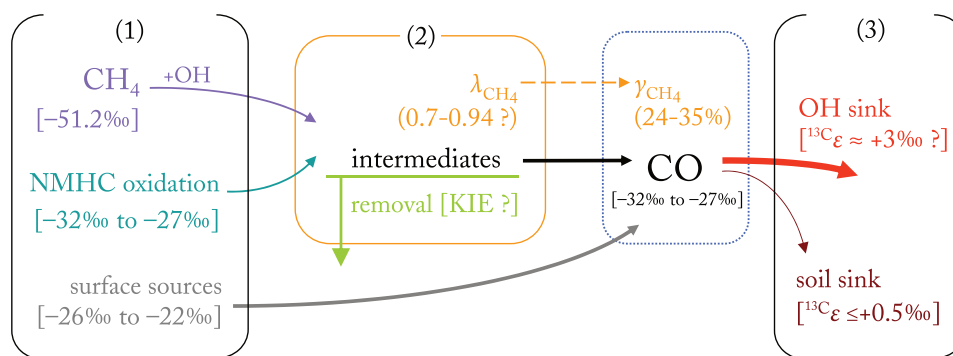
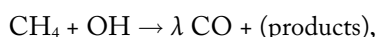


Figure 6.1 Primary sources, photochemical processing and sinks determining atmospheric CO. Values in square brackets denote the $\delta^{13}\text{C}$ signatures of the respective sources and the effective enrichments $^{13}\text{C}\epsilon$ escorting sinks, respectively (ranges are from the available estimates listed in Table 6.3). Question marks denote unknown or uncertain terms scrutinised in this chapter. Numbers in parentheses denote the key factors determining the CO isotope composition: (1) makeup of the primary sources, (2) photochemical processing and removal of the intermediates and (3) CO sinks and concomitant kinetic isotope effects.

6.1.1.1 CH₄ oxidation by OH

Notably, amongst the sources of CO, only methane is characterised by a distinctly depleted composition of -51‰ , which is much below the average -27‰ of the remaining sources. This difference makes $\delta^{13}\text{C}(\text{CO})$ especially sensitive to the input of methane-derived carbon (*cf.* the large uncertainty of the CH₄ source from the various estimates in Figure 6.3 on p. 161, right panel). By fitting this source into the observations from the ETSH, M97 estimated its contribution to the overall CO budget, γ_{CH_4} , to be around 24%, a significantly lower value than the 32–35% from other studies. A similarly low estimate (28%) was derived in a subsequent study by Bergamaschi *et al.*^[2000] (“B00”), to date the most extensive modelling study on CO carbon and oxygen isotopes employing a similar inversion technique. The higher (compared to M97) γ_{CH_4} values in B00 result from the smaller influence of the CH₄ share counterbalancing the heavier composition of the remaining sources (-24.3‰ *vs.* -22.6‰) and from an updated $\delta^{13}\text{C}$ signature of methane input of -52.1‰ .⁹⁸ In contrast to M97, B00 used a three-dimensional transport model and a significantly larger observational dataset, covering both NH and SH locations. Conversely, these studies share the same simplified chemistry scheme, *i.e.* parameterising the photochemical production of CO using a “net reaction”, that can be written as



where the yield λ approximates the effect of the chemistry regime and the removal of intermediates from the CH₄ oxidation chain, and is duly used as one of the fitting parameters. Any other photochemical production of CO (*e.g.* from NMHC oxidation) in M97/B00 is treated as a constant surface source.

We remark that due to the fairly well studied kinetics in the reaction of CH₄ with OH, the methane oxidation source is expected to be associated with the least uncertainty compared to the other sources of CO (see Sect. 5.2.7, p. 134). On the other hand, the estimates of λ are hitherto inconsistent being derived or assumed in a number of calculations. For instance, Logan *et al.*^[1981] confer the value of 0.5–0.78, similarly to Lelieveld and Crutzen^[1991] who estimate reductions of formaldehyde and other intermediate species of 0.30–0.85 in summer–winter due to the wet scavenging.⁹⁹ Tie *et al.*^[1992] have simulated the spatio-temporal variation of λ using a fairly detailed CH₄ → CO chemistry scheme accounting for CH₃OOH and HCHO removal by precipitation. They derived a global average value of 0.82, with a significantly lower latitudinal and seasonal variation of 0.7–0.9. Smaller yields in summer were attributed to the higher-HO₂ and lower-NO_x conditions favouring elevated CH₃OOH concentrations and hence a more efficient scavenging of the latter. More recent studies report higher λ values. Novelli *et al.*^[1999] estimated 0.95 for the yield of H₂ and CO from CH₄ assuming, on the contrary, small wet removal ($\leq 1\%$) and dry deposition ($\sim 5\%$) terms for HCHO. More recently, Folberth *et al.*^[2006] reported the value of 0.9, reproduced in their model study on the CO global budget employing a consistent

⁹⁸ This value has been derived from the composition of the methane residing in the atmosphere (-47.2‰) and the magnitude of the KIEs in the photochemical removal of CH₄ effectively depleting the carbon reacting further into the chain of by 3.9‰ (see Sects. 3.4.1.1 and 5.2.6). M97 used an earlier CH₄+OH KIE estimate of 5.4‰ (Cantrell *et al.*^[1990]) yielding a composition of -52.6‰ , respectively.

⁹⁹ Since formaldehyde (HCHO) is the main precursor of CO in the atmosphere, and therefore the “bottleneck” for the CH₄-derived carbon (see Sect. 3.3.2.3), the mentioned value is virtually identical to λ .

chemical scheme but a different parameterisation of the dry/wet removal of the intermediates. Alternatively, Duncan *et al.*^[2007] in a study on the global CO budget assume $\lambda = 1$, supposing this value being insensitive to NO_x levels determining the domination of either the HCHO or CH_3OOH channel of the CO production from CH_4 . They argue that the photochemical lifetime of both intermediates is by far shorter compared to that in the wet/dry removal.¹⁰⁰ A similar tropospheric average λ value close to unity was derived with the MOZART4 CTM (Emmons *et al.*^[2010]) which includes comprehensive chemistry and wet/dry removal schemes (L. Emmons and K. Park, pers. comm., 2010).

Recapitulating the above, different assumptions guide one to significantly different estimates of λ ; recent model parameterisations tend to favour almost complete conversion of the carbon from CH_4 to CO. However, as the early isotope-enabled studies contend, the ^{13}C isotope imbalance appears to be a systematic indication of smaller λ values. Indeed, taking both, *a priori* and *a posteriori* estimates of the source signatures and leaving the CH_4 source conversion into CO complete ($\lambda = 1$) renders the average atmospheric $\delta^{13}\text{C}(\text{CO})$ significantly lower than observed. Relative to higher *a posteriori* signatures, the underestimate amounts to approximately 2‰ and 1‰ in M97 and B00, which they compensate by reducing λ from unity to 0.7 and 0.86, respectively. Relative to *a priori* estimates, the equivalent increase of the whole non-methane source signature (still taking $\lambda = 1$) is +4.5‰ for both studies, exceeding the overall uncertainty of ± 2.4 ‰ associated with this source. Since these studies assume nearly identical *a priori* signatures, they both need an overall composition of the non- CH_4 sources of around -21.3‰ to adequately reproduce the observed ratios in case the yield of CO from CH_4 equals unity. Ultimately, however, the missing +4.5‰ in these studies can be obtained for any assumed λ . This permits an adjustment of the non-methane source compositions within the given uncertainties, *i.e.* the compensation of the missing ^{13}C enrichment is distributed between the reduction of the CH_4 source and an enrichment of the other sources in ^{13}C .

Notwithstanding that, M97 note that the seasonality in $\delta^{13}\text{C}$ and CO mixing ratio itself plays an important role in constraining λ , because of the interplay of the sources throughout the year. Upon relaxing the constraints on the fitted $\delta^{13}\text{C}$ values, they find that the seasonal cycle of $[\text{CO}]$ ¹⁰¹ is better reproduced when λ increases from general inferred value of 0.7 to 0.8. This implies that the $[\text{CO}]$ seasonality improves when assimilating a greater share of the CH_4 source seasonality; however, the isotope ratios then deteriorate greatly, highlighting an apparent contradiction between the regular and isotope-inclusive inversions of $[\text{CO}]$. Alternatively, fixing λ at 0.8 and relaxing the non- CH_4 sources did not lead to the well-reproduced seasonal cycle of $[\text{CO}]$ in M97. For instance, to compensate the light methane contribution and to obtain an adequate solution for $\delta^{13}\text{C}$, the inversion grants larger input from heavier sources leading to overestimated $[\text{CO}]$. Finally, increasing the initial uncertainties assigned to the *a priori* sources effects in a progressive decrease of λ , and a compensation of the reduced CH_4 source by the larger surface component.

Unfortunately, B00 did not consider a similar analysis, but from their report of the deviation of the model results from the observational data (by means of a chi-square test) one may note the following relationship: Either larger (~ 0.9) or smaller (~ 0.8) yields assumed in various sensitivity simulations are associated with the χ^2 values elevated for $[\text{CO}]$ and lowered for $\delta^{13}\text{C}(\text{CO})$ seasonal cycles, meaning poorer $[\text{CO}]$ and better $\delta^{13}\text{C}(\text{CO})$ temporal fits, respectively. The optimum value for both characteristics is achieved somewhere in the middle, at $\lambda \sim 0.86$ (scenario S2), where χ^2 is least for $[\text{CO}]$ and comparable to that of $\delta^{13}\text{C}(\text{CO})$. Although being different to the M97 result, this is also an indication of the mutual constraint imposed by the CO mixing ratio and $\delta^{13}\text{C}$ signature on the methane oxidation source. The strong bilateral restraint on λ (*i.e.*, worsening of the result upon deviating in any direction from the optimum found) imposed by fitted $[\text{CO}]$ in B00 is likely the result of employing a sufficiently larger observational dataset covering both hemispheres, whereas M97 had only the ETSH data available. Above all, recalling the results of the studies concluding lower CO yields from CH_4 and their dependence on the chemical regimes (*e.g.*, Tie *et al.*^[1992], see above), one should expect λ values to vary with location and season. Hence, using a global constant value may be a too rough approximation and lead to a

¹⁰⁰The argumentation of this study appears somewhat vague, without presenting any reference or a rough calculation for asserts like, *e.g.*, “the (formaldehyde) photochemical lifetime is hours, shorter than the typical frequency of deep convective events. The lifetime with respect to deposition is long ($\sim$ months)”. The counter-arguments for these statements one may find in, for example, Tost *et al.*^[2007] and Guigard *et al.*^[2006] (and references therein). The latter estimate the comparable half-life times of HCHO of 8-19 hours (chemical removal in polluted-clean air), few hours (photolysis) and approximately 19 and 50 hours (dry and wet deposition), respectively. Besides, it is unclear how Duncan *et al.*^[2007] relate the *typical frequency* of the deep-convective events to the *intensity* of the removal in them.

¹⁰¹Hereinafter the squared brackets $[\]$ denote the abundance (concentration or mixing ratio) of the respective species.

significant insensitivity of the inversion results to it, in particular for the statistics on the [CO] and $\delta^{13}\text{C}(\text{CO})$ seasonal cycles, rather than for the averages. Howbeit, the sensitivity analysis of B00 indicates that the λ value decreases nearly linearly if a more negative CH₄ signature is taken¹⁰², and *vice versa*. The result this way unequivocally depends on the choice of the composition arriving from this source, which is essentially the composition of the atmospheric CH₄ modified by all other potential fractionations acting in the chain, before CO is eventually formed.

In addition, some other model simplifications may have lead to further misinterpretations about the methane source in the results of M97 and B00, as both studies use constant distributions of [CH₄] and monthly climatologies of [OH] in their calculations. M97 noted that their simulated [CO] component from the methane source is virtually constant of about 21 ppb¹⁰³ throughout the year in the ETS. Thus the variations of [CO] and $\delta^{13}\text{C}(\text{CO})$ are determined only by the surface source dynamics, but the CH₄ source variation may be underestimated. Analogously, in B00 this source amounts to ~20 ppb of [CO] and shows virtually no seasonal and latitudinal variation, if one reckons the results for the different stations (*cf.* B00, Plate 2). Taking into account that the chemistry regime (primarily OH concentration and temperature determining the CH₄+OH reaction rate) is subject to change with season and latitude, one expects an altering source rather than a constant methane-derived [CO] component. The variation should be more pronounced at low latitudes, whilst at high latitudes the less intensive chemistry and superimposed effects of air transport and mixing are expected to dampen it. All abovementioned is relevant for the CO+OH sink as well, because it is directly affected by the [OH] variation (see further in Sect. 6.1.4.2, p. 152).

The subsequent modelling studies on CO isotopes, *viz.* Emmons *et al.*^[2004] (“E04”) and Park^[2010] (“P10”), do not examine the yield of CO from the methane source in detail. Both approaches account for the detailed CH₄ → CO chemistry incorporating intermediates, and implicitly include the wet/dry removal terms, which is an explicit equivalent of using a prescribed λ value. Their similar parameterisations render the whole-tropospheric value $\lambda \sim 1$, and a consequent significantly larger share of the methane source γ_{CH_4} of 32%–35%. As a result, the overall composition of CO sources in these studies is depleted by a similar 4‰–4.5‰ with respect to that expected from the observed atmospheric composition (after subtracting the CO removal effects by OH and soil uptake). Although a set of ¹²C/¹³C isotopologues for all respective intermediates was introduced in E04¹⁰⁴, other than chemical KIEs (*e.g.* isotope fractionation in removal processes) were not implemented. These were also neglected in the study by P10, who used an inversion technique employing a set of additional tracers representing only the major sources of CO and its isotopologues. The chemical sources and sinks for the latter were accounted for in the reduced chemistry scheme (alike in M97 and B00, but additionally including the NMHC oxidation source) utilising the pre-calculated reaction rates derived from the model simulation with the full chemistry mechanism. To reconcile the simulated mixing and isotope ratios with the observations, both studies apply the adjustment of the sources strengths and signatures; the potentially large (*i.e.* λ is significantly below unity) reduction of the methane source was not considered. The results of the inversion applied in P10 grant a slightly (by a factor of 0.97 to 1.07) adjusted *a posteriori* value of the CH₄ source for different regions, years and inversion methods. This adjustment to the λ value can be regarded only as the refinement of the CH₄ source due to inaccurately reproduced temperature or OH distributions, which primarily affects the CH₄+OH reaction rate. In effect, substantial changes to the yield value in model setups similar to those of E04 and P10 are only feasible if one reconsiders the removal processes parameterisation embodied as such.

Glancing over the results of the present study¹⁰⁵, we note that the overall tropospheric yield of CO from CH₄ reproduced by EMAC amounts to 0.94, being virtually a constant value showing no seasonal variation. The latter, however, is not true, if the value of λ is specifically calculated for distinct tropospheric domains, where the influence of the removal processes is different. For example, the average value of λ in the lowest model layer (*i.e.*, closest to the surface) in EMAC is significantly lower: 0.72. This result appears to be in line with the estimates of M97 or B00 based on the observational data representing the boundary layer air. Although

¹⁰²For example, they have studied the potential effect of the CH₄+Cl reaction escorted with an unusually large KIE of ~70‰ (depleting the reacting carbon and enriching the residual CH₄ in ¹³C). By adjusting the signature of the $\delta^{13}\text{C}(\text{CO})$ from the CH₄ source within the –60‰ to –50‰ range, they inferred λ values from 0.71 to 0.88, respectively (see also below, Sect. 6.1.1.2).

¹⁰³The abbreviation “ppb” (parts-per-billion) is used as an equivalent to a mixing ratio in [nmol/mol].

¹⁰⁴To the knowledge of the author, this is the first and solitary study with a 3D CTM implementing a comprehensive chemistry mechanism accounting for the complete set of isotopologue species and a detailed set of kinetic isotope effects for stable carbon isotopes prior to the current study.

¹⁰⁵The detailed results on the λ values simulated in EMAC are presented below in Sects. 6.2.2 and 6.2.4 (pp. 167, 181).

lower yields are expected to decrease the share of the methane source locally, the estimated tropospheric average γ_{CH_4} value is large ($\sim 32\%$ vs. $\sim 24\%$ from M97), sensibly reflecting the high tropospheric average λ value. A grave result of the reference setup simulation considered in this study (referred to as “REF” hereafter) is that the EMAC-simulated surface $\delta^{13}\text{C}(\text{CO})$ values exhibit systematic biases up to -3% compared to the observations. Despite its low near-surface value, λ rapidly increases with height to nearly unity, thus decreasing the boundary layer and tropospheric CH_4 source effectively less than ~ 0.7 times befitting the ^{13}C mass-balance reckoned at the surface. To resolve the latter in REF, consequently, one needs to adjust the composition of the overall non-methane source of CO from initial -26% by a perennially missing $+4.5\%$. The required composition of -21.5% of the non- CH_4 sources in REF is close to that of M97 and B00 (-21.3% , putting their results in the perspective of the yield being unity, see above) suggesting their *a priori* estimates are similar to the emission setup considered in EMAC. Noteworthy, this value also outreaches the estimate for the overall surface sources composition of $(-25.2 \pm 3)\%$ conferred in the current study (see Sect. 5.2.7).

6.1.1.2 Reactions with Cl and O(¹D)

Complementary to the $\text{CH}_4 + \text{OH}$ source, there are two photochemical pathways leading to production of CO from methane through its reaction with atomic chlorine and O(¹D) radicals. Although both pathways are considered to be of importance only in the stratosphere (the overwhelming tropospheric abundance of OH coerces nearly all of the tropospheric CH_4 sink to proceed via hydroxyl radical), there are studies hypothesising that the chlorine-mediated removal may account for a non-negligible fraction of the CH_4 sink in the troposphere. Thus, Lowe *et al.*^[1999] and Allan *et al.*^[2005] scrutinise the observed variations of $[\text{CH}_4]$ in the ETSH and emphasise that the concomitant variations in $\delta^{13}\text{C}(\text{CH}_4)$, if caused predominantly by the isotope fractionation in its photochemical removal, outreach those expected from the sole OH-initiated sink. The authors conjecture that reaction with active chlorine in the Marine Boundary Layer (MBL) may contribute to the large CH_4 “apparent” sink fractionation derived from the observational data in the ETSH at $(+11 \pm 4)\%$. This value is significantly larger than the $+3.9\%$ fractionation anticipated in the $\text{CH}_4 + \text{OH}$ reaction, in contrast to the reaction with Cl escorted by the large KIE of $65\% - 75\%$.¹⁰⁶ Therefore, a relatively small chlorine methane sink (CMS) proceeding with significant fractionation is capable of adding the missing variation in $\delta^{13}\text{C}(\text{CH}_4)$. In the accompanying model studies employing different global CTMs, Allan *et al.*^[2001] and Allan *et al.*^[2007] (“A07”) simulate adequate ETSH $\delta^{13}\text{C}(\text{CH}_4)$ variations by introducing a synthetic, seasonally varying source of active chlorine in the MBL. They derive a befitting CMS term at $25 \pm 12 \text{ Tg}(\text{CH}_4) \text{ yr}^{-1}$, or $(4.4 \pm 2.1)\%$ of the overall photochemical CH_4 sink in the troposphere. However, there is no concord on the origin of the large variations in tropospheric/MBL $\delta^{13}\text{C}(\text{CH}_4)$ in the literature. An alternative hypothesis attributing these to an extensive stratosphere-troposphere exchange (STE) of air (stratospheric methane displays lower mixing ratios and a distinct enrichment in ^{13}C) finds no firm corroboration amongst related studies. This and other aspects concerning the MBL Cl content and its effect on $\delta^{13}\text{C}(\text{CH}_4)$ are concisely reviewed by Platt *et al.*^[2004]. In a study coeval with A07 by Tyler *et al.*^[2007] on the tropospheric record of ^{13}C and D isotopes in CH_4 , similar $\delta^{13}\text{C}(\text{CH}_4)$ annual variations are presented at two (continental and maritime) US sites. Supplementing the above surmises, they conclude that the observations likely indicate the pronounced seasonality in the ^{13}C -enriched methane source(s) strength, as follows from the poor and strong interdependence between the mixing ratio and $\delta^{13}\text{C}$ and δD signals, respectively. A larger (anti)correlation of $\delta\text{D}(\text{CH}_4)$ with $[\text{CH}_4]$ has two compatible explanations: δD is more sensitive to the sink processes, hence the actual sink fractionation in $^{13}\text{CH}_4$ is indeed smaller and close to that of the OH KIE, or both signals are much more sensitive to the seasonal changes in the sources. Using such mutual $^{13}\text{C}/\text{D}$ isotope constraint would be of benefit when analysing the ETSH observational data (*e.g.*, Quay *et al.*^[1999]) or in view of the results of A07, but has not been attained yet. At last, Tyler *et al.*^[2007] do not confirm any significant inconsistency between their data and a possible existence of a small CMS as well.

The significance of the CMS appears unfavourable, however, regarding CO, whose isotope composition is largely sensitive to the methane carbon input: The $\text{CH}_4 + \text{Cl}$ source should produce an extremely light CO with $\delta^{13}\text{C}$ below -110% . Accommodating the MBL CMS estimate by A07 at $\sim 4.4\%$ of the overall CH_4 tropospheric sink lowers the overall methane-derived carbon source $\delta^{13}\text{C}$ signature by 3.9% (SH tropospheric average) to 9.1% (SH MBL average). This translates into a noticeable concomitant drop in the average

¹⁰⁶ Both fractionation magnitudes are based on the laboratory measurements of carbon KIE in respective reactions (see Sect. 3.4.1.1, p. 39). The $\text{CH}_4 + \text{Cl}$ fractionation value spans the tropospheric temperature and pressure ranges (see Figure 3.7, p. 54).

SH $\delta^{13}\text{C}(\text{CO})$ of about 1.9‰ (tropospheric) to 5.9‰ (MBL), respectively¹⁰⁷, foremost leading to an increased discrepancy in the CO isotope mass-balance already lacking $^{13}\text{C}\text{O}$ (see previous and next sections). Similarly, B00 note that an “apparent” KIE (if it is exclusively driven by the photochemical sink of CH_4) would imply a significantly lower $\delta^{13}\text{C}$ signature of produced CO from methane, which adequately fits the observed compositions only at (unlikely) low CO yields.¹⁰² Nonetheless, the contribution of the here considered CH_4+Cl source to the overall tropospheric $\delta^{13}\text{C}(\text{CO})$ would amount to approximately -1‰, *i.e.* nominally within the uncertainty associated with the surface sources’ $\delta^{13}\text{C}$ (of both CO and its precursors) and with the estimates of $\delta^{13}\text{C}(\text{CO})$ tropospheric average at $\pm(1.2\text{--}1.9)\text{‰}$ (see Sects. 5.2.7, 6.1.5 and Table 6.3).

A more cogent restraint on the CMS may be placed examining relative changes in isotopic CO in the ETS in response to the large interannual variations in the observed “apparent” CH_4 removal KIE. Based on these, A07 deduce the extrema of the CMS fraction at ~6.5% and ~2.3% of the total tropospheric CH_4 sink in transition from 1994–1996 to 1998–2000 conditions, respectively. One can conformably estimate the effect of a $\sim 1/3$ reduction in the CMS on the SH $\delta^{13}\text{C}(\text{CO})$: The corollary relative change in the austral summer-fall period (when the effect of the CMS presence is expected to be largest) must be at least of +1.8‰ (tropospheric average) to +5.2‰ (in the MBL). However, simultaneous isotope CO observations in the ETS show no evidence of such a marked increase in $\delta^{13}\text{C}(\text{CO})$ in 1998–2000: The respective data from Baring Head (BHD, 41.4°S) and Scott Base (SCB, 77.8°S) are presented in Figure 4.3 (Sect. 4.1.1, p. 73). Seasonalities at SCB positively display a CMS-expected relationship in $\delta^{13}\text{C}(\text{CO})$, but the difference in monthly averages barely exceeds +1‰ in November–December. The latter is clearly attributable to varying degree of photochemical processing of CO itself (*i.e.*, effective ^{13}C -enrichment in OH oxidation) associated with large differences in the average [CO]. These reach some 15 ppb, or 20–25% of the total CO seasonal inventory at SCB. Accordingly, a possible increase in CO mixing ratio induced by the CMS (estimated to be 3%–8% for tropospheric-MBL averages, respectively) may remain unnoticed behind the typically larger variability in [CO]. A rather different situation emerges at BHD, where the fall $\delta^{13}\text{C}(\text{CO})$ in 1998–2000 actually shows an inverse (*i.e.*, a CMS-unexpected) relationship with respect to the 1994–1996 levels, reaching the maximum difference of -1.4‰ in March. In the remaining seasons, $\delta^{13}\text{C}(\text{CO})$ averages are much comparable, despite the large [CO] variability in 1998–2000. Noteworthy, the above estimated potential effect of the CMS on $\delta^{13}\text{C}(\text{CO})$ is reckoned for the entire SH, implying even stronger sensitivities in the extratropical domain. Another fact that corroborates the comparison is that the regarded $\delta^{13}\text{C}(\text{CO})$ data pertains to the same ETS locations as the $\delta^{13}\text{C}(\text{CH}_4)$ data of A07. The observed discrepancy in CO and CH_4 $\delta^{13}\text{C}$ signals analogously does not support the assumption of an enhanced STE, as the latter must lead to the CMS-similar consequences for the compositions. Ultimately, the only plausible deduction remains that both, $\delta^{13}\text{C}(\text{CO})$ and $\delta^{13}\text{C}(\text{CH}_4)$, are sensitive to the seasonally (and, perhaps, interannually) varying sources, whilst the methane-derived CO has a $\delta^{13}\text{C}$ signature close to that of atmospheric CH_4 (within the CH_4+OH KIE magnitude).

Whereas the tropospheric CO does not present an evidence of the CMS and $\text{CH}_4+\text{O}(\text{}^1\text{D})$ source, stratospheric isotope compositions likely do so. A unique example is provided by the comprehensive observations of CO and CH_4 isotopologues in the lowermost stratosphere between New Zealand and Antarctic conducted by Brenninkmeijer *et al.*^[1996], which are further compared to the current EMAC results in Sect. 6.2.7.3 (p. 206). Here we only remark that the EMAC-estimated CMS in the lowermost stratosphere (reckoned above 6%) is able to contribute with considerable 5–10‰ to the overall CH_4 sink fractionation, and therefore induce appreciable $\delta^{13}\text{C}(\text{CO})$ depletions, as confirmed by the observational data.

Summing up, within the scope of the comprehensive modelling approaches the yield of CO from CH_4 cannot have as much impact on the share of the CH_4 source in tropospheric CO as presupposed by M97 and B00. Hence, resorting to this parameter in search for the imbalance of the CO isotopic composition due to the highly ^{13}C -depleted CH_4 input should be considered cautiously, and may even be inappropriate. The results of the later and present studies suggest that the λ value is close to unity and methane contributes to at least 60% of the photochemically produced and to one-third of the overall tropospheric CO.¹⁰⁸ With better constraints on

¹⁰⁷This estimate is the projection of the results of the reference simulation considered in this study (REF), assuming the same fraction of the MBL Cl[•] sink of methane in EMAC as in A07 (taken to obtain similar $\delta^{13}\text{C}$ of the CH_4 source). The SH MBL CMS is reckoned at $2/3$ of the global MBL sink term, reflecting the hemispheric ratio of the open ocean surfaces (used as the Cl[•] source mask in A07); the average CH_4+Cl KIE magnitude is taken at 280K.

¹⁰⁸It is interesting to estimate the effect of a diminished CH_4 source share on atmospheric $\delta^{13}\text{C}(\text{CO})$ throughout the 20th century, ensuing from the increased anthropogenic and biomass-burning emissions of CO. Assuming the latter in 1900 at 18% and 70% of their 2000 lev-
(continued on next page)

this source, larger CH₄ input dictates a generally more ¹³C-depleted composition of the CO entering the atmospheric reservoir. The CO isotopologues observations in the ETSH, in turn, put a lower estimate on the methane source δ¹³C signature, close to that expected from the dominance of the CH₄+OH oxidation in the troposphere. They also belie the hypothesis of a CH₄ sink via active Cl leading to the production of highly ¹³C-depleted CO.

Apart from reducing the CH₄ source, reconciling the ¹³C mass-balance of CO calls for addressing the other factors that determine the isotopic composition of atmospheric carbon monoxide (see Figure 6.1, p. 141). In essence, the key parameters determining the CO composition are: (1) the primary sources, (2) the isotope fractionation in the irreversible removal of the photochemical precursors of CO modifying the ¹³C composition of the latter, and (3) the isotope effects in the CO sink processes affecting the composition of the leftover atmospheric CO, primarily the reaction with OH. Further, all three factors are discussed in view of their potential in contributing to the missing atmospheric ¹³CO. The estimates of sources, sinks and related isotope compositions and effects on the resulting CO and δ¹³C(CO) abundances from the aforementioned studies are summarised in Table 6.3 (p. 158) and illustrated in the accompanying Figure 6.3 (p. 161).

6.1.2 ¹³C/¹²C composition of the CO sources

Notably, the bottom-up estimates (including the *a priori* setups for the inverse modelling studies) of the primary sources combined are more depleted in ¹³C and do not vary significantly between different studies, *i.e.* within -35‰ to -33‰ in δ¹³C. The general top-down estimate of -30.3‰ given by SW89 is based on the average of the atmospheric δ¹³C(CO) observed by that time, corrected for the OH removal KIE of ~+3‰. Similarly, the *a posteriori* estimates from the inverse modelling studies favour the overall composition of -31.1‰ to -30.5‰ resulting from the adjusted ¹³C-enriched surface sources and reduced methane source share. The difference between the bottom-up and top-down estimates of the primary sources is 3–4‰, which, if one assumes the CO yield from CH₄ oxidation being nearly unity, causes an even larger disparity in the estimates of the average δ¹³C of the non-CH₄ CO sources. Thus, from M97 and B00 these should be -21.3‰, whereas for the other studies the non-methane CO source signature is much lower, *e.g.* -26.1‰ in E04 and -25.5‰ (this study, REF). From the CO budget considerations of Brenninkmeijer *et al.*^[1999b] (“B99”) and P10, one derives similarly depleted source compositions, when superimposing the respective δ¹³C values from the literature on their reported emission strengths.

Despite the fact that the adjustment of the surface sources towards a more enriched composition may reconcile the overall tropospheric ¹³CO mass-balance¹⁰⁹, the resulting surface δ¹³C(CO) values become only slightly improved. This was also derived from the sensitivity studies of M97 (see previous section) as well as within the present study (REF simulation). From the comparison of the EMAC model results with the station data¹¹⁰ one finds that the discrepancy in δ¹³C(CO) values becomes larger in remote regions and at high latitudes. This manifests that the missing ¹³CO is to a large degree a result of the unaccounted ¹³C enrichment inherent to the atmospheric processing of CO, rather than just the consequence of an underestimated composition of the surface sources. For instance, the total of the global CO emissions is enclosed in the 30°S–60°N latitude band (*cf.* Figures Figure 5.3 and 5.9 from Sects. 5.2.2 and 0, respectively, pp. 122, 132), thus the CO arriving at higher latitudes has undergone chemical ageing during the transport from the source regions. By increasing the ¹³C content of the surface sources one achieves adequately reproduced high-latitude averages of δ¹³C(CO), but then the low-latitude values concomitantly become overestimated, *i.e.* the missing enrichment superimposed on the source composition is proportional to the age of the atmospheric CO and clearly larger than that predicted by the model. Alternatively, a potential culprit may be a particularly large spatial δ¹³C variation of the emitted

els, respectively (Lamarque *et al.*^[2010]), [CH₄] and δ¹³C(CH₄) of around 900 ppb and -49‰ in 1900 (Lassey *et al.*^[2007]), the average tropospheric δ¹³C(CO) at the beginning of the last century must have been lower by (0.8–4.2)‰. This estimate embraces two further assumptions on the CH₄ source of CO, *viz.*: (1) it is reckoned using the present day [OH] levels (yielding ~35% of the overall CO source in 1900), and (2) it scales proportionally with the higher OH abundance expected in 1900 (~47%, respectively). The latter assumption employs the sensitivity of [OH] to the changes in [CH₄] and [CO] inferred in Sect. 6.2.5.3 of this study (p. 190). In any case, a decrease in tropospheric δ¹³C(CO) is expected in the last hundred years, thus opposing the studies regarding the isotope-inclusive measurements of CO from firm air (Assonov *et al.*^[2007], Wang *et al.*^[2010]).

¹⁰⁹ Implied is the mass-balance of the bottom-up estimates compared to the results of M97 and B00 corrected for the larger methane source ($\lambda \approx 1$). However, their overall tropospheric δ¹³C(CO) is a model result, which may be subject to an underestimation either, as only surface observations were available for the model evaluation.

¹¹⁰ Given below in Sect. 6.2.7, see also Figure 6.19 (p. 201).

CO, for example, with significantly more ^{13}C enriched compositions situated at higher latitudes. This, however, does not explain the deviations between the model and the SH. Furthermore, it is not supported by available emission estimates and station data.

A similar conclusion is inferable from the results of E04, who explored to match their simulated ^{13}CO to the observational data. Assuming the biofuel CO source being the most uncertain component, they seasonally adjusted its strength to fit simulated $[\text{CO}]$ to the observed mixing ratios at four NH ground stations. From the isotope mass-balance of the new source apportioning, the respective seasonal $\delta^{13}\text{C}$ signature of the biofuel CO source befitting the observed composition was derived, indicating that generally more ^{13}C -enriched CO is expected in the model. For each station, the missing enrichments varied seasonally within $\sim 10\%$ and were temporally correlated; however, the averages of the required source composition increases were 3–4 times larger for the remote locations. For example, for Barbados (13°N) an average adjustment of only $+2.4\%$ was deduced (with respect to the initially assumed composition of -25% of the biofuel CO source in E04). This station is expected to be significantly influenced by the freshly emitted CO, hence the fitted biofuel source strength resulted in a good agreement with the observations. On the contrary, for the more remote stations Izaña (28°N), Mauna Loa (19°N) and Spitsbergen (79°N), the remarkably larger missing enrichments of $+8.4\%$ to $+10.4\%$ were diagnosed. These are inconsistent with the finding for Barbados, although the $\delta^{13}\text{C}(\text{CO})$ at Spitsbergen may reflect a sufficiently different source distribution. Unfortunately, E04 did not extend their analysis to the SH, where their model significantly underestimated the $\delta^{13}\text{C}(\text{CO})$ as well, but the mixing ratios were reproduced much closer to the observations. Compared to the NH, the background SH mixing ratios of CO are much lower and the photochemical sources account for more than 60% of the total CO^{111} , thus if one resorts to adjusting the surface source compositions to reconcile the ^{13}CO , the respective enrichment must be significantly large. For instance, the missing $\sim +3\%$ at Scott Base (78°S) is equivalent to the enrichment of the SH surface sources by $\sim +8\%$, similar to those found for Spitsbergen. Nevertheless, analogously adjusting the biofuel source strength and signature will not be effective in the SH, as the relative contribution of this source is extenuated by the dominating biomass burning emissions. Currently the amount of SH observational data (especially those influenced by the fresh CO emissions) is insufficient to conclude that the SH model discrepancies in E04 are similar to those for the NH.

One notes that a particular similarity of the results of E04 with those of the REF setup of the current model study exists: The larger enrichments of all remote data can be agreeably explained by the stronger influence of the in-situ fractionation that concurs with the age of the atmospheric CO. Similarly to the conclusions by M97 and REF, in E04 the necessary adjustment of the emission strengths (*i.e.*, CO mixing ratios better reproduced) adequately suits either aged or fresh CO isotope ratios only, if distinctly different surface source compositions are chosen, with the aged CO requiring more ^{13}C -enriched sources. Therefore, any underestimation of primary sources can only partly explain the discrepancies between the simulated and observed isotopic CO, corroborating the need to revisit the remaining factors.

6.1.3 ^{13}C fractionation in intermediates

Disregarding so far the isotope effects in CO sink processes, the differences between the bottom-up estimates of $\delta^{13}\text{C}(\text{CO})$ and their top-down evaluation should be attributed solely to the possibly missing enrichment in the photochemically produced CO accumulated from the isotope fractionation escorting the intermediates removal processes. We remark that none of the previous studies have investigated this aspect intently. B00 note that an appreciable enrichment of the photochemically produced CO can be introduced through an intermediate that is subject to an even relatively small removal term, if the latter is escorted with a significant KIE. For example, a 10% scavenging of an intermediate with the preferential removal of ^{12}C isotopologues at a nominal KIE value of 10‰ introduces an effective enrichment of 1‰ in the remaining reservoir, hence the subsequent products and ultimately generated CO. The same reasoning is valid for NMHC/VOC $\rightarrow$ CO oxidation pathways that include intermediates affected by dry deposition and wet removal. How large must the overall nominal enrichment due to the removal KIEs in the photochemical CO production chain, $^{13}\text{C}\eta_{\text{rem}}$, be, taking the more realistic CH_4 source (*i.e.* $\lambda \sim 1$, see the previous section) and reckoning the results of M97 and B00? For the 6% removal term as a surmise ($\lambda = 0.94$ from REF simulation with EMAC), and *a priori* sources yielding

¹¹¹This is an estimate from the REF simulation of the current study for the troposphere. The share of the photochemical sources in the total CO budget amounts to $\sim 52\%$ and $\sim 64\%$ for the NH and SH, respectively.

the fraction of photochemically produced CO of ~ 0.5 , $^{13}\text{C}\eta_{\text{rem}}$ must be slightly larger than +100‰ to compensate the missing 3.1‰ in both studies. Considering the *a posteriori* estimates and yet $\lambda = 0.94$, the value of $^{13}\text{C}\eta_{\text{rem}}$ decreases to +44‰ for B00; however, it surpasses +120‰ for M97. That is because the required removal KIE increases to befit the lower fraction of the photochemical sources of 0.4 in the former, whereas for the latter it remains virtually unaltered (0.49). Besides, the inversion in B00 does not favour such a strong reduction of the CH_4 source, further enriching the remaining sources in ^{13}C . The expected values of $^{13}\text{C}\eta_{\text{rem}}$ are even larger regarding the more ^{13}C -depleted sources from the later (bottom-up) approaches that consider more ^{13}C -depleted surface sources. Overall, such large kinetic effects in (non-photochemical) removal processes are implausible for the relatively heavy isotopes of carbon: The estimates given in Sect. 5.1.5 confer the nominal removal KIEs within +10‰, with weaker effects for the heavier molecules, *e.g.* isoprene. Likewise, the chemical removal of certain intermediates outside of the CO production chain is also unlikely to be escorted with such strong kinetic effects (see Sect. 3.4.1).

The estimates of the ^{13}C enrichments in the carbonaceous intermediates escorting their removal were obtained in the sensitivity simulations of the present study. While these are discussed in detail further in Sect. 6.2.4, here for brevity we conclude the resulting enrichments for CO. In EMAC, the KIEs of dry deposition deliver a mere additional +0.15‰ to the overall tropospheric $\delta^{13}\text{C}(\text{CO})$, this is the aggregate of the KIEs of the removal of all considered intermediates that lead to CO. The magnitude of the effect is small but reasonable, corresponding to the average enrichment of $^{13}\text{C}\eta_{\text{rem}} \sim +2.3\text{‰}$ for the 6% removal term. The latter itself was probed for the sensitivity to the changes in the dry deposition process parameterisation in EMAC (see *ibid.*, p. 181). Thus, the increase of the tracer deposition velocities and solubility coefficients to and above their estimated upper limits has only a small effect on the overall removal intensity. For example, a doubling of the dry deposition velocities for HCHO and other methane oxidation chain intermediates decreases λ_{CH_4} by 0.02 at most, which is negligible in view of the changes to the effective isotope enrichments. Importantly, in the model surface layer, the reproduced enrichments are larger owing to the locality of the deposition process and vary for different precursors. For example, the preferential removal of ^{12}C isotopologues adds on average +1‰ and +3‰ to $\delta^{13}\text{C}(\text{HCHO})$ and $\delta^{13}\text{C}(\text{CH}_3\text{OH})$, respectively, reflecting the species properties and type of the surface they get deposited onto. Generally, the largest enrichments are associated with the dry deposition of the tracers over the continents in summer, driven by the uptake by vegetation. Finally, depending on the fraction of the photochemically produced CO in its total budget, the surface layer $\delta^{13}\text{C}(\text{CO})$ may acquire additionally up to +0.4‰ in some regions. Nevertheless, the enrichment of CO due to in the KIEs in the removal of its precursors (both CH_4 - and NMHCs-derived) is an order of magnitude smaller term than the overall missing 3‰–4‰ in the simulated $\delta^{13}\text{C}(\text{CO})$.

6.1.4 KIEs in the removal of atmospheric CO

Inasmuch as the composition of the sources and fractionation in removal of the intermediates of CO cannot entirely account for the missing enrichment, one is impelled to attribute the remaining discrepancy to the last factor, namely the isotopic fractionation associated with the removal of CO itself from the atmosphere. Because of its relatively short lifetime, the effective isotope enrichment escorting the CO sink is largely governed by the interplay between the current emission/production and removal terms, with the former attenuating the nominal removal KIEs. Besides, because the sink operates on the whole atmospheric CO reservoir, the isotope composition of the latter is much more sensitive to the uncertainties in the sink KIEs than to those associated with the composition of a particular (*i.e.* constituting only some fraction of the total budget) surface source. To illustrate this, a hypothetical underestimation of 1‰ of the surface sources' $\delta^{13}\text{C}$ value will propagate as the missing 0.48‰–0.36‰ into the NH–SH $\delta^{13}\text{C}(\text{CO})$, decreasing with the larger fraction of the photochemical sources in the SH CO budget¹¹¹. The underestimation of the same magnitude in the CO+OH removal KIEs will, in turn, propagate with the missing 0.64‰–0.91‰, increasing with the smaller CO burden in the SH. This demonstrates that the larger NH surface sources and burden of CO cause the weaker sensitivity of its isotope composition to the removal effects. Regrettably, the analysis of the important isotope effects in the removal of CO received little attention in the scope of the previous studies. In particular, the analysis of the spatial and temporal variation in the sink KIEs and their effect on the final $\delta^{13}\text{C}(\text{CO})$ was never presented. This, however, is crucially important when model results and observations are contemplated in the atmospheric domains where these effects may either have a large efficacy (soil uptake over the continents) or variation (OH sink in the re-

mote areas), *e.g.* at the ground stations. Below these sink effects resulting from the different global model approaches for isotopic CO are estimated.

6.1.4.1 Dry deposition of CO

The dry deposition constitutes a minor but significant sink of CO that may range up to one tenth of its global budget according to various estimates (presented in Table 6.1). The dry deposition is essentially the net loss of the atmospheric tracer due to its interaction with the surface vegetation and soils; in addition, some gases like CH₄, H₂ and CO are involved in the concurrent soil microbiological processes (see Conrad^[1996] and references therein). The net balance between the abiotic production from the soil organic matter and production/consumption by various soil microorganisms commonly causes an uptake of CO by soils (Moxley and Smith^[1998], Yonemura *et al.*^[2000b], Sanderson^[2002]), although the dynamics of these processes is complex. For instance, CO uptake was also shown to correlate with the soil temperature and moisture content, suggesting the large influence of the diffusive properties of soil itself (Sanhueza *et al.*^[1998], Yonemura *et al.*^[1999], Yonemura *et al.*^[2000a]). On the other hand, the close correlation of the large uptake variation for CO and H₂ was also attributed to their microbiological oxidation in the thin uppermost soil layer. In that case, the interrelation of a multitude of important factors such as soil/vegetation and land-use types, optimum moisture level, ecosystem and climate conditions, *etc.*, is decisive for the activity of the biogenic oxidisers and yet not well understood (Yonemura *et al.*^[2000a]). Owing to these peculiarities, different parameterisations of the dry deposition processes in global models implement more or less simplified approaches, resorting to various simpler proxies assumed to be decisive for CO uptake in soils.

Among the model studies regarded here, M97 and B00 use the simplest schemes implementing constant CO deposition velocities¹¹² over land, excluding desert regions and cases of monthly average soil temperatures below 0°C, representing a first-order approximation of the uptake as a microbiologically controlled process. The most sophisticated schemes of E04 and P10 calculate the uptake online (*i.e.* from the simulated variables at each time step, hence resolving finer temporal scales) and include the empirical relation of the deposition velocity with the soil moisture content and vegetation/land cover type (Emmons *et al.*^[2010], Yonemura *et al.*^[2000a]). Some studies assume the CO soil uptake proportional to the net primary productivity (NPP), *i.e.* the variation of the leaf biomass load depending on the particular ecosystem or geographical location (Müller and Brasseur^[1995]). Overall, the latter approaches yield a factor of two smaller removal terms (~140 Tg(CO)/yr) than the simplified ones (~300 Tg(CO)/yr). Another simplified parameterisation of CO dry deposition analogous to that of M97 and B00 was probed in the sensitivity study by Pozzer *et al.*^[2007] based on the EVAL model setup that is being followed closely in the present study. Although their estimate grants a considerably smaller removal term of 72 Tg(CO)/yr, this result is consistent in view of the stricter conditions triggering CO uptake (higher soil temperatures and relative humidity thresholds).

A few other studies implemented deposition schemes which introduce the dependence of the deposition velocities on the land cover type and vegetation/soil moisture content indirectly, *e.g.* theoretically considering the similarity in physical and chemical properties between the tracers (such as solubility and oxidation capacity, see details in Sects. 0 and 5.1.5). However, usually the deposition velocities, or equivalent “resistances”, for the tracers are proportionally scaled with respect to the other well-studied species such as O₃ and SO₂ (Wesely and Hicks^[2000]), which apparently are not related to the microbiological aspects that are crucial for the CO soil uptake. Therefore, such “indirect” schemes may confer inconsistent results, for which an interpretation is difficult. For instance, the dry deposition scheme implemented in MOZART2 (Horowitz *et al.*^[2003], different than the one used in the isotope-enabled version of this CTM by E04) produces a negligibly small CO deposition term of 2 Tg(CO)/yr, two orders of magnitude less than the lower limits reported by the majority of the studies. In addition to the differences introduced by different approaches to soil uptake representation, the inter-study uncertainty of the deposition term is largely determined by the uncertainty of the overall budget of CO itself, forasmuch as the removal term is proportional to the atmospheric load of the tracer. To estimate the effect of fractionation escorting the dry deposition of CO on its atmospheric isotope composition, it is expedient to use its proportionality to the nominal soil sink KIE, $^{13}\text{C}\eta_{\text{soil}}$, and the ratio of the CO residing in the atmosphere to the amount being removed undergoing certain KIE. In Table 6.1, the estimates of the effective en-

¹¹²Deposition velocity (usually expressed in [cm/s]) is essentially the proportionality factor between the atmospheric burden of the tracer and the dry deposition term, *i.e.* the first order rate constant of the removal process (see details in Sects. 0 and 5.1.5).

richment in the average tropospheric and continental boundary layer (CBL) air ^{13}C content due to soil deposition are presented, projected from the results of the abovementioned studies. Although the analysis is rather crude¹¹³, it provides the magnitudes that are directly comparable with the uncertainties and discrepancies in the simulated ^{13}C .

Table 6.1 CO dry deposition and respective ^{13}C fractionation estimates from selected model studies

Study	<i>isotope-inclusive</i>				<i>non-isotope</i>			
	M97	B00	E04	P10	MS05	F06	H03	P07
Total CO source	2600 (722)	2860 (794)	2890 (803)	2872 (798)	2760 (767)	3019 (839)	2696 (749)	2547 (708)
Dry deposition sink	347	288	143	135	186	135	2	74
deposition velocity	0.04 ^{a,c}	0.03 ^{b,c}	var. ^d	var. ^d	var. ^{e,c}	var. ^e	var. ^f	0.04 ^g
Deposited fraction	13.4% (48.0%)	10.1% (36.3%)	5.0% (17.9%)	4.7% (16.9%)	6.7% (24.3%)	4.5% (16.1%)	0.1% (0.3%)	2.9% (10.5%)
Effective ^{13}C enrichment, $^{13}\text{C}\epsilon_{\text{soil}}$ ^h	+0.71‰ (+1.95‰)	+0.55‰ (+1.60‰)	+0.28‰ (+0.91‰)	+0.27‰ (+0.87‰)	+0.38‰ (+1.17‰)	+0.26‰ (+0.83‰)	+0.004‰ (+0.02‰)	+0.17‰ (+0.57‰)

Notes:

Abbreviations refer to: M97 – Manning *et al.*^[1997] (case 2); B00 – Bergamaschi *et al.*^[2000] (scenario S2); E04 – Emmons *et al.*^[2004]; P10 – Park^[2010]; MS05 – Müller and Stavrakou^[2005] (case B); F06 – Folberth *et al.*^[2006]; H03 – Horowitz *et al.*^[2003]; P07 – Pozzer *et al.*^[2007] (simulation S1a).

Emission and sink terms are given in $[\text{Tg}(\text{CO})/\text{yr}]$, deposition velocity in $[\text{cm s}^{-1}]$. Plain numbers refer to the tropospheric integrals, the values in parentheses denote the upper estimates for the continental boundary layer air.

- ^{a)} Constant; deposition occurs over ice-free land. The sink term for M97 is derived from the result of the similar approach implemented in B00 by scaling with respect to the total emissions and different deposition velocity. Because M97 distinguish only ice-free land (but not non-freezing soils) as the deposition criteria, this value may be underestimated.
- ^{b)} Constant; deposition occurs over non-freezing soils (temperature above 0°C), excluding deserts (annual precipitation rate < 100 mm/yr).
- ^{c)} Monthly/annual climatologies or calculated fields of temperature, moisture, *etc.* are used.
- ^{d)} Variable; the parameterisation implements the empirical relation between the deposition velocity and soil moisture content.
- ^{e)} Variable; CO deposition velocity is assumed proportional to the net primary productivity (see text). For comparison, this approach applied by Hauglustaine and Ehrlert^[2002] yields the average CO deposition velocities over the continental areas of 0.016–0.024 for January–July, respectively (derived from the diagnosed deposition velocities for H_2 soil uptake taken linearly proportional to those of CO).
- ^{f)} Variable; employs the scaling of the CO deposition velocity with respect to those of well-known tracers (see text).
- ^{g)} Constant; deposition occurs over the regions where the soil temperatures are above 5°C and the relative humidity exceeds 40%.
- ^{h)} Reckoning the nominal soil sink ^{13}C KIE equivalent to the enrichment of $^{13}\text{C}\epsilon_{\text{soil}} = +6\text{‰}$.

For the CO deposition process, all isotope-enabled studies account for the concomitant ^{13}C fractionation of $^{13}\text{C}\epsilon_{\text{soil}} = +6\text{‰}$ from SW89, assuming the KIE value being identical for all types of soil, as no details on the soil type, experimental procedure, *etc.* were given for these unpublished results. More recently, a by one-third higher estimate of +8‰ was reported by Tsunogai *et al.*^[2002] for the temperate forested soils in Japan. Similar to these estimates, Komatsu *et al.*^[2003] reported the fractionation magnitudes spanning within +6‰ to +8‰ for the forest soils and +3‰ to +9‰ for the arable land in Japan, respectively. They argue that the microbial activity largely influences the KIE in addition to the molecular diffusion term, but the relationship between the KIE magnitude and any general proxy like temperature or soil moisture was not reported. Due to the scarcity of estimates, one can merely conclude a significant uncertainty of $\pm 3\text{‰}$ associated with the soil uptake ^{13}C KIE. Superimposed on the uncertainty of the dry deposition term itself, when the latter may be as large as 10% of the total CO budget, the uncertainty in dry deposition KIE may propagate with as much as $\pm 0.8\text{‰}$ into the final simulated $\delta^{13}\text{C}(\text{CO})$ of the BL air.

Looking into the results of the model studies, the implemented dry deposition KIE of +6‰ should produce an effective enrichment, $^{13}\text{C}\epsilon_{\text{soil}}$, of +0.7‰ (M97), +0.5‰ (B00) and +0.3‰ (E04, P10) in the overall tropospheric $\delta^{13}\text{C}(\text{CO})$, reckoning their reported soil sink terms of ~13%, ~10% and ~5%, respectively. In the CBL air, the effect should be at least a factor of three larger than the tropospheric average due to the deposition

¹¹³ One can roughly assess the effective enrichment in the surface layer air, assuming that the deposition operates on the whole CO burden in the boundary layer (BL), which makes up ~28% of the overall tropospheric budget. The latter estimate is derived from the mass fractions of the tropospheric (below 100 hPa, ~85%) and BL (below 750 hPa, ~24%) air of the whole atmosphere (Jacob^[1999], p. 15). This analysis also relies on the assumption that the major part of the CO emissions is located over the continents, where deposition occurs. Applying the approach introduced in Sect. 5.1.5 and substituting the respective boundary layer fraction of the overall budget for the long-term fraction f_a and the total soil sink term for the continuously removed fraction f_i in Eq. (5.8), one obtains the resulting enrichments that scale with respect to the emission and deposition rates.

at the surface, and hence is significant for CO residing or being transported over the continents. All studies project that the CO component extensively exposed to the soil uptake may acquire significant ^{13}C enrichments of +1‰ or larger. Thus, for M97 and B00 the dry removal terms are equal or greater than 10% of the overall CO budget, resulting in $^{13}\text{C}_{\text{soil}}$ values larger than +1.6‰ when projected onto the CBL CO abundance. Notably, the overall influence of the dry deposition fractionation on ^{13}CO is comparable to the effect of reducing the CH_4 source in these studies (see Sect. 6.1.1). Such a potentially large contribution was not examined (or presented) by the authors; moreover, if the CO deposition term is overestimated, this should affect the inversion results by consequently underestimating the surface sources' composition.

In the studies employing more sophisticated CO soil uptake parameterisations (E04, P10) the reproduced removal terms are similar, ranging from 4.7% to 5% and resulting in CBL CO enrichments of up to +0.9‰. A somewhat larger deposition term given by MS05 (6.7%, with an equivalent of one-quarter of the CBL abundance deposited) is perhaps a consequence of the different parameterisation for CO uptake in this study, relating the latter to the leaf biomass proxy instead of the soil moisture, and using the monthly means of parameter values. A similar approach by F06 uses the on-line calculation of NPP and produces a removal term of 4.5% (comparable to E04 and P10). Finally, according to the results of Pozzer *et al.*^[2007] (hereafter referred to as "P07"), the dry deposition processes account for a CO sink of ~3% of its overall budget. Because of the virtual identity of the model setups of P07 and the present study, the above estimate can be adopted here. Thus, if the dry deposition of CO would be included in EMAC¹¹⁴, it would add +0.2‰ and +0.6‰ to the average tropospheric and BL air $\delta^{13}\text{C}(\text{CO})$, respectively. Together with the ^{13}C fractionation in the removal processes for the intermediates of CO (see Sect. 6.1.3), these two processes are capable of adding ~0.4‰ to the average tropospheric $\delta^{13}\text{C}(\text{CO})$ and potentially up to 1‰ in near surface air.

Unfortunately, from the analysis of the reported global terms it is not possible to conclude the effect of the CO deposition KIE simulated in the model studies at the observational stations, because one needs a full-fledged CTM simulation to account for the aggregate effect of transport, varying deposition term and surface sources. Nevertheless, for the simulated ETSH surface component of CO in M97, the effective enrichments should be weaker than the estimated averages above, as the tracers are less susceptible to the dry deposition owing to the smaller land/ocean area fraction in the SH. Conversely, $^{13}\text{C}_{\text{soil}}$ values should be larger for the NH surface CO station data regarded in B00, for example. With the model setup analogous to that of E04, Emmons *et al.*^[2006] estimate that less than 3% of the whole CO dry deposition occurs at latitudes south of 30°S, with the tropical and extra-tropical NH (above 30°N) domains sharing the remaining dominant part as ~6:4, respectively. A nearly equal partitioning of the CO deposition term was found in the model study by Huijnen *et al.*^[2010] predicting an ETSH fraction of ~3% of the overall CO deposited. This implies that the remote SH CO experiences virtually no isotope enrichment due to the deposition effects, and reflects the composition of the low-latitude (tropical) sources equilibrated with the soil sink, further modified only by the OH oxidation KIE during transport. Having recourse to this feature, although based on the scarce observational data by that time, SW89 concluded that the global CO soil sink is much smaller than 10%, relating the opposite KIEs of C^{18}O in the reaction with OH (−10‰) and soil uptake (+11‰). The latter, exclusively operating in the NH but not in the SH high latitudes, should add a significant ^{18}O enrichment to NH remote CO, however, the hemispheric difference between the observed background $\delta^{18}\text{O}(\text{CO})$ was likely attributed to the difference in the strengths and compositions of the surface sources. Similar to this example, the characteristic discrepancies between the simulated and observed $\delta^{13}\text{C}(\text{CO})$ in remote locations (described in Sect. 6.1.2) can attribute the underestimated CO dry deposition to the NH cases, but not to the ETSH disagreements. Applying the same analysis as in Table 6.1 to the estimates of P07 projected on the partitioning of Emmons *et al.*^[2006], one derives that on average the dry deposition of CO in EMAC may account for additional +0.09‰, +0.62‰ and +0.7‰ in the BL $\delta^{13}\text{C}(\text{CO})$ in the ETSH, tropics and Extratropical Northern Hemisphere (ETNH), respectively. With respect to more likely consistent results of Emmons *et al.*^[2006], these numbers will scale to +0.15‰, +0.95‰ and +1.06‰, correspondingly.

Recapitulating, reckoning the results of the studies employing sophisticated and seemingly more consistent parameterisations, a CO deposition term equivalent to ~5% of the total CO budget is a plausible estimate. Whereas the effect on the overall tropospheric $\delta^{13}\text{C}(\text{CO})$ is expected to be small (on the order of +0.3‰), the locality of the deposition process may induce moderate enrichments up to +1‰ in the tropical and

¹¹⁴The dry deposition in the current study is neglected following the original setup of the EVAL simulation (see details in Sect. 5.1.3).

NH extra-tropical $\delta^{13}\text{C}(\text{CO})$; dry deposition of CO in the ETS is likely negligible. A pursuant revisiting of the influence of dry deposition on the isotope composition of CO in a separate model study would be valuable, noticing that none of the foregoing studies devoted enough attention to it; moreover, the estimates derived here are subject to large uncertainty. Nonetheless, the ^{13}C enrichments induced in dry deposition of CO are by far insufficient to resolve the abovementioned discrepancies of a few permil in $\delta^{13}\text{C}$ between the simulated and observed isotope composition of CO. If implemented for the present study in EMAC, the CO deposition term would be of lesser significance, as shown by the estimates from the sensitivity studies based on the similar model setup (P07). Conclusively, an underestimation of 0.6‰–0.7‰ in the EMAC-simulated boundary layer air $\delta^{13}\text{C}(\text{CO})$ in the tropics and NH in the summer-autumn seasons is expected due to neglecting the dry deposition of CO in the current study.

6.1.4.2 Oxidation by OH radical

The dominant fraction (greater than 90%) of the atmospheric CO loss is due to the reaction with hydroxyl radical, giving the kinetic isotope effects escorting this reaction a cardinal effect on the CO isotope composition in the atmosphere. Contrary to the majority of the CO production reactions in the atmosphere, CO+OH removal kinetics is little sensitive to the temperature but shows a moderate pressure dependence, dropping to $\sim 2/3$ of its surface pressure value at 100 hPa. The ^{13}C KIE escorting this reaction experiences a strong change from a normal (+6.5‰) to an inverse (−4.5‰) mode within this pressure range (see details in Sect. 3.4.4, p. 47). Owing to the pressure dependence, the BL air-averaged nominal KIE magnitude, $^{13}\text{C}\eta_{\text{CO+OH}}$, is larger than that for the whole troposphere. Aside of the kinetics, the effective magnitude of the OH oxidation KIE, $^{13}\text{C}\epsilon_{\text{CO+OH}}$, is controlled by the presence of OH and dampened by the surface influx and (horizontal and vertical) transport of CO in the atmosphere, with both terms largely varying spatially and seasonally. The aggregate of these factors imposes a variable and significant modification on the isotope composition of CO ensuing from its surface and in-situ sources.

Evidently, different parameterisations of the KIE in conjunction with the distribution of the atmospheric CO and OH dynamics deliver different nominal KIE magnitudes and respective effective fractionations in CO due to the OH sink. Because of the strong pressure dependence of $^{13}\text{C}\eta_{\text{CO+OH}}$, the calculated KIE value may be significantly sensitive to the parameterisation applied in the model. For instance, the slightly different formulation of the KIE magnitude (as a second-order fit with respect to the pressure) of M97 and B00 leads to the difference between the tropospheric and surface average values of $^{13}\text{C}\eta_{\text{CO+OH}}$ of $\sim 0.4\text{‰}$ and $\sim 0.6\text{‰}$, respectively. Moreover, to derive the pressure fits of the ^{13}C KIE magnitude, these earlier studies exploit the laboratory data of Stevens *et al.*^[1980], which appear to be systematically lower by $\sim 1\text{‰}$ in the 400–800 hPa range, compared to the results of the subsequent KIE examination by Röckmann *et al.*^[1998b].¹¹⁵ Therefore, the later studies (E04 and current work, REF) crediting more recent data to construct the fit, have significantly higher tropospheric and surface $^{13}\text{C}\eta_{\text{CO+OH}}$ values, specifically taking into account that the turnover of the CO+OH reaction is most intensive within the 600–900 hPa pressure range. In addition to the conventional parameterisations of the KIE, a revised *composite* KIE approach based on the detailed kinetics of the CO+OH reaction is considered in this study. The latter, in addition to the pressure dependence, conjectures a temperature dependence of the KIE that renders slightly higher $^{13}\text{C}\eta_{\text{CO+OH}}$ values at lower reaction temperatures (see Sect. 3.4.4, p. 47, for details). The composite KIE was implemented in the alternative model setup in this study and used for the sensitivity simulation hereafter referred to as “AK”; except for the composite approach KIE substituting the conventional parameterisation for the CO+OH KIE, the setup of AK is identical to that of REF. Below the results of the current approach are contemplated in line with estimates from the other studies, while the detailed comparison of the two parameterisations implemented in EMAC and their effect on $\delta^{13}\text{C}(\text{CO})$ are presented further in Sect. 6.2.5.

Except for E04, previous isotope-inclusive studies on CO do not report the direct estimates of $^{13}\text{C}\eta_{\text{CO+OH}}$ inferred from the model simulations. To obtain an approximately close estimate, nonetheless, one can compare the values ensuing from the different parameterisations computed using the same proxy (with respect to the air pressure and density) of the CO+OH sink term distribution in the atmosphere. Figure 6.2a (left panel) presents the vertical distributions of the $^{13}\text{C}\eta_{\text{CO+OH}}$ value calculated from the abovementioned studies’ KIE fits on top of the corresponding simulated CO+OH sink term from the REF simulation of this study. Notably, in the

¹¹⁵These data are presented in Figure 3.5, Sect. 3.4.4 (p. 53).

range of altitudes below 300 hPa (where ~90% of the overall CO+OH sink is situated), the nominal KIEs of M97 and B00 are lower by 1–2‰, giving sensibly lower tropospheric averages of +2.5‰ and +2.3‰ compared to those of ~+4‰ from E04 and +3.6‰ from REF. The composite T -dependent KIE employed in AK shows a vertical distribution which is clearly distinguishable from the conventional KIE, with the largest tropospheric average of +4.6‰. Notably, the composite KIE value exhibits a significant variation of up to +3‰/–1‰ with respect to the averages calculated at the same reaction pressures in the troposphere. Owing to the temperature changes, higher and lower KIE values reflect colder and warmer reaction conditions, respectively, generally providing a larger positive KIE at high latitudes compared to the magnitudes at low latitudes and in the tropics.

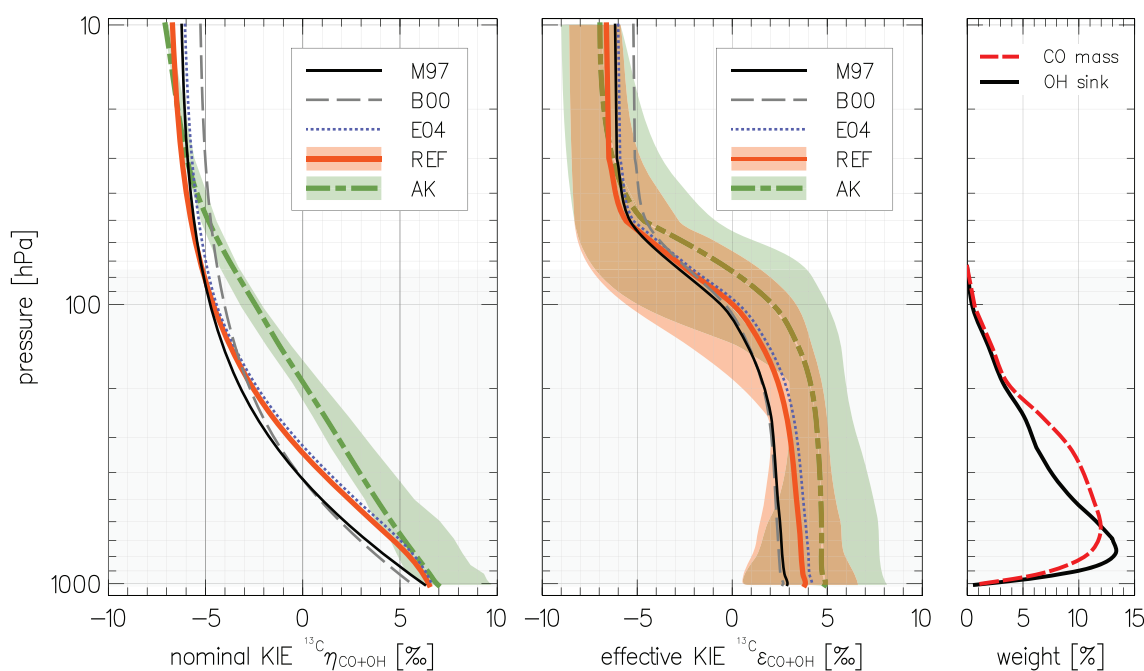


Figure 6.2a Comparison of the nominal CO+OH reaction KIE and corresponding effective ^{13}C enrichment in CO from previous and present studies. Abbreviations refer to those listed in Table 6.2. Left: Vertical distribution of the average $^{13}\text{C}\eta_{\text{CO+OH}}$ value as a function of atmospheric pressure. The distribution for E04 is calculated by averaging the distributions for M97, B00 and EMAC (REF, conventional fit) and fitting into the reported ~4‰ tropospheric average. The shaded area denotes the variation in the composite approach KIE (AK) due to the introduced temperature dependence (see text). Middle: Respective effective enrichments as result of the CO sink, emission, transport and mixing processes. Shaded areas denote the variation in EMAC-simulated $^{13}\text{C}\epsilon_{\text{CO+OH}}$ values resulting from the conventional (REF) and composite (AK) KIE parameterisations. Right: distribution of the tropospheric CO+OH sink and CO mass terms used as the weightings for $^{13}\text{C}\eta_{\text{CO+OH}}$ and $^{13}\text{C}\epsilon_{\text{CO+OH}}$ tropospheric averages, respectively.

Insofar the nominal value merely reflects the dependence of the reaction KIE on the current pressure (temperature) at which the CO+OH reaction proceeds, the effective enrichment experienced by atmospheric CO emerges as complex function of the nominal KIE and mixing and transport processes. Thus, for instance, despite the sink of CO via OH occurring in the wide range of $^{13}\text{C}\eta_{\text{CO+OH}}$ values altering with height, the resulting distribution of the effective enrichment $^{13}\text{C}\epsilon_{\text{CO+OH}}$ shows a much weaker vertical gradient. Subject to large surface emission, BL CO always becomes less enriched compared to the value of $^{13}\text{C}\eta_{\text{CO+OH}}$ expected at the steady-state, since a significant fraction of the tracer is not oxidised in-place, but effectively removed by transport into the free troposphere. Subsequently, this partly enriched CO effectively outbalances the lower or negative KIE escorting the CO+OH sink at higher altitudes/lower pressures, maintaining this way the propagation of the positive enrichments further up into the troposphere. Ultimately, one finds the comparable tropospheric averages of $^{13}\text{C}\eta_{\text{CO+OH}}$ and $^{13}\text{C}\epsilon_{\text{CO+OH}}$, when these are calculated mass-weighted by the CO+OH sink term and the CO content, respectively, with the tropospheric distribution of the effective enrichment being rather uniform with height. A relevant example of the $^{13}\text{C}\epsilon_{\text{CO+OH}}$ values estimated from the studies regarded here is presented in Figure 6.2a (middle panel), with corresponding averages for the nominal KIE and effective enrichments over the different tropospheric domains listed in Table 6.2. Noteworthy, whereas the results of the present study obtained with EMAC (REF and AK) were directly diagnosed from the model simulations, tabled estimates for the other studies should nearly reflect their actual model results, unless the simulated [CO] and [OH] distributions and CO+OH kinetics between these studies and EMAC are crucially dissimilar.

From Table 6.2 one notes that for the conventional parameterisations, the resulting overall tropospheric enrichments are actually lower than those anticipated from the nominal KIE averages. The inter-study differences in tropospheric and surface $^{13}\text{C}_{\text{CO+OH}}$ values are drastic, suggesting that the isotope mass-balance in M97 and B00 is settled at at least 1‰ lower enrichments than in the other studies. The estimates of the overall enrichments in M97 and B00 inferred here (*i.e.*, aggregate of the soil and OH sink KIEs) are in fact close to the value of $\sim +3\text{‰}$ from SW89, which was imposed as the constraint on the global average CO sources influx composition in the inversion routine. This value, however, is the result of a significant input from the relatively large ($>10\%$ of the overall sink) CO soil deposition term escorted with a KIE comparable to that of CO+OH sink at the surface. For B00, nevertheless, the actual overall enrichment of $+2.67\text{‰}$ in the CO sink is lower than the anticipated $+3\text{‰}$, which may have led to a slight inconsistency of the inversion result. That is because the simulated tropospheric average and station data $\delta^{13}\text{C}(\text{CO})$ were inverted with respect to different tropospheric integrals of $^{13}\text{C}_{\text{CO+OH}}$, *viz.* a higher presupposed value from SW89, and a lower actual simulated value, respectively.

Table 6.2 CO+OH sink and ^{13}C nominal and effective enrichments estimates from selected model studies

Study	M97	B00	E04	REF	AK	
Total CO source ^a	2600	2860	2890	2525	2525	
CO+OH sink ^b	2097 (80.6%)	2409 (84.3%)	2652 (91.8%)	2472 (97.9%)	2472 (97.9%)	
CO+OH KIE parameterisation	— <i>conventional</i> —			— <i>composite</i> —		
Nominal OH KIE and effective enrichment						
Domain	Tropospheric	+2.51‰	+2.25‰	+3.85‰ ^c	+3.39‰	+4.58‰
		(+2.35‰)	(+2.12‰)	(+3.72‰)	(+3.40‰)	(+4.59‰)
	Free troposphere	+1.93‰	+1.72‰	+3.38‰	+3.06‰	+4.22‰
		(+2.18‰)	(+1.97‰)	(+3.65‰)	(+3.39‰)	(+4.61‰)
	Boundary layer	+5.63‰	+5.06‰	+6.39‰	+6.19‰	+6.52‰
		(+2.82‰)	(+2.29‰)	(+4.19‰)	(+3.45‰)	(+4.38‰)
	Surface	+6.04‰	+5.45‰	+6.55‰	+6.39‰	+6.70‰
		(+2.44‰)	(+2.27‰)	(+3.69‰)	(+3.34‰)	(+4.23‰)
Overall tropospheric enrichment ^d	+3.06‰	+2.67‰	+4.13‰	+3.54‰	+4.74‰	

Notes:

Abbreviations refer to: M97 – Manning *et al.*^[1997] (case 2); B00 – Bergamaschi *et al.*^[2000] (scenario S2); E04 – Emmons *et al.*^[2004]; REF – present study, reference simulation (implementing conventional KIE parameterisation); AK – present study, sensitivity simulation (implementing composite KIE parameterisation).

Tabled isotope effect values are the annual averages obtained with the same CO+OH sink term distribution adopted from REF simulation.

Plain numbers refer to the nominal KIE magnitude, $^{13}\text{C}_{\text{CO+OH}}$. Numbers in parentheses denote the estimated effective enrichment, $^{13}\text{C}_{\text{CO+OH}}$.

^{a)} Source and sink terms are given in $[\text{Tg}(\text{CO})/\text{yr}]$ over the tropospheric domain.

^{b)} Bracketed values refer to the fraction of CO+OH sink with respect to the overall CO sink.

^{c)} Fitted value for the current comparison (see text), the reported tropospheric value is $\sim +4\text{‰}$.

^{d)} Effective, including fractionations due to the dry deposition and/or removal processes.

A further ambiguity in the estimates of the CO+OH KIE effect on $\delta^{13}\text{C}(\text{CO})$ in M97 and B00 is introduced by the simplified treatment of the model OH represented by the climatological monthly averages. It is likely that in this way the actual [OH] variation is underestimated, which causes an unexpectedly low seasonal variation of the CH_4+OH source of CO (mentioned above in Sect. 6.1.1, p. 143), as opposed to that of the model studies explicitly implementing OH chemistry. For instance, EMAC-simulated methane-derived CO at the two particular surface locations, Izaña (IZA, 28.3°N) and Baring Head (BHD, 41.4°S), varies within 5.8 and 1.3 ppb throughout the year, respectively. This characteristic is at least halved in B00 at IZA (below 3 ppb) and in M97 at BHD (0.48 ppb; in B00 it is comparable at ~ 1.3 ppb, however). Correcting for a lower than unity yield of CO from CH_4 in these studies (the latter proportionally reduces this source' variation by a factor 0.7–0.86, see Sect. 6.1.1) nonetheless increases the annual variation in [OH] climatology-driven CH_4+OH source in M97/B00 only to $\sim 60\%$ of that of EMAC. Notably, apart from the reduced variation in OH (whose abundance generally serves as a limiting factor for the CH_4+OH reaction), other relevant terms

(*viz.* temperature and $[\text{CH}_4]$) determining the rate of $\text{CH}_4 \rightarrow \text{CO}$ conversion are not capable of introducing such a large reduction in its variation.¹¹⁶

Consequently, a reduced $[\text{OH}]$ variability is expected to impair the effective fractionation escorting the OH-mediated CO sink. In essence, a more moderate $[\text{OH}]$ variation similarly leads to slower temporal changes and an underestimated variation in $^{13}\text{C}_{\text{CO+OH}}$, even though its annual average may be adequately reproduced. This pertains, for example, to the dynamics of the extratropical CO sink, which virtually stops in the fall-winter season due to the quickly vanishing OH: The underestimated $[\text{OH}]$ variability (in this case overestimated OH levels) slows down the decrease of $^{13}\text{C}_{\text{CO+OH}}$, and raises its minima. Conversely, the underestimated OH in spring-summer suppresses a quick growth of the effective enrichment, as well as attenuates $^{13}\text{C}_{\text{CO+OH}}$ maxima. This can be tracked in Figure 6.2b depicting the monthly averages of the overall enrichment due to the CO sink simulated at BHD in the regarded studies. Reckoning that the effect of dry deposition on $\delta^{13}\text{C}(\text{CO})$ in the ETS is small (see previous section), the marked difference between the average values of the overall atmospheric CO enrichment is generally attributed to the different $^{13}\text{C}_{\text{CO+OH}}$ reproduced by each model. The averages of the effective enrichments distinctly scale according to the $^{13}\text{C}_{\eta_{\text{CO+OH}}}$ values determining them. Nonetheless, M97 and B00 reproduce a smaller $^{13}\text{C}_{\text{CO+OH}}$ variation of $\sim 1\%$ compared to $\sim 1.5\%$ of REF, although the latter employs a much similar conventional KIE parameterisation, and the simulated $[\text{CO}]$ correlates well between the studies. Furthermore, M97 and B00 reproduce slightly larger $[\text{CO}]$ variations (owing to lower spring-summer levels) that generally yield amplified variations in the effective enrichment. Therefore, at the $[\text{CO}]$ dynamics similar to that of REF the span of simulated $^{13}\text{C}_{\text{CO+OH}}$ in M97/B00 is anticipated to be even lower. To obtain adequate $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ cycles in these studies, the inversion routine is inclined to compensate the missing variability in the CH_4 -derived CO component and the effective sink enrichment at the expense of other (surface) sources by enhancing their variation (recall the contradiction between the regular and isotope-inclusive inversions results in M97/B00, see above, p. 142). Finally, looking at the enrichments simulated by REF and AK, one notes that their similar variation of $+1.5\%$ is hardly influenced by the differences in $^{13}\text{C}_{\eta_{\text{CO+OH}}}$, being rather determined by the dynamics of the CO sources and sinks. The simulated minima and maxima of $^{13}\text{C}_{\text{CO+OH}}$ in AK are delayed compared to the other studies, owing to the nominal KIE variation of 2% reflecting the seasonal temperature variations, with the largest fractionation occurring during austral winter.

Compared to the inverse modelling studies, the input of the sink fractionations to the global $\delta^{13}\text{C}(\text{CO})$ of E04 and REF is significantly larger, albeit their estimates of the soil deposition fractionation is much lower or neglected. Principally, in search for the missing atmospheric ^{13}CO , none of the $^{13}\text{C}_{\text{CO+OH}}$ values granted by conventional KIE parameterisations appear to be sufficient to close the atmospheric $\delta^{13}\text{C}(\text{CO})$ isotope mass-balance and to reconcile the models with observational data. Recalling the assessment of the $\delta^{13}\text{C}$ value of CO sources given in Sect. 6.1.2, the overall enrichment compensating the ^{13}C -depleted composition of either bottom-up or inverse estimates (corrected for a more realistic CH_4 source) should be on the order of $+5\%$, still $\sim 1\%$ more than the largest estimate given by E04. It is notable, that at an early stage SW89 already remarked that the larger KIE of $+5\%$ would be a plausible explanation for the disagreement arising from the mutual atmospheric ^{13}CO and C^{18}O mass-balance of the sources and sinks. They, however, distrusted their estimated $^{13}\text{C}_{\text{CO+OH}}$ value of $+3\%$, arguing that the vertical distribution of the CO+OH sink term may be different, *e.g.* circumscribed within a range of significantly lower altitudes, thus giving a higher tropospheric $^{13}\text{C}_{\eta_{\text{CO+OH}}}$ average (*cf.* Figure 6.2a, right panel). The latter, according to Table 6.2, is indeed confirmed at $(+3 \pm 0.8)\%$ for the conventional parameterisation relying on the consistently simulated sink distribution and measured KIE pressure dependence.

¹¹⁶ One can apparently exclude the annual variation in the tropospheric methane mixing ratio that does not exceed 0.05% of the annual average $[\text{CH}_4]$ (see Sect. 5.2.7, Table 5.10, p. 136). From the kinetics of the $\text{CH}_4 + \text{OH}$ reaction, the rate of the latter in the troposphere is nearly proportional to the temperature. Thus, an implausible reduction of the variation in the simulated temperature of equivalent $\sim 60\%$ is required to explain the missing variations in the overall $\text{CH}_4 + \text{OH}$ source, if OH is simulated correctly.

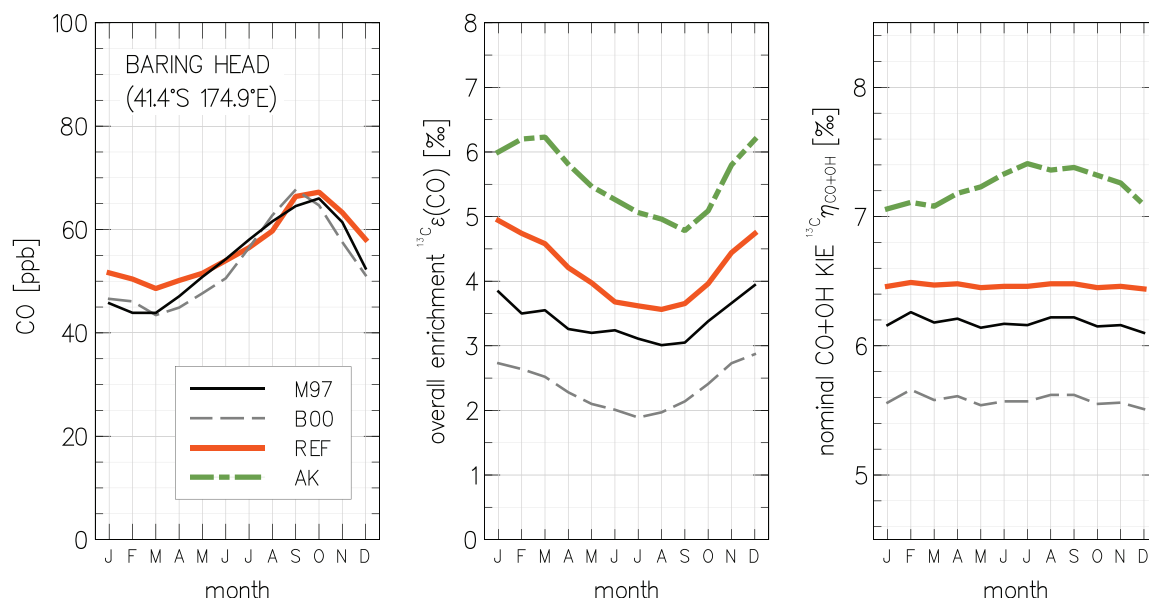


Figure 6.2b Monthly averages of the simulated CO mixing ratio (left), effective ^{13}C enrichment due to CO sinks (middle) and nominal CO+OH KIE value, $^{13}\text{C}\eta_{\text{CO+OH}}$ (right) at Baring Head, New Zealand, according to the selected model studies. Abbreviations refer to those listed in Table 6.2.

A befitting larger tropospheric average of $^{13}\text{C}\eta_{\text{CO+OH}}$, if it were feasible to achieve with a conventional KIE approach, is nonetheless unlikely to improve the underestimated simulated surface $\delta^{13}\text{C}(\text{CO})$, if we revert to the troublesome cases with REF at high latitudes described above in Sect. 6.1.2. Being quite analogous to enriching the overall source composition, adjusting (towards higher average) the nominal KIE values would be nearly equal along all latitudes, due to the narrow range of surface pressures. A case distinctly different to that is the composite KIE approach that introduces, owing to the introduced temperature dependence, a substantial gradient in surface $^{13}\text{C}\eta_{\text{CO+OH}}$ of +2‰ from the equator towards the poles, concurrently augmenting the tropospheric average enrichment up to more congruent +4.75‰. It is shown further in this study (see Sect. 6.2.6, p. 196) that the simulated surface $\delta^{13}\text{C}(\text{CO})$ in AK and other model setups implementing the composite KIE are found in cardinally better agreement with the observations. The concept of the latitude-dependent effective KIE also befits well the cases in the ETSH, where low CO mixing ratios are well captured by the model, and hence the discord in simulated $\delta^{13}\text{C}(\text{CO})$ is more difficult to attribute to the underestimated surface sources.

Recapitulating, the analysis given above suggests that (1) all studies account for appreciably different magnitudes of ^{13}C fractionation in the CO sink processes, with tropospheric averages varying by more than 2‰. The estimated CO+OH sink terms ranging from 81% to 98% of the overall scavenged CO proportionally scale the resulting $^{13}\text{C}\epsilon_{\text{CO+OH}}$ value. For the approaches predicting a lower CO+OH sink and concomitant enrichments (*i.e.* M97 and B00), the latter are largely compensated by the soil sink term escorted with a KIE of a comparable magnitude. The results of these studies also may suffer from misconceptions introduced by the simplified approach to the OH distribution used, and hence the underestimated dynamics of the chemical sources of CO and sink isotope effects. Finally, lower sink enrichments demand significant increases in surface sources ratios and (likely overestimated) reductions of the CH_4 source to mass-balance the ^{13}CO in the inverse modelling studies. (2) The subsequent forward-model studies, even provided with larger sink fractionations, nonetheless experience missing ^{13}CO using bottom-up estimates of the sources' isotope composition. Amongst all above scrutinised factors affecting the isotope composition of the atmospheric CO (Figure 6.1, p. 141), however, only the uncertainty associated with the CO+OH sink KIE holds the potential to explain the gap between the bottom-up and top-down model estimates maintaining the isotope compositions of the CO sources within their given uncertainty range. This is feasible under the assumption that the CO+OH kinetic isotope effect for ^{13}C is actually larger and more variable than predicted by the conventional assumption accounting only for its pressure-induced variability evaluated in the laboratory. One notes withal that since in the present study the reaction with OH uniquely comprises the sink of atmospheric CO, the model may be oversensitive to the reproduced $^{13}\text{C}\epsilon_{\text{CO+OH}}$, as the soil sink of CO is omitted. The latter, however, is not likely to be influential in the remote SH (see previous section), thus EMAC results are expected to bear the least uncertainty in the $\delta^{13}\text{C}(\text{CO})$ simulated in the ETSH.

6.1.5 Global CO turnover

To complement the above analysis of the factors determining the carbon isotope ratios of atmospheric CO, it is mandatory to analyse the underlying CO budget itself. Figure 6.3 (p. 161, left panel) presents the comparison of the global CO turnover by category from the body of selected non-isotope and aforementioned isotope-enabled studies. The large range of 2500–2900 Tg(CO) yr⁻¹ of these estimates is generally attributed to the differences in the implementation of inverted surface emission strengths.¹¹⁷ Noteworthy, neither bottom-up nor top-down estimates show correlated tendencies, suggesting the overall CO budget being uncertain within at least ± 200 Tg(CO) yr⁻¹. A similar estimate of $\sim 2700 \pm 280$ Tg(CO) yr⁻¹ one infers from the results of the ensemble of the inverse modelling approaches summarised by Duncan *et al.*^{[2007]¹¹⁸}, narrowed down to $\sim 2500 \pm 185$ Tg(CO) yr⁻¹ for the year 2000. Regarding the variation range of individual CO sources between the models, the largest spread of ~ 280 Tg(CO) yr⁻¹ (or equivalent $\sim 50\%$ of its average value) is attributed to the biomass burning (BB) source. The most ambiguous biogenic source (including oceanic emission) is varying within $\sim 70\%$ of its average, or ~ 90 Tg(CO) yr⁻¹, but is nonetheless least influential in the aggregate emission composition. The moderately uncertain fossil fuel/biofuel (FF/BF) and VOCs oxidation sources range within $\sim 25\%$ and $\sim 30\%$ (~ 170 and ~ 150 Tg(CO) yr⁻¹), respectively. Disregarding the rather low estimates of M97 and B00, the methane source of CO appears the most certain one ranging only $\sim 15\%$, or roughly 110 Tg(CO) yr⁻¹ around its average value.

Amongst the previous isotope-enabled studies, the *a priori* and bottom up derived sources sum up to ~ 2900 Tg(CO) yr⁻¹, *i.e.* lie at the upper end of the conferred range. The *a posteriori* sources in M97 are generally reduced at the expense of the smaller CH₄ source. In contrast to it, B00 decrease the methane-derived CO less and compensate it by other sources, thus keeping the final emission strengths close to the initial guess. Noteworthy, these two studies also infer the largest BB emission sources exceeding the inter-study average by a factor of $\frac{2}{3}$ and $\frac{1}{3}$, respectively. A significantly lower CO budget in M97 is most probably the drawback of using the fairly limited observational data from the ETSH, where the inversion results are less sensitive to the NH sources, or their underestimation. For example, a comparably low simulated CO turnover in REF is likely to result from the underestimated surface CO emissions in the emission setup for EMAC considered here. Indeed, the simulated NH high-latitude CO mixing ratios in REF are systematically lower than the surface station data, particularly in winter. A similar feature was observed in the study with EMAC (Pozzer *et al.*^[2007]) whose setup is closely followed here (EVAL, see Sect. 5.1). To achieve more adequately reproduced CO mixing ratios, an amended emission setup, hereafter referred to as “AE”, was implemented for this study. The latter, having recourse to the sensitivity studies performed by P07, implies an increase of the industrial (FF and BF) emissions over India and China, surmising these as having been the most underestimated. In contrast to P07 probing the adjustment of only CO emission, the AE setup accounts for the enhanced influx of the other concomitantly emitted tracers (*e.g.*, hydrocarbons), yielding a larger increase of the overall CO source to 2754 *vs.* 2525 Tg(CO) yr⁻¹ in REF.¹¹⁹ It is shown below (see Sect. 6.2.3, p. 172) that the simulations based on the AE emission setup reproduce the background ETNH CO mixing ratios generally better, rendering a consistent comparison of the superimposed isotope ratios feasible. Nevertheless, similar to the results of P07, it is clear that the strength and spatial distribution of the missing CO sources requires a more thorough quantification that is not undertaken within this study.

¹¹⁷ Quoted range refers to the year 2000 or to the interannual averages conferred by the regarded studies.

¹¹⁸ See references therein; quoted are the ensemble averages ± 1 standard deviation, respectively.

¹¹⁹ A detailed analysis of the emission setups and differences in the resulting CO turnover is given in Sect. 6.2.3 (p. 172) further.

Table 6.3 Tropospheric CO turnover and its isotopic composition from the present and previous studies

Study	MS05 ^{a,b}	F06 ^c	A06 ^{a,b}	D07 ^a	P07 ^c	SW89	B99	
Model	IMAGES	LMDz-INCA	GEOS-CHEM	GEOS-CHEM	ECHAM5/MESSy1	–	–	
Emission inventories ^d	1997	1995 [*]	2000	1988–1997	2000 [*]			
Sources	CH ₄ oxidation	825	854	820	778–861	834	(–55‰)	400–1000 (–52.6‰)
	NMHC oxidation	695	635	394	501–542	579	(–32‰)	200–600 (–32.2‰)
	Fossil fuel / Biofuel usage	730	672	841	391–411 / 159	318 / 250	(–27.5‰)	300–550 (–27.5‰)
	Biomass burning	356	811	501	406–516	452	(–24.5‰)	300–700 (–24.5‰)
	Biogenic / Oceans	128 / 26	– / 50		75–380 ^c	100 / 13		60–160 (–) / 20–200 (–13.5‰)
	All photochem. sources	1520	1489	1214	1279–1403	1414	(–35.6‰) ^f	805+460 (–45.2‰) ^g
	All surface sources	1240	1533	1342	956–1086	1133		489+575+146+75 (–24.8‰) ^g
	Total sources	2760	3022	2556	2235–2489	2547	(–30.3‰)	2550 (–34.9‰)
	Overall uncertainty		–	±80				
	Sinks	Reaction with OH		2653		2164–2295		(+3‰)
Soil uptake		186	135	–	115–240 ^e	74	(< +0.2‰) ^h	250–640 (+0.5‰)
Loss to stratosphere			231		65–71			~100
Removal processes ⁱ		92	95	91	96	93		
Total sinks			3019		2231–2366		2800 (+3‰)	2100–3000 (+3.5‰)
CO tropospheric burden ^{j,k}	366			305–350	376	(–27.4‰)	(–31.4‰)	
λ _{CH₄} (CO) ^l	0.925	0.9	0.95	~1	0.94	signif. < 1		
γ _{CH₄} (CO) ^l	29.9%	28.3%	32.1%	31.7%	32.8%		31.6%	
(CH ₄ /photo) photo/total ^m	(0.54) 0.55	(0.57) 0.49	(0.68) 0.47	(0.69) 0.46	(0.59) 0.56	(0.15) ^f	(0.64) 0.50	
CH ₄ sink [Tg(CH ₄)/yr]	510	542	493	445–492	507			
trop. OH [10 ⁶ molec./cm ³]		9.6		8.7–9.3	10.8[12.7]			
τ _{CH₄} [yr] / τ _{MCF} [yr] ^{k,n}	9.1 / 5.4 [*]	9.2 / 5.5	10.7 [*] / 6.4	8.1 / 4.9	8.0[4.1] / –			
τ _{CO} [dy] ^{k,n}	49		61		54 [*]			

Notes:

The source/sink terms are given in [Tg(CO)/yr] with the corresponding $\delta^{13}\text{C}$ composition of the sources or estimated effective enrichments $^{13}\text{C}_\text{e}$ escorting sinks in parentheses. Values are the tropospheric averages, with the squared brackets denoting the values diagnosed for the surface conditions.

Abbreviations refer to: MS05 – Müller and Stavrakou^[2005] (case B); F06 – Folberth *et al.*^[2006]; A06 – Abou El-Nour *et al.*^[1977]; D07 – Duncan *et al.*^[2007]; P07 – Pozzer *et al.*^[2007] (simulation S1a); SW89 – Stevens and Wagner^[1989]; M97 – Manning *et al.*^[1997] (case 2); B99 – Brenninkmeijer *et al.*^[1999b]; B00 – Bergamaschi *et al.*^[2000] (scenario S2); E04 – Emmons *et al.*^[2004]; P10 – Park^[2010]; REF, AEK – this study, reference and AEK setup (see text).

^{a)} Employs a simplified chemistry scheme (no intermediates in the CH₄ → CO chain, no NMHC chemistry).

^{b)} Employs an inversion technique to improve the emission strengths/isotope signatures.

^{c)} Employs a detailed chemistry scheme (*e.g.*, CH₄ and NMHC chemistry with intermediates and removal processes).

^{d)} Reports the year(s) the aggregate of the emission inventories correspond closest to; the plus signs indicate that the transient biomass burning inventory was used, with the listed year referring to the anthropogenic emissions revision.

^{e)} Biogenic and ocean sources were assumed to be counterbalanced by the soil sink term, thus not implemented in the model.

^{f)} This value is apparently overestimated due to assuming too high NMHC:CH₄ source fluxes partitioning of 5.5.

^{g)} The average signature results from the respective source terms (denoted as the sum) assumed within the given limits.

^{h)} Estimated to be significantly smaller than 10% of the overall CO sink, based on the background $\delta^{18}\text{O}(\text{CO})$ values.

ⁱ⁾ The CO-equivalent term of the CH₄ source reduction is given (not to be included in the budget).

^{j)} Given is the estimated tropospheric burden in [Tg(CO)] and its $\delta^{13}\text{C}(\text{CO})$ resulting from the sources and fractionation escorting the sinks; for EMAC, values are diagnosed.

^{k)} Asterisks (*) denote the values calculated from the relation of the CH₄/MCF lifetimes against OH. Daggers (†) indicate the values derived from CO budget closure and lifetimes.

^{l)} Estimated fraction (γ) and yield (λ) of CO from the methane source.

^{m)} The ratios of the respective source terms.

ⁿ⁾ Tropospheric lifetimes against OH removal (CH₄, MCF) and OH and soil uptake (CO).

Table 6.3 Tropospheric CO turnover and its isotopic composition (*continued*)

Study	M97 ^{a,b}	B00 ^{a,b}	E04 ^c	P10 ^{a,b,o}	REF ^c	AEK ^{c,k}
Model	GFDL (2D)	TM2	MOZART2 ^{a,b}	MOZART4	EMAC	EMAC
Emission inventories ^d	1987–1995	1991–1995	1997–1999	2000 ⁺	2000 ⁺	2000 ⁺
<i>Sources</i>						
CH ₄ oxidation	624 (–52.6‰)	795 (–51.1‰)	1022 (–51‰)	922 (–51‰)	834 (–51.2‰)	811 (–51.2‰)
NMHC oxidation	403 (–29.3‰)	607 (–23.9‰)	453 (–30‰)	496 (–32.2‰)	579 (–26.1‰)	622 (–26.1‰)
Fossil fuel / Biofuel usage	595 (–27‰)	641 (–26.7‰)	361 (–27‰) / 306 (–25‰)	359 (–27.5‰) / 470 (–25‰)	272 (–27.4‰) / 285 (–25‰)	376 (–27.2‰) / 397 (–25‰)
Biomass burning	909 (–21‰)	768 (–20‰)	570 (–21.8‰)	495 (–24.5‰)	434 (–24.1‰)	434 (–24.1‰)
Biogenic / Oceans	– / 57 (–13.5‰)	– / 49 (5.1‰)	158 (–32‰) / 20 (–12‰)	118 (–32.2‰) / 20 (–40‰)	102 (–25.7‰) / 13 (–13.5‰)	102 (–25.7‰) / 13 (–13.5‰)
All photochem. sources	1027 (–43.4‰)	1402 (–39.9‰)	1475 (–44.6‰)	1417 (–44.4‰)	1413 (–40.9‰)	1416 (–40.3‰)
All surface sources	1561 (–23‰)	1458 (–22.1‰)	1415 (–24.8‰)	1455 (–26.2‰)	1105 (–25.2‰)	1321 (–25.3‰)
Total sources	2588 (–31.1‰)	2860 (–30.5‰)	2890 (–34.9‰)	2872 (–35.2‰)	2525 (–34.0‰)	2754 (–33.1‰)
Overall uncertainty	±58 (±1.5‰)	±31 (±1.1‰)		±32	±351 (±1.5‰)	±382 (±1.6‰)
<i>Sinks</i>						
Reaction with OH ^p	2097 [†] (+2.4‰)	2409 (+2.1‰)	2652 (+3.7‰)	2650 (+3.7‰)	2472 (+3.4‰)	2709 (+4.6‰)
Soil uptake ^p	347 [†] (+0.7‰)	288 (+0.5‰)	143 (+0.3‰)	135 (+0.3‰)	{ 73 (+0.2‰) }	{ 80 (+0.2‰) }
Loss to stratosphere ^{j,q}	156	161	95	79	53	61
Removal processes ⁱ	267	129			97 (+0.17‰)	100 (+0.16‰)
Total sinks	2600 (+3.1‰)	2858 (+2.7‰)	2890 (+4‰)	2872 (+4‰)	2524 (+3.54‰[+3.50‰])	2770 (+4.75‰[+4.39‰])
CO tropospheric burden ^{j,k}	370 [†] (–28.1‰)	350 [†] (–27.9‰)	429 [†] (–30.6‰)	450 [†] (–31.7‰)	321 (–30.5‰[–29.3‰])	368 (–28.4‰[–27.7‰])
$\lambda_{\text{CH}_4}(\text{CO})$ ^l	0.7	0.86	~1	~1	0.94[0.72]	0.93[0.72]
$\gamma_{\text{CH}_4}(\text{CO})$ ^l	24.1%	27.8%	35.4%	32.1%	33.1%[28.1%]	29.1%[24.6%]
(CH ₄ /photo) photo/total ^m	(0.61) 0.40	(0.57) 0.49	(0.69) 0.51	(0.65) 0.49	(0.59) 0.56	(0.57) 0.52
CH ₄ sink [Tg(CH ₄)/yr]	507	528	584	527	510	498
trop. OH [10 ⁶ molec./cm ³]	10.0			~10 ^{rs}	11.1[12.7] ^s	10.7[12.4] ^s
τ_{CH_4} [yr] / τ_{MCF} [yr] ^{k,n}	– / 4.8	– / 5.2	~10 / –	10.5 / –	8.0[4.1] / –	8.2[4.2] / –
τ_{CO} [dy] ^{k,n}	52	53 [*]	56 [*]	60 [*]	47[37]	50[39]

Notes:

The source/sink terms are given in [Tg(CO)/yr] with the corresponding $\delta^{13}\text{C}$ composition of the sources or estimated effective enrichments $^{13}\text{C}_\text{e}$ escorting sinks in parentheses. Values are the tropospheric averages, with the squared brackets denoting the values diagnosed for the surface conditions.

Abbreviations refer to: MS05 – Müller and Stavrakou^[2005] (case B); F06 – Folberth *et al.*^[2006]; A06 – Abou El-Nour *et al.*^[1977]; D07 – Duncan *et al.*^[2007]; P07 – Pozzer *et al.*^[2007] (simulation S1a); SW89 – Stevens and Wagner^[1989]; M97 – Manning *et al.*^[1997] (case 2); B99 – Brenninkmeijer *et al.*^[1999b]; B00 – Bergamaschi *et al.*^[2000] (scenario S2); E04 – Emmons *et al.*^[2004]; P10 – Park^[2010]; REF, AEK – this study, reference and AEK setup (see text).

^{o)} The inversion is done with respect to the $^{18}\text{O}/^{16}\text{O}$ isotopes, the ^{13}C signatures are adopted from B99, E04.

^{p)} These values are purposely estimated in the present study, see Sect. 6.1.4. Sink isotope effects for P10 are assumed identical to those of E04. Soil sink terms quoted for REF, AEK (parenthesised in curly brackets, not to be included in the final turnover) are the estimates in case dry deposition of CO would be included in the EMAC setup used in present study.

^{q)} For EMAC, the photochemical terms are integrated over the online diagnosed tropospheric domain. The stratospheric loss term is calculated as the difference between the simulated overall and tropospheric sink terms, reduced by the production term in the stratosphere (~5.2% of total methane source, ~1.8% of the total non-methane photochemical sources).

^{r)} A rough estimate from the comparison against the OH climatology (Spivakovsky *et al.*^[2000]) provided by Emmons *et al.*^[2010].

^{s)} For the studies employing EMAC (including P07) and P10, the mass-weighted (according to Lawrence *et al.*^[2001]) average tropospheric OH concentrations are quoted; for the other studies the weighting method is unknown.

For conciseness of the comparison, Figure 6.3 incorporates the result of the simulation referred to as “AEK” implementing both of the improvements introduced in the present study, *viz.* the revised CO+OH KIE parameterisation (AK) and the adjusted emissions (AE). Hence by comparing the estimates from REF and AEK, one perceives the differences in the source strengths, their isotope composition and on top of that, the different sink fractionation that ultimately lead to different average tropospheric $\delta^{13}\text{C}(\text{CO})$ values. Further, analogously to the comparison of the CO sources strengths, the right panel in Figure 6.3 elucidates the individual contribution of every source composition and sink fractionation to the final tropospheric $\delta^{13}\text{C}(\text{CO})$ for the isotope-inclusive model inquiries. The source terms (wide bars) are calculated as the products ($f_i \cdot \delta_i$), where f_i is the fractional contribution and δ_i is the $\delta^{13}\text{C}$ of a particular CO source, respectively. This way one grasps how large each individual source enriches/depletes the final composition with respect to the reference ratio of 0‰. Because the majority of the CO sources is depleted, the calculated contributions are always negative, with an exception of the minute term of +0.1‰ for B00 derived from the oceanic source with a corresponding $\delta_i = +5.1$ ‰. Due to the appreciably ^{13}C -depleted composition of methane ($\delta_i \sim -51.2$ ‰), the overall sink composition reflects a high sensitivity to the CH_4 source input, with clearly smaller contributions in M97 and B00. The depicted enrichments associated with the sinks of CO (narrow bars) are effective, *i.e.* damped from their nominal values by the tracer emission and transport in the atmospheric reservoir. Contrary to the inputs of the sources, all isotope effects escorting the sinks are positive, thus leading to the augmentation of atmospheric $\delta^{13}\text{C}(\text{CO})$. Finally, the expected overall composition of tropospheric CO is denoted with solid symbols, which are shifted from the bottom line of the sources upwards in conformity with the overall sink enrichment.

Figure 6.3 is intended to conclude quantitatively the relationship between the factors determining the isotope composition of CO from the analysis given in the previous sections, thus actualising Figure 6.1 (p. 141) for every regarded study. First of all, one notes a prominent change to the sources composition in *the a posteriori* estimates given by the inverse studies. It is important to remark that the presented *a priori* and *a posteriori* source contributions refer to different isotope compositions (prior and posterior, respectively) of the sources on top of their changed strengths. From that one concludes that the posterior repartitioning of the non-methane sources is virtually ineffective in M97: An increase of +2.7‰ in δ_i of the VOC oxidation source counterbalances the sufficiently larger BB source in the optimised emissions, thus the increase in tropospheric $\delta^{13}\text{C}(\text{CO})$ is merely promoted by adjusting the CH_4 source. As it was noted above, the reduction of the methane component in B00 is less marginal, whilst the non-methane sources also deplete the final $\delta^{13}\text{C}(\text{CO})$ less, being enriched by a similar adjustment of the VOC signature by +2.5‰. Despite the fact that the CH_4 source strength inferred by B00 is comparable to the majority of the estimates presented in Figure 6.3 (left panel), its relative contribution to the overall CO is diminished by a larger fraction of the other sources, which is a direct consequence of the reduced CO yield from CH_4 . The remaining studies suggest almost complete conversion of the $\text{CH}_4 + \text{OH}$ source to CO, and this way confine the overall source $\delta^{13}\text{C}$ to the -35‰ to -33‰ range.

In view of a likely underestimation of the CH_4 source in M97 and B00 (see Sect. 6.1.1), the adjustment of the remaining sources (both strengths and signatures) equivalent to $\sim +3$ ‰ caused by the reduction of the CH_4 component, appears difficult if not unfeasible (*cf.* the rather low range of the contributions in E04, REF and AEK based on significantly different source strengths, for instance; see also Sect. 6.1.1). Irrespective from the fact that the source composition and sink enrichments may have been erroneously estimated, the results of the inversion studies (including the top-down estimate of SW89) importantly retain the *expected* tropospheric average of around -28‰ “assimilated” to a considerable extent from the observational data.¹²⁰ Regarding the bottom-up estimates, it becomes clear that the lower sink fractionations predicted by the conventional-type CO+OH KIE are capable of bringing the tropospheric $\delta^{13}\text{C}(\text{CO})$ at most to -30.5‰ (REF). A more befitting estimate of -28.3‰ granted by AEK is comprised of extra +0.9‰ in the sources $\delta^{13}\text{C}$ owing to the readjustment of the source contributions and, more importantly, additional +1.2‰ pertaining to the larger sink fractionation from the revised T -dependent KIE. For completeness, Table 6.4 compares the terms defining the tropospheric average of $\delta^{13}\text{C}(\text{CO})$ inferred in all four setups of the present study.

¹²⁰ Although the latter pertains to the surface or BL air measurements, the actual tropospheric estimate must be near this value, recalling, for example, how efficiently the nominal CO+OH KIE is “stirred” in effective enrichment throughout the troposphere (see previous section).

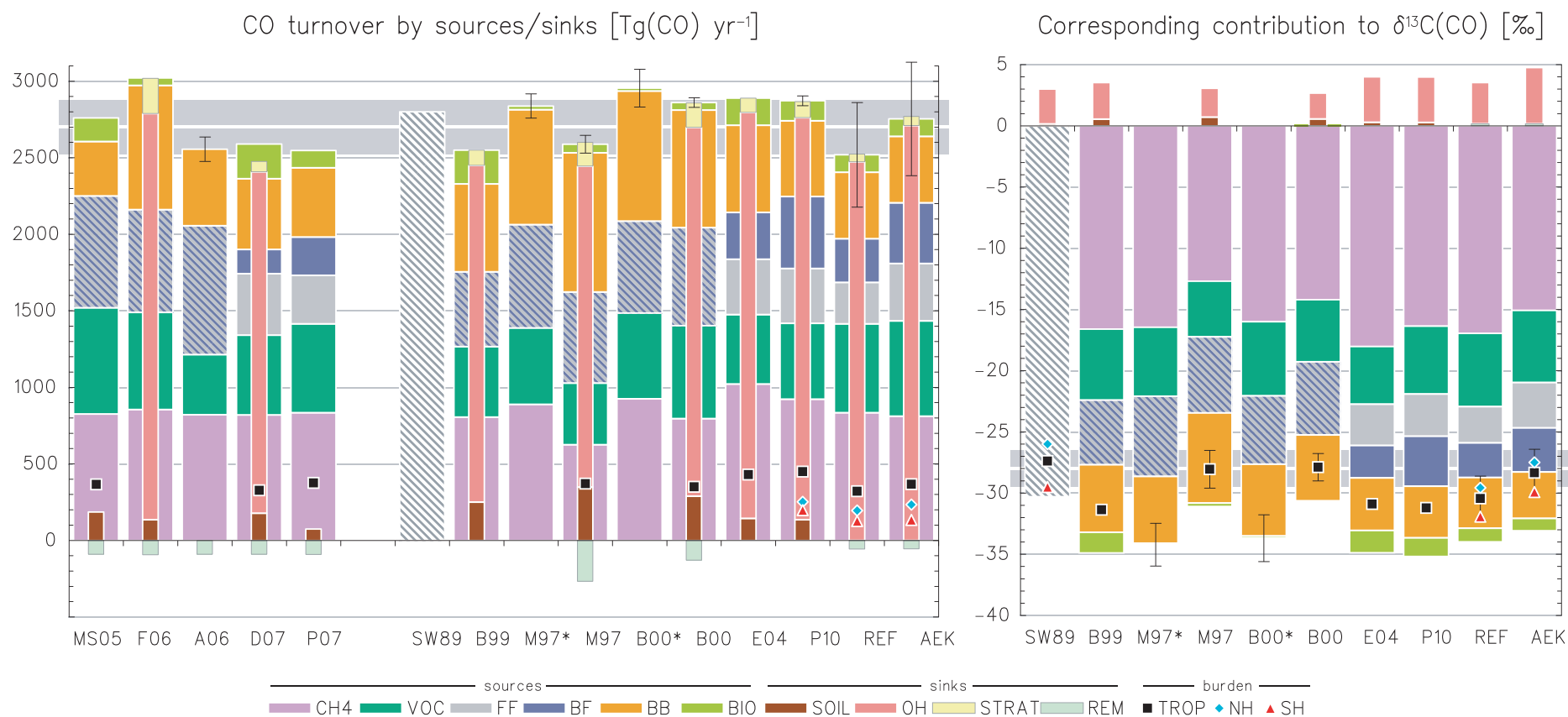


Figure 6.3 Estimates of the tropospheric CO turnover and its isotopic composition from previous and the present studies (refers to Table 6.3). Abbreviations refer to: MS05 – Müller and Stavrakou^[2005] (case B); F06 – Folberth *et al.*^[2006]; A06 – Arellano *et al.*^[2006]; D07 – Duncan *et al.*^[2007]; SW89 – Stevens and Wagner^[1989]; M97 – Manning *et al.*^[1997] (case 2); B99 – Brenninkmeijer *et al.*^[1999b]; B00 – Bergamaschi *et al.*^[2000] (scenario S2); E04 – Emmons *et al.*^[2004]; P10 – Park^[2010]; REF, AEK – this study, reference and AEK setup (see text). Asterisks denote *a priori* estimates of the corresponding inverse modelling studies. Note: For SW89, only the values referring to the total source/burden are plotted (grey hatched bars). Blue-grey hatched bars denote the aggregate industrial emission, as FF and BF sources are not distinguished. Left: Sources and sinks by category. Wide and narrow bars represent the source and sink terms, respectively. Symbols denote the overall and hemispheric tropospheric burden in [Tg(CO)]. The removal category (REM) presents essentially not a sink term, but the CO-equivalent amount of the intermediates scavenged from the $\text{CO} \rightarrow \text{CH}_4$ chain, *i.e.* the reduction of the methane-derived CO term. The grey shaded area denotes the ensemble average and standard deviation of $\sim 2700 \pm 280 \text{ Tg(CO) yr}^{-1}$ of the top-down estimates from D07 (see references therein). Right: Individual contribution of each source composition and fractionation in sink process on the overall source $\delta^{13}\text{C(CO)}$. The expected overall composition of the tropospheric CO is denoted with solid symbols. The results of the AEK setup reflect the updated emission strengths (AE) and implementation of the composite temperature-dependent CO+OH KIE in the model setup (AK) (see text for details). The grey shaded area denotes the average of $(-28 \pm 1.5)\text{‰}$ inferred from the top-down estimates of M97 and B00.

Summing up, the budgets of CO simulated with EMAC appear to be in line with the results of the majority of the recent studies, of which neither bottom-up nor top-down approaches converge within less than $\pm 10\%$ of the average of $\sim 2700 \text{ Tg(CO) yr}^{-1}$. Two probed emission setups, REF and AE, are found at the lower end and close to this estimate, respectively. The inter-model scatter ensues mainly from the range of surface emission estimates, whose uncertainty and inter-annual variation is sufficiently large. Meanwhile the studies implementing more comprehensive chemical schemes expectedly better constrain the methane source estimate owing to less ambiguous atmospheric CH_4 load and its OH-driven sink kinetics. Overall, these predict CH_4 to comprise at least one-third of the whole CO source. The reader is further referred to Table 6.3 for the detailed overview of the constituents and decisive parameters for CO turnover conferred in the abovementioned studies. There are a few noticeable extremes amongst these fairly congruent estimates, namely:

(1) Compared to the average given by other studies, the CH_4 sink in E04 is $\sim 15\%$ larger, which in conjunction with the relatively long methane lifetime of $\tau_{\text{CH}_4} \sim 10$ years points to the likely overestimated $[\text{CH}_4]$. A cross-evidence of the latter is the significantly larger CO burden and its longer lifetime, as a consequence of the smaller $[\text{OH}]$. A similar relationship is noted for P10, who uses the MOZART4 CTM and reports a lower hydroxyl radical abundance (Emmons *et al.*^[2010]). Opposite to E04 and P10, the results of REF and P07 simulate $\tau_{\text{CH}_4} \sim 8$ years, a CO lifetime at the lower and $[\text{OH}]$ at the upper ends of presented estimates. Nonetheless, larger $[\text{OH}]$ in EMAC yet results in smaller simulated CH_4 sink terms than those in the MOZART CTM, despite that all model setups utilise nearly identical prescribed (“nudged”) methane boundary conditions and $\text{CH}_4 + \text{OH}$ kinetics. While the reason for such inconsistency remains unknown, E04 appears to overestimate the input of methane to CO. Concerning remaining studies, their estimates fall within the above-mentioned range of τ_{CH_4} of 8 to 10.5 years yielding CO tropospheric lifetimes spanning from 48 to 60 days, respectively.

(2) The lowest contribution of the photochemical sources (0.4) in the overall CO is conferred by M97, as a consequence of the large reduction of the CH_4 source, hence the overestimated fraction of the surface component in their posterior estimates. Analogously, the largest fraction (0.54) of photochemically produced CO by P07 and REF is clearly an indication of the underestimated surface source strengths in the EVAL emission setup, later modified in AE and AEK. An appreciable increase of $\sim +9\%$ of the total CO source results in lower $[\text{OH}]$ and CH_4 source terms in AE; nonetheless, the overall photochemical CO source remains unchanged with respect to that of REF, being repartitioned between methane and VOCs oxidation.

(3) Finally, one remarks substantially different uncertainties given by the top-down and bottom-up estimates, respectively. It is specific to the inversion analyses to conclude uncertainties lower than those of the initial guess (*e.g.*, emissions), being constrained by much more certain observations. Thus, the *a priori* overall uncertainties of ± 79 and $\pm 123 \text{ Tg(CO) yr}^{-1}$ in M97 and B00, respectively, are decreased to *a posteriori* ± 58 and $\pm 31 \text{ Tg(CO) yr}^{-1}$, with a much greater reduction in B00 owing to the larger set of observational data. We note, however, that the *a priori* uncertainties in the inverse studies are taken at least by a factor of two smaller than those pertaining to the CO budget in EMAC, owing to much larger uncertainties in the bottom-up emissions propagating into the final model result (see also Sect. 5.2.7, p. 134). The uncertainties in superimposed $\delta^{13}\text{C}(\text{CO})$ in all studies are comparable though (*cf.* Table 6.4).

Table 6.4 Tropospheric ^{13}C isotope mass-balance from selected studies

Study	SW89	M97	B00	E04	REF	AE	AK	AEK
CO+OH KIE parameterisation	<i>conventional</i>				<i>composite</i>			
Total CO source [Tg(CO) yr^{-1}]	2800	2600 $\pm$ 58	2860 $\pm$ 31	2890	2525 $\pm$ 351	2754 $\pm$ 382	2525 $\pm$ 351	2754 $\pm$ 382
Tropospheric burden [Tg(CO)]		370	350	429	321	368	321	368
Overall sources $\delta^{13}\text{C}$ [‰]	-30.3	-31.1	-30.5	-34.9	-34.0	-33.1	-34.0	-33.1
Sink fractionation [‰]	+3	+3.1	+2.7	+4	+3.5	+3.5	+4.8	+4.8
Tropospheric $\delta^{13}\text{C}(\text{CO})$ [‰]	-27.4	-28.1 $\pm$ 1.5	-27.9 $\pm$ 1.1	-30.6	-30.5 $\pm$ 1.5	-29.6 $\pm$ 1.6	-29.3 $\pm$ 1.5	-28.3 $\pm$ 1.6
Bias [‰] ^a	+0.6	-0.1	+0.1	-2.6	-2.5	-2.6	-1.3	-0.3

Notes:

Abbreviations refer to those listed in Table 6.3; REF, AK, AE and AEK denote the simulations performed in the present study (see text). Given values are the annual tropospheric averages.

^a With respect to the top-down estimate of -28‰ taken as the average of the tropospheric $\delta^{13}\text{C}(\text{CO})$ inferred by M97 and B00.

6.1.6 Synopsis: New investigations and improvements in the present study

We conclude this reviewing part of the chapter briefing the questions on atmospheric isotopic CO addressed here to complement the findings of the previous studies, also enumerating the model improvements introduced. These are, *viz.*:

- Revisiting the methane source of CO: EMAC uses a sufficiently more detailed chemistry scheme equipped with an additional diagnostic of the $\text{CH}_4 \rightarrow \text{CO}$ chain. In particular, the yields of CO from the photochemical sources are examined and a more adequate reproduction of the CH_4 -derived CO component is anticipated (Sect. 6.2.2.1).
- Non-methane sources of CO: A reassessment of the carbonaceous precursors' surface emissions and their isotope composition is made, with improvements of the biosphere-related constituents and an adequate analysis of the uncertainties (Sects. 5.2, 6.2.2).
- In-situ isotope fractionation in precursors of CO: Prior to the present study, no attempts to look into the kinetic isotope effects of the removal processes of the atmospheric carbonaceous tracers were made. An additional sensitivity study probing the removal processes efficiency in EMAC has been performed (Sect. 6.2.4).
- Revisiting the CO+OH KIE: A reassessment of the isotope fractionation escorting the atmospheric sink of CO via the hydroxyl radical is proposed through comparing the conventional (pressure-dependent) and new composite (pressure- and temperature-dependent) KIE parameterisations implemented in EMAC (Sect. 6.2.5).
- Expanded observational data: A more complete series of background station data are analysed (Sect. 4.1) and used for the evaluation of the model results, compared to the previous studies. An emphasis is put on the ETSH compositions insufficiently scrutinised to date. For the first time, the unique aircraft observations of CO isotopes from CARIBIC platform are included (Sect. 4.2).
- Use of dedicated sensitivity studies: The individual contribution of every component modifying the final atmospheric $\delta^{13}\text{C}(\text{CO})$ is inferred directly (see Sects. 6.2.1). This is favourable when a sophisticated modelling setup is used, and indispensable for studying the combined effect of non-linearly coupled processes, *e.g.* the chemical interaction (including the isotope effects) of the tracers and their transport and mixing in the atmosphere.
- In addition to the stable carbon isotopes, for the first time the simulation of the anomalous stable oxygen isotope composition (*i.e.* $\Delta^{17}\text{O}$) of CO and the related atmospheric tracers is undertaken in the present study (see Sect. 6.2.8).

6.2 3D model simulations with EMAC

This section presents the highlights of the results obtained in the 3D model simulations with EMAC. The overview of the model setups and simulations including stable carbon isotopes (Sect. 6.2.1) is followed by the comparison of the model results with the observational data in Sect. 6.2.7 (p. 199). The analysis of the simulated anomalous isotope oxygen composition is presented in the closing Sect. 6.2.8 (p. 210).

6.2.1 Overview

The model simulations performed with EMAC are listed in Table 6.5 (p. 165) and generally categorised as the control and sensitivity simulations. The former represent the model results that pertain to the initial (also called reference, “REF”) and improved (denoted as “AEK”, see below) model setups that contrast the modifications eventually leading to the significant amendments of the simulated characteristics, first of all the stable carbon isotopologues of CO. The latter, sensitivity simulations, describe individual setups probing several aspects of the atmospheric system surmised being crucial for CO. Some of the model setups serve as the base setup for the other ones, however, they all ultimately originate from REF to make the comparison between them consistent. The graphic presented in Figure 6.4 (p. 165) aids the reader in tracing back the origin of every model setup. It also ascribes particular setups to the aspects regarded, *e.g.* one reads that the simulation DEP investigates the kinetic isotope effects in conjunction with the removal processes in the atmosphere. Of the listed aspects, “ZERO” denotes the special set of simulations designed to investigate the intertwined alteration of the tracers’ isotope ratios due to the isotope effects and transport processes in the atmosphere, but not owing to the variations in the isotope composition of the emissions. To achieve this, the isotope ratios of all emitted tracers were set to 0‰ with respect to the given isotope standard, which coined the abbreviation. Similarly, the abbreviations of the setups starting with “A” (for *a*djusted, or *a*mmended) and “S” (for *s*ensitivity) are chosen to help the reader in recollecting an individual setup or simulation.

Table 6.5 further lists the tagging configurations employed in each simulation. Thus, abbreviations “IC” and “AO” denote that the stable isotope carbon and oxygen composition were simulated, respectively (see Sect. 5.1.4.1, p. 113 for details). Because these two substantially large configurations induce high computational strain, they were usually simulated separately, however including the diagnostic configurations listed (FM/FN/FI). An exceptional case is the set of ZERO simulations (Z/ZE/ZK), in which the configurations were employed simultaneously to study the evolvement of both ^{13}C and ^{18}O effective isotope enrichments in tracers undergoing the same atmospheric dynamics. The model analysis with EMAC presented here is thus comprised of sixteen control/sensitivity simulations. In addition to those, a set of test simulations based on REF setup were conducted in order to elucidate the sensitivity of the simulated characteristics for the key species¹²¹ to the selected model resolution and atmospheric dynamics.

¹²¹Those are CH_4 , isoprene, CH_3OH , CO, HCHO, O_3 mixing and isotope ratios, *i.e.* the respective $\delta^{13}\text{C}$ and/or $\Delta^{17}\text{O}$ characteristic.

Table 6.5 List of EMAC simulations performed within this study

Abbr.	Description	Main goals / Differences with base setup	Base setup	Tagging conf.
<i>Control simulations</i>				
REF	Reference simulation	Introduction of the stable C and O isotopes extension, incl. deposition effects, $^{13}\text{C}/^{12}\text{C}$ ratios and $\Delta^{17}\text{O}$ in emissions; diagnostic tagging of the chemical mechanism	EVAL ^a	IC, AO, FM, FN, FI
AEK	Improved setup	Aggregate of amendments introduced by the AE and AK setups	AK/AE	"
<i>Sensitivity simulations</i>				
AE	<u>A</u> ddjusted <u>E</u> missions	Improvement of the simulated remote NH [CO] / Increased emissions of CO and NMHCs over India and China	REF	"
AK	<u>A</u> ddjusted (revised) <u>K</u> IE	Improvement of the simulated CO isotope composition / An improved (composite) CO+OH sink KIE is implemented	REF	"
<i>Carbon isotope effects</i>				
Z	" <u>Z</u> ERO"	Estimation of the sink fractionation effects on $\delta^{13}\text{C}(\text{CO})$, $\delta^{18}\text{O}(\text{CO})$ and $\Delta^{17}\text{O}(\text{CO})$ / All CO sources are set to $\delta^{13}\text{C} = 0\text{‰}$, all KIEs except for CO+OH are switched off	REF	IC, AO, FM, FN, FI
ZK/ZE	Z for AK/AE	Same as "ZERO", but for the revised emissions/CO+OH KIE	AK/AE	"
DEP	Deposition effects	Estimation of the isotope effects related to the deposition of atmospheric tracers / All chemical KIEs are switched off, all removal KIEs are switched on	REF	IC, FM
<i>Other (sensitivity) simulations</i>				
SMK	<u>S</u> ensitivity to <u>m</u> ethanol <u>K</u> IE	Probing the effect of uncertain KIE in reaction of methanol with OH ($^{13}\text{C}_{\text{CH}_3\text{OH}+\text{OH}} = +31\text{‰}$) on $\delta^{13}\text{C}(\text{CO})$	REF	IC, FM
SBE	<u>S</u> ensitivity to <u>b</u> iofuel <u>e</u> mission signature	Probing the alternative emission isotope composition / Tracers' bio-fuel emission $\delta^{13}\text{C}$ is changed from -25‰ to -12.9‰	REF	IC
SR2/SRU	<u>S</u> ensitivity to doubled/ <u>u</u> pper-limit <u>r</u> emoval	Probing the sensitivity of the simulated budgets to the removal processes / Doubled and ~quintupled removal efficiency applied	REF	FM

Notes:

Abbreviations refer to the Isotope Carbon (IC), Anomalous Oxygen (AO), carbon fraction (FM/FN/FI) tagging configurations (see Sect. 5.1.4.1, also Table 5.3 on p. 114). Except for Z, the configurations IC and AO were usually simulated separately (see text).

^a) Refers to the setup of the re-evaluation simulation EMAC2 (Jöckel *et al.*^[2010]), see details in Sect. 5.1.2 (p. 108).

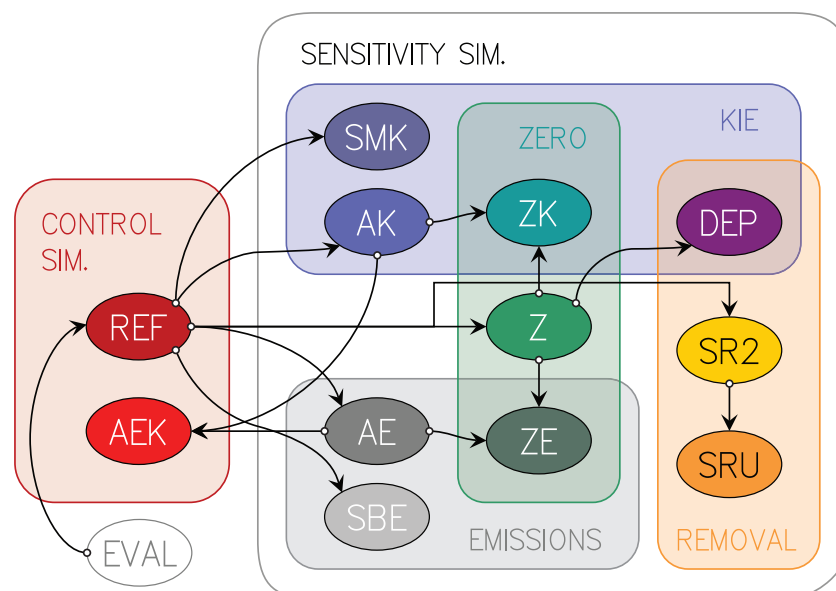


Figure 6.4 (complements Table 6.5) Overview of the EMAC simulations performed within the current study, their hierarchy and relation to the problems studied, *viz.* chosen emission setup, kinetic isotope effects (KIE) and removal processes. Arrows designate which setups contributed to the particular simulation performed. Thus, EVAL refers to the EMAC evaluation simulation setup used as the base model setup for the reference simulation REF here (see Sect. 5.1.2).

Regarding the former, choosing a coarser horizontal resolution conformably yielded a reduced spatial variability of the isotopologues' burdens and ratios having, however, little influence on the simulated averages (annual and monthly were compared), specifically in the tropospheric domain¹²². Being of small dependency on the chosen horizontal resolution, an overestimated vertical mixing in the troposphere was seen at all tested vertical resolutions (L19, L31ECMWF, L39MA and L90MA), which was also confirmed for the CO isotope ratios in comparison with the aircraft data (see further Sects. [406] and 6.2.7.3, pp. 203–206). The test simulations were furthermore benchmarked to assess their overall accuracy with respect to the numerical integration effort. The best computational benefit was achieved with the T42L31ECMWF resolution, which was therefore opted for the production simulations. This decision was partially supported by the results of Aghedo *et al.*^[2010] who evaluate a comparable, well reproduced chemical tracer transport in simulations with the ECHAM5 GCM using the less expensive T42L31 and more realistic T63L31 resolutions, respectively.

Test simulations were also used to investigate whether the simulated species' averages/variabilities are comparable under the different modes of the simulated atmospheric dynamics, *viz.* relaxed towards the observations¹²³ ("nudged") and not ("free-run"). Importantly, both the model setup and observational data need to be brought into a common framework in order to be compared consistently. For instance, current model emission data represent the estimates for the year 2000 (see the details on the emission setup of EMAC in Sect. 5.2). To match this period, the sporadic observational data on CO isotopes (that pertain to the different time frames prior to and beyond 2000) were analysed and processed to create the "climatological" dataset for comparison, with the representative values being the monthly median and intra-monthly variation (IMV¹²⁴, denoted hereinafter also with σ_m) that are in turn to be compared with the corresponding simulated characteristics. Somewhat analogous "representativeness" tests for the simulated tracer abundances/isotope ratios were conducted with the test simulations. Thus, the REF and Z setups were integrated throughout a decade (1996–2005), each with the 'perpetual' emission scenario for 2000 in free-running mode, and with the transient emissions in the regime with atmospheric dynamics relaxed towards the observations.^{123,125} Further, for the key species and their isotope ratios¹²¹ the IMV $\sigma_m(n_y)$ as a function of the number of simulated years n_y was derived. For example, at $n_y = 4$ and January, $\sigma_m(n_y)$ equals the IMV of a given characteristic simulated in all Januaries in a four-year period, *e.g.* the statistic is gathered throughout 1997–2000 (or any other set of four different years considered). Values of σ_m at the various model domains¹²² and at the model grid cells corresponding to the location of the observational data were analysed.

The results assert that $\sigma_m(n_y)$ typically increases with n_y until reaching a certain "saturation" value at a given number of years n_s . The latter denotes the typical period throughout which the model reproduces the largest possible IMV resulting from relevant atmospheric processes. Interestingly, comparable n_s values were found for the sets of both, sequentially and randomly picked years, constrained between 3 and 4 for the mixing ratio of CO. For the simulated $\delta^{13}\text{C}(\text{CO})$ values, n_s is on average one year less for the Z setup compared to REF due to the larger IMV driven by the variations in the emissions, whereas the Z setup was probing only the effective enrichment in the tracers, *i.e.* mostly the IMV due to atmospheric dynamics. Secondly, test simulations with the "nudged" dynamics/transient emissions showed generally larger $\sigma_m(n_y)$ than those in the "free-running" modes, however, only for the mixing ratios. The respective $\delta^{13}\text{C}(\text{CO})$ IMV, on the contrary, remained comparable: The enhancement of the [CO] IMV was predominantly associated with the regions of large emissions, which, being characterised by similar $\delta^{13}\text{C}$ values, had smaller relative impact on the respective isotope ratios' variation. At last, all test cases were analysed in the period excluding the years 1997–1998, when the large biomass burning-related global-scale perturbation to [CO] has occurred; noteworthy, the observational data from this period were discarded from the time series used for the comparison here (see above, p. 69, also throughout Sect. 4). In this case, the respective $\sigma_m(n_s)$ for CO mixing and isotope ratios from both, the "nudged" and "free-run" simulations were found in a close agreement at the n_s of 4 years and above. Alike for the IMV, the monthly climatological medians for [CO] showed a larger relative divergence than those for $\delta^{13}\text{C}(\text{CO})$, however for both setups they never exceeded one-half of the respective σ_m value.

¹²²The analysed domains and averaging used are enumerated in Appendix D (p. 255).

¹²³The ECMWF operational analysis data is implied (see details in Sect. 5.1.1, p. 107).

¹²⁴The term intra-monthly variation denotes here the IQR of the given characteristic (*e.g.*, [CO] observed or simulated) in a particular month. It is also applied to characterise the variation in the station data, as detailed in Sect. 4.1.1, see also Table 4.2 (p. 72) and note⁴⁸.

¹²⁵Transient emissions imply the variable biomass burning emission component (spans 1997–2005) on top of other components estimated for 2000. The emission data for the test simulations' spin-up year (1996) were set to the 'perpetual' 2000 conditions.

Based on the above analysis, the sufficient integration period for the production simulations was determined to be 1998–2002, with the first year dedicated to the model spin-up. The tracers' climatological means for January 1999–2005 obtained in the test simulations were used as the initial conditions for the control simulations, and, after the appropriate adjustments (*e.g.* setting the initial tracers' $\delta^{13}\text{C}/\Delta^{17}\text{O}$ to 0‰ in Z setups), for the sensitivity simulations. Unless stated otherwise, the model results are presented hereinafter for the simulated climatological monthly means and corresponding IMVs, respectively. Exceptionally, the error bars given to the presented annual averages (*e.g.* in the zonal average plots) denote the span of the corresponding monthly means. The quoted averages for the tracer mixing ratios, chemical yields, production/sink terms are air mass-weighted. The averages of the isotope ratios and effective enrichments are additionally weighted by the mixing ratio of the corresponding tracer. Last but not least, the detailed results for the selected characteristics simulated with EMAC are presented in figure plates aggregated in Appendix D separately (p. 255). For conciseness of presenting the results, the reader is often referred to these. The following sections highlight the particularities of the setup and findings pertaining to each simulation.

6.2.2 Control simulations (REF, AEK)

In order to ascertain that the changes introduced in the isotope-enabled setup of EMAC does yield adequate results, the abundances of the key species¹²¹ simulated with REF were examined to be in a close agreement with those reproduced in the EVAL simulation (see Sect. 5.1, p. 109, also note⁷⁷). Regarding CO, the comparison of the observed (NOAA/ESRL) and simulated (REF) near-surface mixing ratios conformably reveals discrepancies much similar to those detailed by Jöckel *et al.*^[2010] (Sect. 9.2). In particular, winter-spring [CO] simulated by EVAL/REF in the high northern latitudes is underestimated substantially (up to 40 ppb, or ~22% of the expected seasonal maximum value). A systematically low [CO] was simulated at the mid-latitude NH locations as well (see *ibid.*, Sect. 4.1 in the supplementary material). Although a moderate sensitivity of CO to the biomass burning emissions in EVAL was inferred, the anomalies reproduced in the simulations with climatological and transient biomass burning emissions were found poorly correlated. From that, Jöckel *et al.*^[2010] concluded that other factors (*e.g.* underestimated anthropogenic emissions) are likely responsible for the missing ETNH CO. Another inquiry into the CO simulated with EMAC1 was conducted by Pozzer *et al.*^[2007] (P07), who probed the effect of nearly doubling the fossil fuel emissions of CO over India and China. The resulting increase of 36 Tg(CO)/yr (or ~2.2% of the overall NH CO source) had, however, a comparably small effect on the resulting background [CO], and primarily over the Northern Pacific. P07 conclude that a strong evidence for the missing, although not clearly quantifiable, Chinese CO emissions exists.

The above-mentioned discrepancy is manifested in the comparison of REF with the isotope CO data, too. Shown in Figure 6.5, the surface and MBL zonal averages of [CO] present a similar seasonal variation north of 70°N, with the maxima and annual averages underestimated by ~30 and ~10 ppb with respect to the background levels, respectively.¹²⁶ Regarding the mixing ratios simulated at particular stations (black symbols), the missing CO amounts on average to at least 20 ppb at BAR, IZA, SBK, ALE and SPI, *i.e.* at all stations pertaining to the background and remote conditions (see above, p. 71 in Sect. 4.1.1). As the average NH [CO] drops towards the equator, the relative missing component can be quantified to be ~11% at ALE/SPI, ~15% at SBK and nearly 20% at BAR/IZA, which is up to an order of magnitude larger than the increase considered by P07. Projected onto the overall NH CO source reckoned in REF (see Table 6.3, p. 158), a rough calculation yields an average underestimated CO source of ~214 Tg(CO)/yr, conformably. We note again that the discrepancies seen at the background locations point at the global CO component missing. Regarding the ETSH [CO], the simulated MBL abundances are slightly higher (by 4–5 ppb, though also ~10% of the averages) than those observed for 2000, and are in agreement with the 20-year climatology. This is consistent in view that the lowest biomass-burning emissions throughout 1997–2005 were reckoned for 2000 (Randerson *et al.*^[2007]) and shown results are the climatological averages. The excellently reproduced ETSH annual variation of 25 ppb is nonetheless a robust indicator for the SH CO characteristic for the period around 2000.

In order to achieve the simulated NH [CO] levels adequate for the isotope ratios comparison, several adjustments to the direct (surface) emissions of CO and its precursors in REF were considered. As discussed below (see Sect. 6.2.3.1), the best matching results for [CO] were found with the increased anthropogenic emissions from India and China, which adds some 229 Tg(CO) yr⁻¹ (or ~14.3%) to the overall NH CO source in

¹²⁶The detailed distributions of CO mixing ratio and $\delta^{13}\text{C}(\text{CO})$ simulated in REF are presented in Plates D.1 and D.2 (pp. 256–258).

REF, and is the best option that delivers the adequate reproduction of the Arctic BL CO mixing ratios in EMAC. This adjustment was further incorporated into the AE (“adjusted emission”) and subsequently AEK setups (see Table 6.5). The CO resulting from the AE simulation (shown in Figure 6.5 with dotted curve) has a conformably larger NH abundance, with the average MBL mixing ratios above 40°N being ~20 ppb higher than that in REF. A comparable enhancement in [CO] is marked for the annual variation, mostly at the expense of the winter/spring maxima. Regarding the simulated station data, the improvement is seen for all NH locations, particularly for the background/remote stations (IZA, SBK, ALE/SPI), yet with slightly underestimated annual amplitudes. In the ETSH, a 1–2 ppb increase in the respective [CO] appears to be small; however, changes to the respective $\delta^{13}\text{C}(\text{CO})$ simulated in AE (see below, Sect. 6.2.3) ascertain that a substantial amount of Indian and Chinese CO is being exported from the tropics, but barely survives the encounter with abundant tropical and sub-tropical OH.

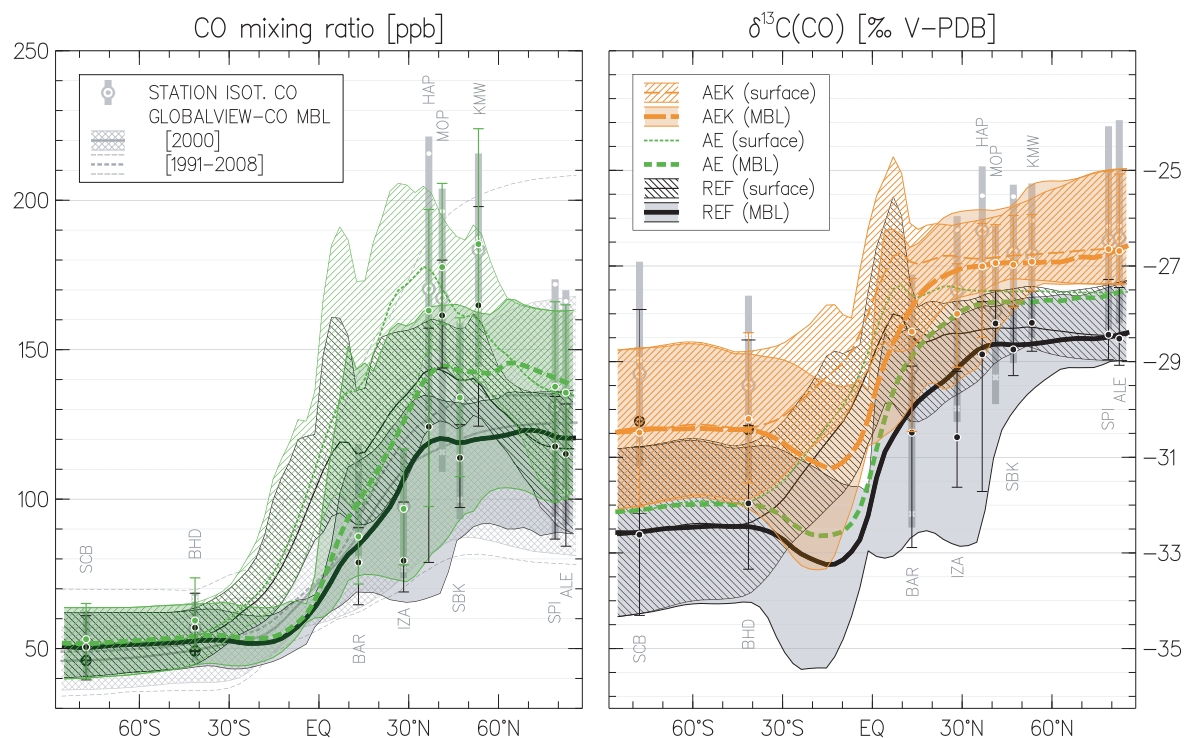


Figure 6.5 CO mixing ratio and $\delta^{13}\text{C}(\text{CO})$ simulated in REF, AE and AEK simulations. Lines refer to the zonal averages in the MBL (thick) and at the surface (thin). Grey curves and symbols refer to the climatology of the MBL [CO] from the NOAA ESRL GLOBALVIEW-CO product and isotope CO data from the surface stations, respectively (see Figure 4.7, p. 83, for references). Symbols denote the values simulated at the locations of the surface station data in respective setup. The CO mixing ratios simulated in AE and AEK are identical.

On top of the discrepancies seen in [CO], a substantially larger underestimation of the relative ^{13}C abundance is marked in REF (shown in the right panel of Figure 6.5). Thus, the simulated station $\delta^{13}\text{C}(\text{CO})$ is typically low by (2–2.5)‰ and (3–3.5)‰ in the NH and SH, respectively, including the polluted NH locations (HAP, MOP, KMW). Whereas for the NH the discrepancy may pertain to the underestimated emissions, an even larger missing ^{13}C component on top of the adequately simulated [CO] in the ETSH presents an exceptional case. That is, the model may crucially underestimate one or more key factors determining the isotope CO composition in the atmosphere.¹²⁷ To scrutinise these, the sophisticated chemical mechanism of EMAC was equipped with the diagnostic tagging to quantify the simulated tracers’ photochemical components and transformations exactly. Thus the integrals and distributions of the sink, production and chemical yields from the oxidation of methane (CO_M), non-methane hydrocarbons (CO_N) and isoprene (CO_I) were derived for CO. Likewise, the share of the remaining surface-emitted carbon monoxide (CO_S) was inferred. Such component-wise budgeting allowed further deriving the approximate (bottom-up) uncertainties $\langle \text{CO} \rangle$ and $\langle \delta^{13}\text{C}(\text{CO}) \rangle$ propagating into the simulated CO mixing and isotope ratio from the uncertainties associated with the strength

¹²⁷ Reviewed in Sects. 6.1.1–6.1.4 (see also Figure 6.1, p. 141).

and isotope composition of each source, respectively.¹²⁸ The resulting $\langle \text{CO} \rangle / \langle \delta^{13}\text{C}(\text{CO}) \rangle$ simulated in REF are presented in Figure 6.6; these peak at 100–200 ppb/2.0–2.4‰ in the areas subject to intensive surface emissions, as the latter bear the largest strengths and $\delta^{13}\text{C}$ uncertainties. Actually, the overall $\langle \text{CO} \rangle$ is mainly determined by the mixing ratio variations in the CO_S , CO_N and CO_I components, whose large individual uncertainties (equivalent to (60–200)%, see Table 5.11, p. 137) oppose the low $\langle \text{CO}_\text{M} \rangle$ (below 1%, respectively). For example, between the ETNH and ETSH, the average $\langle \text{CO} \rangle$ relates as ~3:1 (BL) and ~2:1 (FT), or strictly proportional to the share of the non- CO_M components. For $\langle \delta^{13}\text{C}(\text{CO}) \rangle$, however, this relationship holds at different values owing to less diverse uncertainties of the sources' $\delta^{13}\text{C}$ signatures, and equals ~1.5:1 and ~1.3:1, respectively. The MBL averages of $\langle \text{CO} \rangle$ are much more moderate than those over land, although hardly below the considerable 20% of $[\text{CO}]$ in both hemispheres. The lowest values (~17 ppb/~0.9‰, respectively) are found in the Southern Pacific BL, where the methane-derived CO_M (it is characterised by the least uncertain $\delta^{13}\text{C}$ signature) is the largest contribution to the overall CO abundance. For instance, the detailed results (see, *e.g.*, Plate D.4, p. 262) suggest that the observations made around March in the area enclosed within 180°N–120°N and 15°S–30°S (roughly between Samoa and Cook Islands) can provide the most accurate comparison for the CO ensuing from the emission inventory and atmospheric dynamics in EMAC. Essentially, with the simulated $\langle \text{CO} \rangle$ below 9 ppb and $\langle \delta^{13}\text{C}(\text{CO}) \rangle$ below 0.7‰ there, the model $\delta^{13}\text{C}(\text{CO})$ has the largest sensitivity to CO_M . Analogously, the isotope composition of formaldehyde measured in this region may provide the best estimate for the $\delta^{13}\text{C}/\delta^{18}\text{O}$ signatures of the $\text{CH}_4 + \text{OH}$ oxidation source.

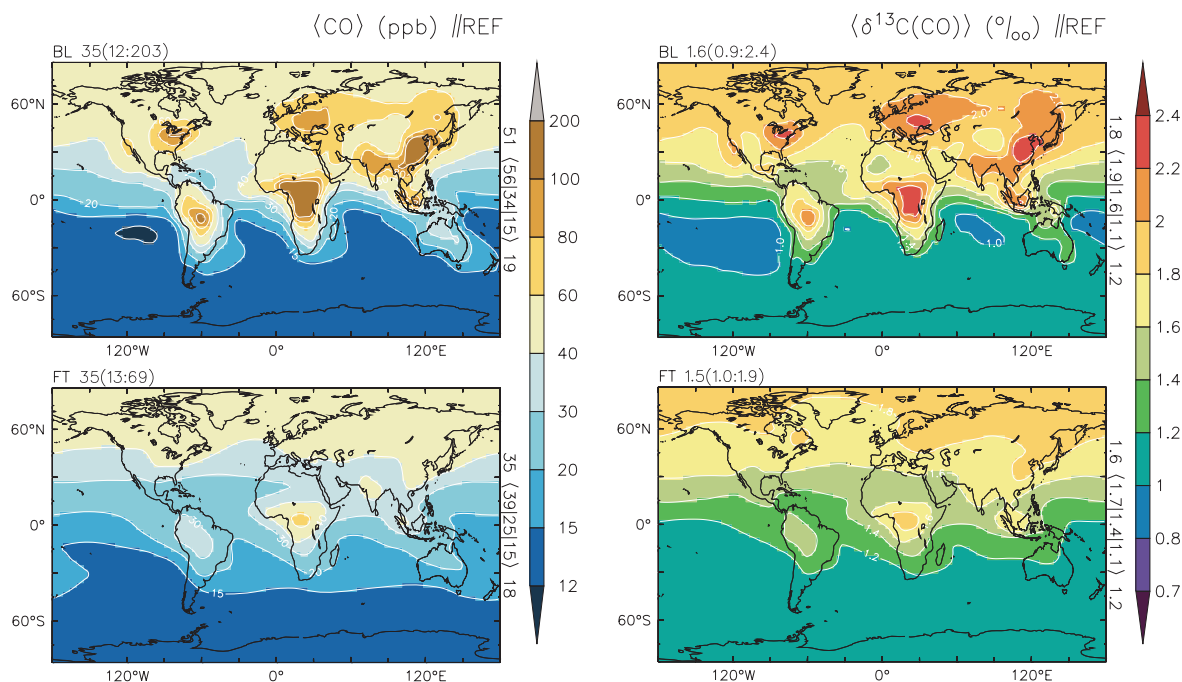


Figure 6.6 Bottom-up estimates of the uncertainties in the CO mixing ratio (left) and $\delta^{13}\text{C}(\text{CO})$ in the boundary layer (upper panels) and free troposphere (lower panels) simulated in REF. Annual averages are shown. See Figure D.1 (p. 255) for the legend.

6.2.2.1 Photochemical yields of CO

Ironically, the least uncertain $\delta^{13}\text{C}$ signature and the largest ambiguity in the simulated $\delta^{13}\text{C}(\text{CO})$ are associated with the same CO_M component. That is because the CO stemming from the oxidation of CH_4 is largely depleted in ^{13}C compared to the other, relatively enriched, sources. The balance between the former and the latter chiefly determines the $\delta^{13}\text{C}$ of the overall CO source: The smaller the contribution of CO_M , the larger the resulting $\delta^{13}\text{C}(\text{CO})$ entering the atmospheric reservoir. As earlier modelling studies conjecture (see Sect. 6.1.1), a reduction of the CO_M share (with a corresponding increase in the other sources) to 0.7–0.8 of its value simulated in REF matches the observed ETSH $\delta^{13}\text{C}(\text{CO})$. In absolute terms, this is equivalent to some 7.2–4.8 ppb of CO_M repartitioned into other sources, yet too small to be unambiguously singled out with

¹²⁸The emission uncertainty analysis follows that described in Sect. 5.2.7 (p. 134). The detailed distributions of $\langle \text{CO} \rangle$, $\langle \delta^{13}\text{C}(\text{CO}) \rangle$ and each CO component simulated in REF are shown in Plates D.3–D.8 (pp. 260–270).

EMAC, considering the average $\langle \text{CO} \rangle$ of ~ 20 ppb in REF. On the other hand, the kinetics and distribution of CH_4 and OH dictate that the reduction of CO_M is only possible assuming a conformably lower (*i.e.*, of 0.7–0.8) chemical yield (λ_{CH_4}) of CO from CH_4 . The simulations with EMAC suggest that the λ_{CH_4} matter is somewhat more complex, as described below.

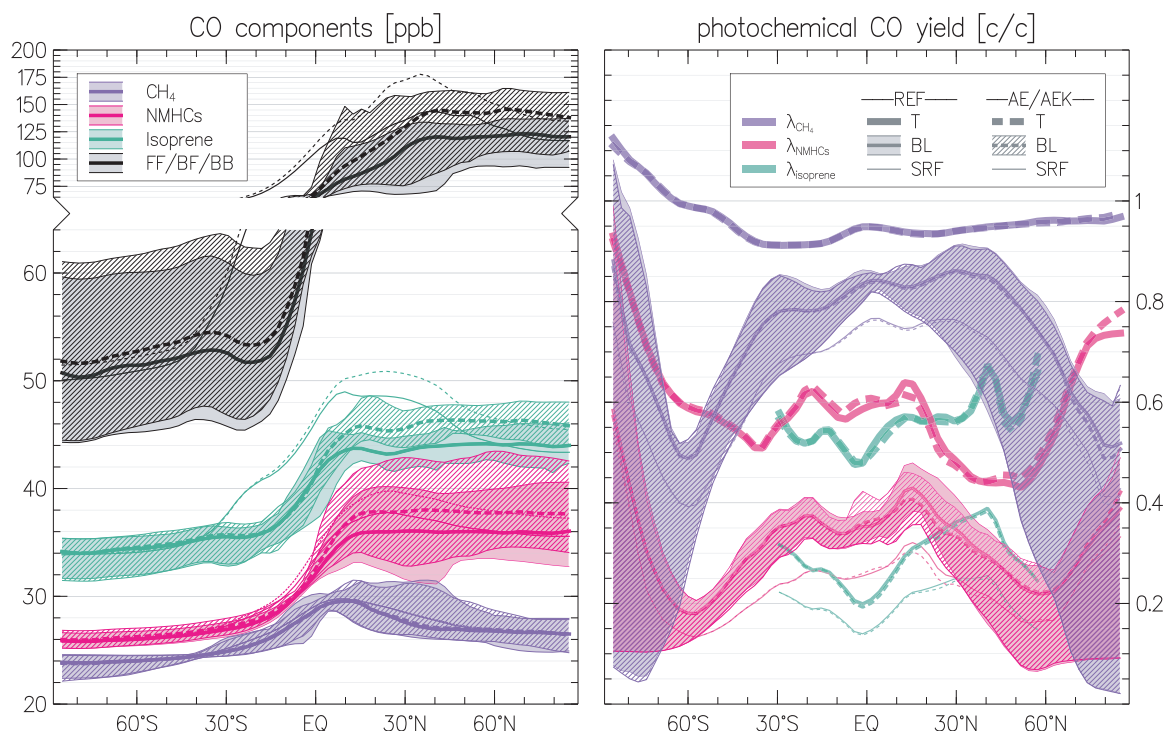


Figure 6.7 Left: Zonal averages of the CO photochemical/surface components simulated with EMAC. Shown values are stacked, *e.g.* the exact surface component equals the difference between the black and green curves, respectively. The upper and lower axes' scales relate as $\sim 10:1$. Thick and thin lines refer to the BL and surface averages, respectively. Right: Zonal averages of the photochemical yields of CO from the methane, non-methane hydrocarbon and isoprene oxidation sources. Thin, medium and thick lines denote the surface, BL and tropospheric averages, respectively. Solid and dashed lines refer to the REF and AE/AEK simulations, respectively. The error bars denote the annual variation of the monthly averages. Units [c/c] denote that the yields are calculated on a per carbon basis.

In Figure 6.7, the meridional profiles of the simulated CO components and photochemical yields λ for CO from CH_4 , NMHCs and isoprene oxidation sources are presented.¹²⁹ The averages of λ progressively increase with altitude as one regards the surface, BL and tropospheric domains. This is partly explicable in terms of the removal processes' (RPs) location, *i.e.* the intermediates of the CO production chains are efficiently removed in the lowest layers (wet scavenging) and at the surface (dry deposition). Noteworthy, the intensity of the latter simulated in EMAC is about an order of magnitude larger than that of the former globally (see Sect. 5.1.5, p. 114). Nonetheless, the efficiency of the intermediates' photochemical processing and/or transport in a given region were found to be much more important factors determining the spatial distribution of λ , than the efficiency of the RPs. Thus, contrasting its monotonic vertical gradient, the horizontal variations in λ_{CH_4} in the BL closely correspond the changes in the chemistry regimes: The relatively high values of λ_{CH_4} around 0.8 spanning between 30°S–60°N are associated with the available OH and HO_2 (as well as NO_y in the NH) that propel the rapid conversion of CH_4 into CO (see also Figure 6.8, panel (b)). The intermediates outside these latitudes are more likely to be scavenged out/transported away before they react to CO. For instance, the lowest λ_{CH_4} averages seen in the BL around 60°S are due to the efficacious convective transport of the intermediates over the oceans. Around one-half of the reacted CH_4 carbon at this latitude is uplifted in form of formaldehyde and methanol to the free troposphere. The estimated contribution of these species to the local λ_{CH_4} value amounts to 0.13 and 0.38, respectively, and clearly reflects a $\sim 1:3$ proportion of their mixing ratios.

¹²⁹The detailed distributions of λ_{CH_4} and λ_{NMHCs} diagnosed in REF are shown in Plates D.9 and D.10 (pp. 272–274).

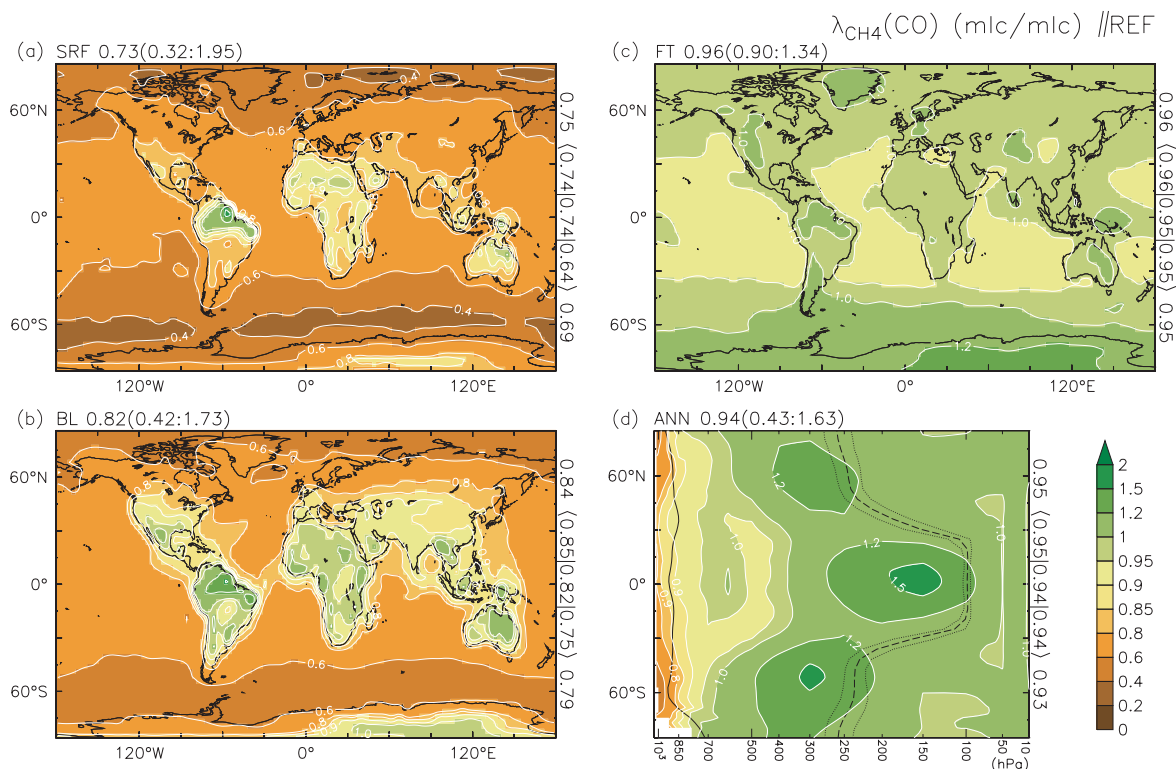


Figure 6.8 Distribution of the photochemical yield λ_{CH_4} of CO from methane simulated in REF. Panels (a)–(c) refer to the surface, BL and FT averages, respectively. Panel (d) shows the zonal averages in vertical direction. Annual averages are shown. See Plate D.9 (p. 272) for the details and Figure D.1 (p. 255) for the legend.

The effect of the intermediates' vertical transport is marked in the free tropospheric CO yields above unity, allocated in accordance with the general circulation pattern, as shown in Figure 6.8, panel (d) (see additionally Plate D.10, p. 274, for λ_{NMHCs}). As such, λ_{CH_4} values of 1.2–1.6 found within the ITCZ and at the verge of the Ferrel and Polar cells are not an artefact, but an indication that locally the production of methane-derived CO exceeds the destruction of CH_4 by (20–60)%, respectively. Averaged over the entire tropospheric domain, however, the integral λ_{CH_4} value amounts to 0.94 and appears to be a very robust characteristic in EMAC.¹³⁰ The total reduction of the CO_M component is therefore of very moderate 6%, and is accounted to the surface/BL RPs, whereas the large spatiotemporal variations in λ_{CH_4} are mostly caused by the transport processes and changes to the photochemical regime. Regarding the NMHCs and isoprene sources, substantially lower integral tropospheric CO yields of 0.53 and 0.55 were diagnosed, respectively, calculated on a per carbon basis. That is, one $\text{C}_5\text{H}_8/\text{NMHC}$ molecule reacted produces on average 2.7 molecules of CO in the chemical mechanism of EMAC (MIM). Both non- CH_4 chains have much comparable CO yields because they share a large set of intermediates, in particular HCHO , CH_3OH , CH_3CHO and CH_3OOH that are predominantly subject to the removal through deposition and scavenging (see Sect. 5.1.5.3, p. 117). Whereas the estimate of λ_{NMHCs} in EMAC is obtained here for the first time, the result for $\lambda_{\text{isoprene}}$ corroborates earlier budgeting of MIM in EMAC1 by Butler *et al.*^[2008] and is slightly more accurate, being direct. An earlier estimate of $\lambda_{\text{isoprene}}$ for MIM in MATCH-MPIC CTM by von Kuhlmann *et al.*^[2004] is about 50% lower than that in EMAC, and may be a shortcoming of the indirect assessment approach these authors used.

By matching the differences between the surface/BL and overall tropospheric λ values, one can infer a rough estimate of the average lifetime of the intermediates in each CO production chain against the deposition processes or export from the BL. Thus, the 'transport residue' in the BL λ values is reckoned at 0.21 for λ_{CH_4} , 0.28 for λ_{NMHCs} and 0.36 for $\lambda_{\text{isoprene}}$, taking the global averages. This denotes, *e.g.*, that the conversion of carbon (or, analogously, the lifetime of the longest-living intermediate in the chain against the removal by transport) in the isoprene $\rightarrow$ CO chain is about 27% and 69% faster (analogously, shorter) than that in the NMHCs $\rightarrow$ CO and $\text{CH}_4 \rightarrow$ CO chains, respectively. Nonetheless, these are the global average estimates; the intertwined effects of the emission, RPs and transport/mixing on a large set of tracers generate much different distributions for each

¹³⁰ See below Sect. 6.2.4 on the model sensitivity to the efficiency of the removal processes parameterization.

λ . Hence, the estimates above are expected to vary substantially for different locations and/or timeframes regarded.

We recur to the methane-derived CO component determining the $\delta^{13}\text{C}$ of the overall atmospheric CO source. The simulated overall λ_{CH_4} value of 0.94 suggests that the reduction to the tropospheric CO_M is minor; can, nonetheless, the local values of 0.7–0.8 significantly affect the respective $\delta^{13}\text{C}(\text{CO})$ in the BL? Importantly, the large horizontal and vertical gradients in λ_{CH_4} (*e.g.*, from ~ 0.7 at the surface up to ~ 1.0 at around 500 hPa altitude, see Plate D.9, panels (u)–(w), p. 273) have a marginal effect on the corresponding distribution of CO_M , as EMAC results confirm. Therefore, a reduction in the near-surface CO_M that, as a surmise, might have had a positive effect on the station $\delta^{13}\text{C}(\text{CO})$, can be singled out. A slight (within 3–5 ppb/month in tropics and ET summer) lowering in the surface CO_M production due to the RPs was diagnosed globally in REF (not shown), however it affects the vertical distribution of CO_M only in the tropics as a ~ 1 ppb reduction at the surface (see Plate D.5, panels (u)–(w), p. 265). The reason for this is the increase in the CO chemical lifetime, τ_{CO} , as one goes from the tropics toward higher latitudes: Once τ_{CO} surpasses the characteristic CO atmospheric mixing lifetime¹³¹, the transport and vertical mixing start efficiently levelling off the BL CO inventory. A conspicuous case of that is the background CO in the ETS¹³¹ found well mixed throughout the entire troposphere (see, *e.g.*, Seiler and Fishman^[1981], Fishman *et al.*^[1987], Marengo *et al.*^[1989]). A similar, strongly mixed ETS¹³¹ CO_M is simulated in REF up to ~ 500 hPa, at the average of 24.5 ppb (23.8 ppb above 40°S) and temporal and latitudinal variations not exceeding ± 1 ppb and ± 1.5 ppb, respectively (see Plate D.5, p. 265). The mere fact that CO is efficiently mixed in the in ETS¹³¹ renders the “low λ_{CH_4} ” hypothesis less plausible, as the larger methane-derived CO component from the FT (where λ_{CH_4} is generally higher) is expected to dilute the BL average to a higher value. Recapitulating, the largest discrepancy in ^{13}CO simulated in REF pertains to the domain most sensitive to CO_M , however our current understanding, as well as the modelling approach to the atmospheric chemistry and removal processes, strongly suggest it is unlikely to be caused by the overestimated yields of CO from atmospheric CH_4 .

To seek for the missing ^{13}CO , two other key factors determining atmospheric $\delta^{13}\text{C}(\text{CO})$ were scrutinised in this model study, *viz.* chosen surface emissions, and effective isotope fractionation of CO and its precursors in the atmosphere. Regarding the former, a better matching emission inventory was proposed in the AE setup of EMAC. As briefly outlined above, it allows a consistent comparison of the CO isotope ratios simulated in the NH; it also has non-negligible implications in the resulting sources’ $\delta^{13}\text{C}$. The following section describes this and another sensitivity study related to the emissions. Regarding the latter factor, alteration of the tracers’ isotope ratios due to the chemical transformations and RPs were thoroughly examined. Essentially, none of these were found to be decisive for $\delta^{13}\text{C}(\text{CO})$, except for the effective isotope enrichment in the CO reaction with the OH radical. Escorting the principal CO sink in the atmosphere, the kinetic isotope effect (KIE) in $\text{CO}+\text{OH}$ has the ultimate impact on the resulting $\delta^{13}\text{C}(\text{CO})$. In addition, implemented in the AK setup of EMAC, the revisited parameterisation of this KIE proposed in this study yields a substantially better agreement between the simulated and observed $\delta^{13}\text{C}(\text{CO})$. In particular, no alternative elucidation of the ETS¹³¹ $\delta^{13}\text{C}(\text{CO})$ is found. Sections 6.2.4 and 6.2.5 below review the sensitivity simulations dedicated to the isotope effects and CO sink KIE. At last, the amendments introduced in the AE and AK setups are aggregated in the AEK setup. Whilst the general improvement to $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ was briefly presented to the reader in Figure 6.5 above, the detailed comparison of the results from these simulations, also with the observational data (Sect. 6.2.7), follows.

6.2.3 Sensitivity to emission strengths and isotope signatures

Several adjustments to the direct (surface) emissions of CO and its precursors in REF were probed in the series of test simulations with EMAC in order to infer the sensitivity of the underestimated NH $[\text{CO}]$ to the location and strength of the potentially underestimated sources. Thus, the largest constituents, *viz.* biomass-burning and anthropogenic emissions, were considered and individually increased within their uncertainty ranges in the four regions predominantly associated with CO emissions, *viz.* Northern America (NA), Europe (EU), Central Africa (CA) and East Asia (EA) (see Sect. 5.1.5 for details, also Figure 5.9, p. 132). Although not being as powerful as an inverse modelling approach, these test simulations have clearly highlighted two par-

¹³¹Judging by the variation in the simulated $[\text{CO}_\text{M}]$, this is at around $45^\circ\text{N}/40^\circ\text{S}$, which is equivalent to surpassing τ_{CO} values above two months, respectively. The distribution of the simulated τ_{CO} (REF setup) is detailed in Plate D.11 (p. 276).

ticularities: (1) In order to sufficiently augment both, sub-tropical and mid-latitude background CO mixing ratios, a sufficient part of the missing component must originate from outside the tropics and be further transported latitude-wise through both, the BL and FT. Alternatively, a mere increasing of the tropical sources (*e.g.*, in Central Africa) leads to generally overestimated SH and underestimated ETNH burdens but adequately simulated tropics; besides, the large fraction of augmented CO gets quickly transported to the upper FT via the tropical general circulation instead of supplying the NH BL domain. (2) Not every source, due to its strength or location, is capable of sufficiently contributing to the NH high-latitude CO inventory, however. For instance, scaling the aggregate of NA emissions to their upper limit (about 140 Tg(CO)/yr added) results in an average 10–12 ppb increase in the Arctic winter-spring [CO], or mere one-half of the missing 20–30 ppb there. Besides, generally slower mid-latitude transport and photochemistry dilute the NA/EU CO arriving at the high latitudes more, as opposed to an equivalent increase in the EA emissions.

Consecutively, the test simulations indicate that the largest response in the missing [CO] component is associated with scaling up the East Asian emissions. The cases probing adjustments in the alternative regions separately, as well as combined in several regions (*i.e.*, NA/CA/EU), were discarded. These suggested that larger (than for EA only) emissions are needed to match the Arctic [CO], which, in addition, substantially worsen the low- and mid-latitude CO inventory. Similar findings were obtained by Liu *et al.*^[2011] (L11), who used satellite measurements to evaluate the CO emission inventories implemented in different 3D AC-GCMs/CTMs, including EMAC with a setup analogous to that used in REF. They infer that the emissions over East China are particularly underestimated, as well as the [CO] simulated close to the surface. L11 also conjecture that the uncertainties in the EA emission factors are likely much larger than those associated with the amount of burned biomass. Likewise, the test simulations regarded here did not provide a clear indication which anthropogenic emission component, industrial or biomass-burning, is missing over EA. An insight into this matter can be given by the simulated/observed $\delta^{18}\text{O}(\text{CO})$ values in the region, as the BB source is more depleted in ^{18}O . The respective source average $\delta^{13}\text{C}$ signatures are, however, similar (-25.9‰ from the BB *vs.* -25.7‰ from the FF/BF mix), hence augmenting either source leads to an identical impact on the NH background $\delta^{13}\text{C}(\text{CO})$.

The extra EA emission fluxes required to yield the best-matching simulated [CO] are reckoned slightly greater than the overall industrial component emitted over this region. Implemented in the AE setup, these are summarised in Table 6.6. Noteworthy, the same emission $\delta^{13}\text{C}$ signatures as in REF are considered in AE. Besides, the proportional increase in the anthropogenic NMHCs influx over EA is applied, taking into account that the original anthropogenic emissions for CO and NMVOCs are derived using the same proxies (van Aardenne *et al.*^[2005]). The fairly large enhancements in CO/NMHCs emissions in the AE setup are nonetheless well comparable (as $\sim 30\%$ / $\sim 60\%$, respectively) to the overall uncertainties associated with the NH and tropical anthropogenic emissions (see Table 5.11, p. 137).

In addition to the AE setup, another study probing the sensitivity of the simulated $\delta^{13}\text{C}(\text{CO})$ to the chosen biofuel emission $\delta^{13}\text{C}$ signature was devised. Abbreviated as “SBE”, this setup mimics the original REF emissions, with an exception for the biofuel emission class, whose $\delta^{13}\text{C}$ signature is increased from -25.0‰ to -12.9‰ . Such drastic change in the isotope ratio of the constituent that makes up about $1/4$ of the total surface CO source occurs if one considers the alternative proxy for its ^{13}C content. As detailed in Sect. 5.2.2 (p. 120), the original signature of -25‰ is derived from an abstract assumption on the precursor carbon composition. A few data on (industrial) biofuel production suggest, however, that the dominant part of the BF is comprised of ethanol, which, in turn, predominantly stems from sugarcane and corn crops rich in ^{13}C . The alternative estimate of -12.9‰ is considered the upper limit associated with this hypothesis. Table 6.6 lists the changes to the respective CO and NMHCs emissions’ $\delta^{13}\text{C}$ upon assuming the new BF signature. Whilst the effect on the global non-BB NMHCs emission component is moderate ($+1.6\text{‰}$), for CO it is pronounced ($+4.6\text{‰}$) and important regarding the prevalence of the surface emissions in the tropics and ETNH. The most apparent changes pertain to CA and EA, where the BF-derived share of the surface emissions is highest; the respective increase in the $\delta^{13}\text{C}$ of the anthropogenic CO emission is around $+9\text{‰}$ there. To note, changes listed in Table 6.6 pertain to about $1/4$ of the total tropospheric CO source, whose $\delta^{13}\text{C}$ ultimately gets augmented by $+1.2\text{‰}$ in the SBE setup.

Table 6.6 Integrals of the surface emissions and respective $\delta^{13}\text{C}$ signatures in the REF, AE and SBE setups

Region	CO [Tg/yr^{-1}] ($\delta^{13}\text{C}(\text{CO})$ [‰])			NMHCs [Tg(C)/yr^{-1}] ($\delta^{13}\text{C}(\text{C})$ [‰]) ^a		
	REF	Δ AE ^b	Δ SBE ^c	REF	Δ AE ^b	Δ SBE ^c
ETNH	351.7 (-26.3‰)	+140.6 (+0.12‰)	(+3.78‰)	90.6 (-26.6‰)	+18.9 (+0.03‰)	(+1.88‰)
Tropics	280.4 (-25.3‰)	+69.8 (-0.03‰)	(+6.05‰)	105.6 (-25.9‰)	+9.9 (-0.03‰)	(+1.60‰)
ETSH	29.0 (-23.3‰)		(+2.08‰)	10.3 (-23.4‰)		(+0.77‰)
NA	77.4 (-26.9‰)		(+1.10‰)	20.5 (-26.5‰)		(+0.81‰)
EU	85.1 (-26.6‰)		(+1.59‰)	26.4 (-26.9‰)		(+1.02‰)
CA	61.9 (-25.1‰)		(+8.36‰)	17.4 (-25.3‰)		(+2.83‰)
EA	202.1 (-25.6‰)	+210.3 (-0.04‰)	(+8.40‰)	39.9 (-25.9‰)	+28.8 (-0.14‰)	(+4.85‰)
Global	661.1 (-25.2‰)	+210.3 (+0.003‰)	(+4.60‰)	206.5 (-26.1‰)	+28.8 (-0.03‰)	(+1.59‰)

Notes:

Values refer to the annual surface emission over the given area (biomass-burning component is not included). Values in parentheses denote the $\delta^{13}\text{C}$ signatures. For the AE and SBE setups, changes to the emission fluxes (or $\delta^{13}\text{C}$) with respect to those implemented in REF setup are shown.

Abbreviations denote the following regions: NA – North America (100°W–50°W/15°N–50°N), EU – Europe (20°W–50°E/30°N–60°N), CA – Central Africa (30°W–60°E/EQ–20°N), EA – East Asia (50°E–120°E/EQ–50°N).

^{a)} Quoted is the overall amount of the emitted NMHCs calculated per carbon atom, and respective average $\delta^{13}\text{C}$.

^{b)} Emission $\delta^{13}\text{C}$ signatures identical to those implemented in the REF setup are applied. The small changes to the emission $\delta^{13}\text{C}$ are caused by the repartitioning of the sources in the overall mixture.

^{c)} Only changes to the emission $\delta^{13}\text{C}$ due to the different biofuel source signature are quoted; emission fluxes are identical to those in REF.

6.2.3.1 Amended emissions (AE)

The evolution of the extra CO component (ΔCO) and its effect on the respective $\delta^{13}\text{C}(\text{CO})$, simulated in the AE setup, are shown in Figure 6.9. The BL distributions are detailed for June and September, when the remote NH maxima and minima of $\delta^{13}\text{C}(\text{CO})$ are typically observed, respectively. As expected, a substantially higher [CO] within +(50–200) ppb is seen over India and China, as well as the enhancements of up to +40 ppb denoting the outflow region over the Far East, through which a substantial fraction of the augmented CO gets faster transported to the higher latitudes. The increase in the EA emissions affects the mixing ratios in the entire NH MBL and BL north of 60°N, ranging from +(5–10) ppb in October to +40 ppb and more in May. In panel (c) of Figure 6.9, the timing of the seasonal ΔCO extrema highlights the latitudinal transport of the augmented component: The maximum MBL [ΔCO] in March around 30°N develops north of 70°N in May, correspondingly. Likewise, the respective high-latitude minima lag by about two months. Such latitudinal “transport” dynamics, as detailed above in Sect. 4.1.2 (p. 81), are rather characteristic for $\delta^{13}\text{C}(\text{CO})$ than [CO]; however, these are expected to be seen in the sensitivity plots. An enhancement comparable to that in the MBL appears in the NH FT [ΔCO] only above ~40°N, suggesting that the transport of ΔCO in low latitudes occurs mostly through the BL. On the other hand, synchronous seasonal variations in the extratropical MBL/FT ΔCO denote that the vertical mixing of the high-latitude CO inventory is much quicker compared to the zonal transport.

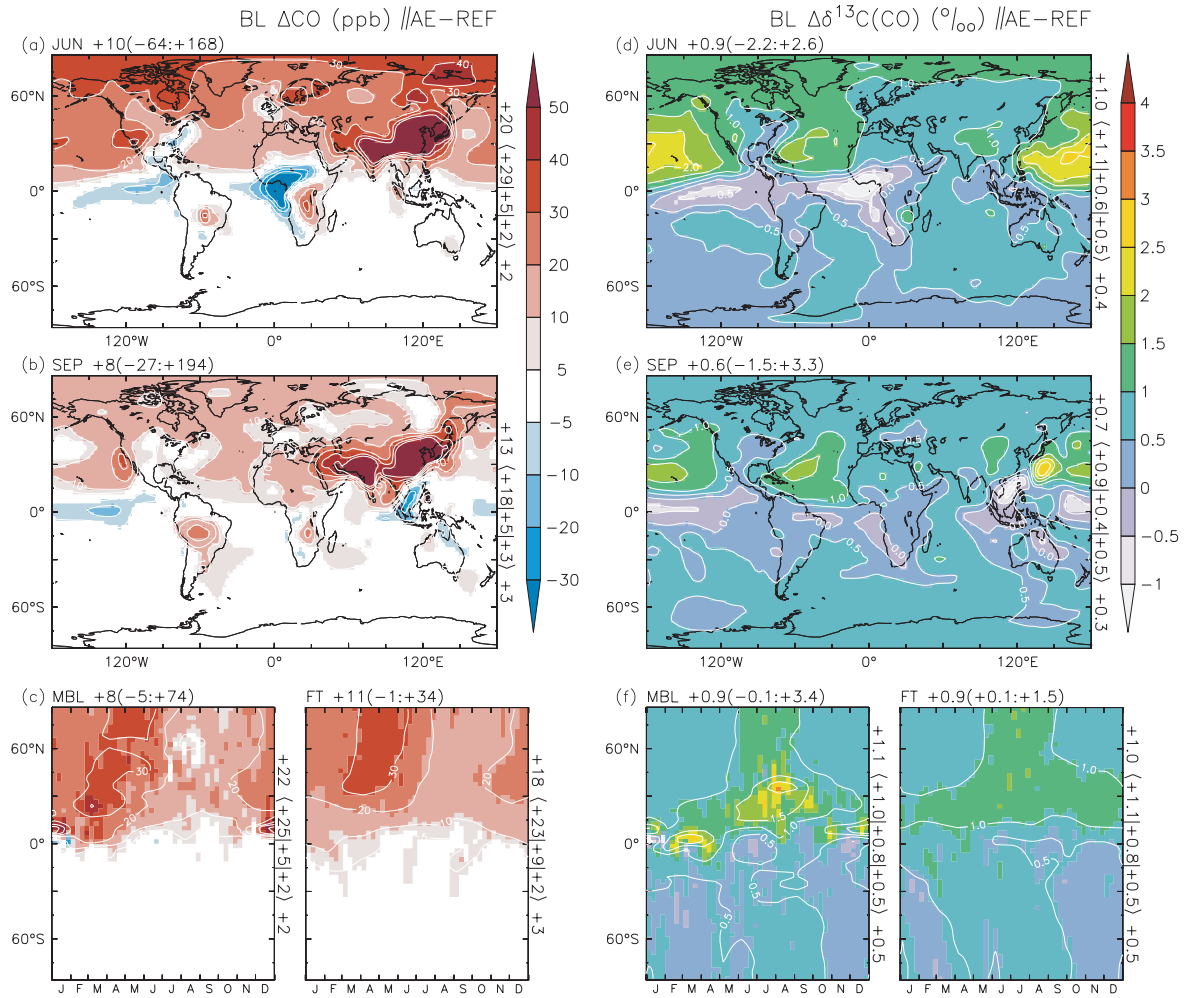


Figure 6.9 Sensitivity of the $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ to the changes in the surface emissions as considered in the AE compared to REF setup. Panels (a), (b) and (d), (e) present the BL averages for June and September, respectively. The seasonal evolution of the MBL/FT zonal averages is shown in panels (c) and (f), respectively. The detailed distributions of ΔCO and $\Delta\delta^{13}\text{C}(\text{CO})$ are presented in Plates D.13 and D.14 (pp. 280–282). See Figure D.1 (p. 255) for the legend.

Changes to the corresponding $\delta^{13}\text{C}(\text{CO})$, denoted hereinafter as “ $\Delta\delta^{13}\text{C}$ ”, contrast those for CO. In particular, large $\Delta\delta^{13}\text{C}$ values above +1‰ are pronounced in the entire NH MBL throughout the year, peaking at +3‰ in summer-fall in the EA outflow region over the Northern Pacific. The augmented $\delta^{13}\text{C}(\text{CO})$ here occurs due to the decreasing share of the methane source (CO_M), promoted by the reduction of the $\text{CH}_4 + \text{OH}$ sink strength (see below). The seasonal variations in the ETNH $\Delta\delta^{13}\text{C}$ are chiefly driven by the photochemical CO sink and do not resemble those for $\delta^{13}\text{C}(\text{CO})$ (see, *e.g.*, Sect. 4.1.2, Figure 4.8, p. 85): The synchronous $\Delta\delta^{13}\text{C}$ peaks in June–August are seen throughout the NH north of $\sim 30^\circ\text{N}$, not correlated with the seasonal $[\Delta\text{CO}]$ variations. Remarkably, the applied extra EA emissions are capable of significantly affecting the $\delta^{13}\text{C}(\text{CO})$ in both hemispheres. Thus, the annual averages of $\Delta\delta^{13}\text{C}$, being very similar in the MBL and FT, amount to +1‰, +0.8‰ and +0.5‰ in the ETNH, tropics and ETSH, respectively. To compare, the corresponding $[\Delta\text{CO}]$ averages relate as approximately +24, +7 and +2 ppb, respectively, *i.e.* the effect on $\delta^{13}\text{C}(\text{CO})$ is complex and not merely proportional to the $\Delta\text{CO}/\text{CO}$ abundances. For instance, the increase of +0.5‰ in the ETSH $\delta^{13}\text{C}(\text{CO})$ is equivalent to adding extra CO with the $\delta^{13}\text{C}$ signature of the anthropogenic EA source in an amount of some 7–8% of the whole ETSH inventory. The diagnosed respective ΔCO is, however, of +3.9%, or slightly above one-half of what the isotope mass-balance suggests. To resolve the latter taking this amount, alternatively, an additional ^{13}C enrichment on the order of +5‰ (with respect to the $\delta^{13}\text{C}$ of the emitted ΔCO) is required. This inconsistency unravels the fate of the tropical ΔCO in the ETSH: Before arriving at higher latitudes, around one-half of the exported ΔCO gets photochemically oxidised, which enriches the leftover CO. Employing the Rayleigh fractionation model (see, *e.g.*, Eq. (4.2) on p. 93) and the nominal sink fractionation magnitude $^{13}\text{C}\eta$ of +6.5‰ for ^{13}CO reacting with OH suggests that the missing +5‰ correspond to a 43.5% sink of the overall exported ΔCO . A similar Rayleigh-kind enrichment pattern is seen in the vertical profiles of $\Delta\delta^{13}\text{C}$, particularly in

the SH (shown separately in Plate D.14, p. 282). In addition, seasonal variations in the SH $\Delta\delta^{13}\text{C}$ demonstrate the characteristic transport pattern (~ 3 months from the equator to the pole, distinctly seen in the FT) foremost noted in the $\delta^{13}\text{C}(\text{CO})$. This suggests that the EA emissions have a source signature effect on the SH $\delta^{13}\text{C}(\text{CO})$ (but little on $[\text{CO}]$), as opposed to the situation in the NH entailing large changes to the photochemical turnover. Thus, the April–October $\Delta\delta^{13}\text{C}$ value is nearly constant and solely reflects the augmented overall ETSH $\delta^{13}\text{C}(\text{CO})$, due to the tropical ΔCO input. When the austral summer sets in, the fraction of the leftover ΔCO reaches its minimum in February, yielding the corresponding $\Delta\delta^{13}\text{C}$ below $+0.2\text{‰}$.

The extended budgeting of the chemical mechanism included in EMAC in this study further allows inspecting the impact of a $\sim 16\%$ increase in surface emissions (or $\sim 9\%$ increase in the overall source) of carbon monoxide on the photochemical turnover of the key species. Figure 6.10 presents the detailed budgeting of the OH, HO_2 , CO and CH_4 photochemical terms simulated in REF, and their respective changes reckoned for the AE simulation. The diagnostic tagging of the chemical mechanism enables to infer the contribution of each CO component, as well as of a particular set of reactions (*e.g.*, HO_x or NO_x chemistry), separately. For instance, the annual tropospheric sink of OH in the reactions with CO amounts to $36^{+4}_{-3}\%$ outcompeting all other sinks, *e.g.*, oxidation of methane ($14^{+1}_{-1}\%$) and intermediates in the CO production chains (overall $26^{+6}_{-1}\%$).¹³² In the latter, around $1/2^{+1}_{-3}$ of OH is consumed only in the reactions involving species stemming from CH_4 . The intermediate reactions also produce OH, thus during the conversion of CH_4 and NMHCs carbon to CO some $13^{+2}_{-2}\%$ and $14^{+10}_{-3}\%$ of OH become recycled, respectively, with a generally higher efficiency of $18^{+3}_{-2}\%$ in the isoprene chemistry. Nonetheless, generally the recycling of OH during the oxidation of hydrocarbons amounts to a mere 5.5% (3.4% in the tropics) of its overall sink. Quite the opposite is diagnosed for the HO_2 turnover: On average, $2.1^{+2.8}_{-0.8}$, $1.5^{+1.9}_{-1.3}$ and $1.9^{+2.8}_{-2.2}$ molecules are produced per one hydrogen peroxide reacted in the CH_4 , NMHCs and isoprene chains, respectively. The hydrocarbon reactions account for $\sim 30\%$ ($\sim 18\%$ for the $\text{CH}_4 \rightarrow \text{CO}$ chemistry only) of the global HO_2 production, implying a high recycling rate of a factor of ~ 2.05 .

The effect of an increased atmospheric CO source on the species' turnover is highlighted in the panels showing the difference between the budget terms simulated in the AE compared to REF setup. The most prominent changes pertain to the CH_4 and NMHCs chains, which show opposite tendencies. Thus, in reactions with OH, extra CO outcompetes CH_4 , reducing the sink of the latter, therefore decreasing the CO_M component and slightly inhibiting the methane-related chemistry. A similar effect (and even stronger when relative changes are regarded) is noted in the isoprene $\rightarrow$ CO chain. The production of CO from CH_4 and isoprene decreases by ~ 23 and ~ 9 Tg/yr, respectively, or within 2% of its overall photochemical turnover, compensated by ~ 24 Tg/yr increase in the NMHCs $\rightarrow$ CO chain throughput. The largest changes to the CO and OH sink are attributed to the augmented surface component; the ~ 240 Tg/yr of ΔCO (including those produced in-situ from the NMHCs source) are being removed by the additional ~ 160 Tg/yr sink via OH, with the difference contributing to the changes in the NH CO burden. Congruent changes to the radicals' turnover are noted for the NMHCs $\rightarrow$ CO conversion: The extra hydrocarbons emitted in the AE setup typically increase the throughput of OH and HO_2 . The changes to the sink/production of the latter, however, are much more balanced (relating as $+49.5$ to $+38.6$ Tg/yr) than that for OH ($+8.7$ *vs.* $+37.5$ Tg/yr, respectively). Interestingly, the increase in the total HO_2 production in AE occurs mainly through the HO_x chemistry, whereas the increased sink is being shared nearly equally between the NO_x and HO_x cycles.

¹³²The normal, superscript and subscript (*e.g.*, T^N_S) values denote the averages (or integrals) for the tropics, ETNH and ETSH, respectively.

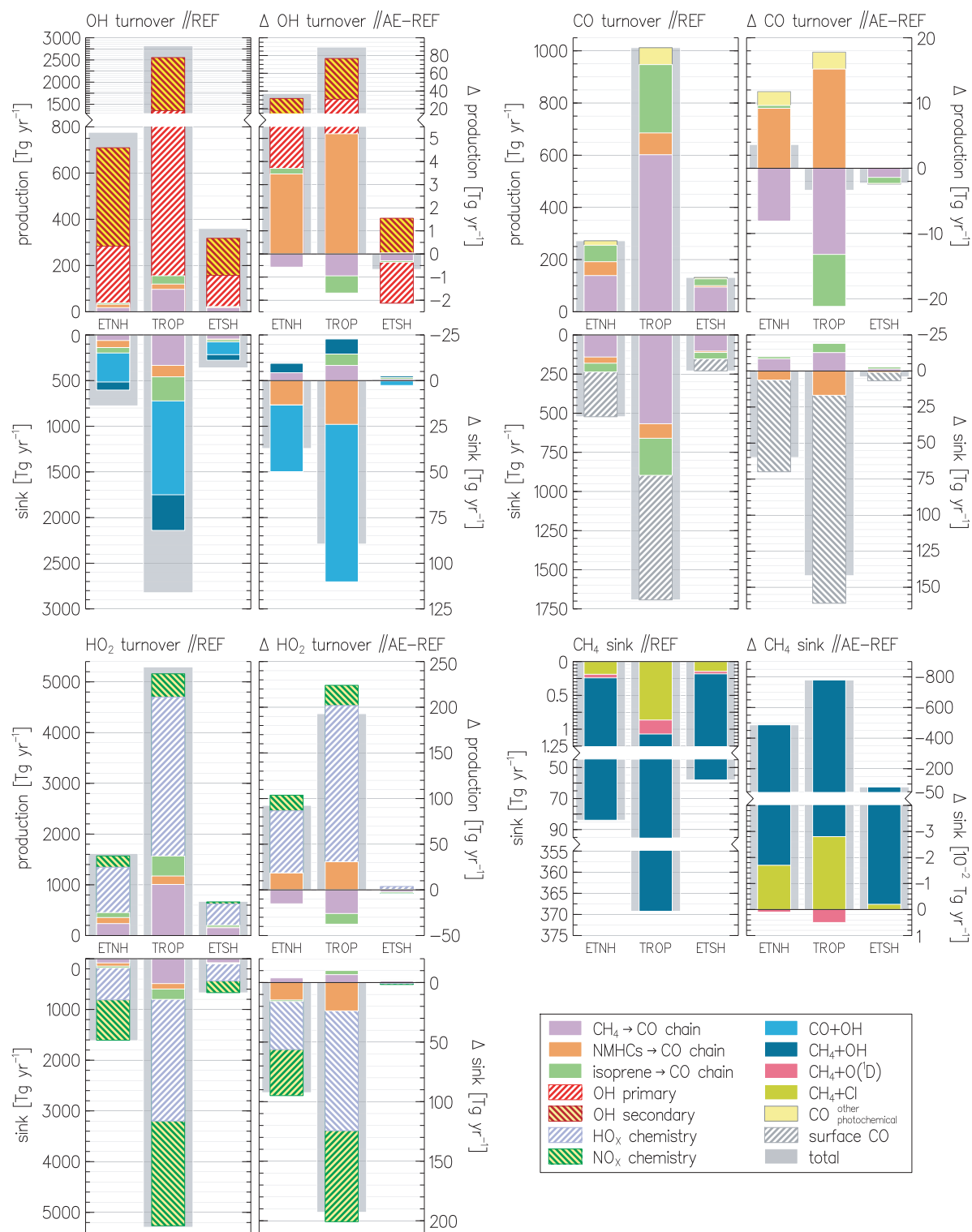


Figure 6.10 Extended budgeting of OH, HO₂, CO and CH₄ photochemical turnover in EMAC. Each panel presents the component-wise in-situ production and sink simulated in REF (left), and their respective differences with those simulated in AE (right) for the given species. For OH, the sinks shown in the CO production chains do not include those of the OH+CO and OH+CH₄ reactions; the production terms include the reactions of H₂O with O(¹D) (denoted as primary) and HO₂ with O₃, NO and NO₃ (denoted as secondary), respectively. The HO_x and NO_x chemistry terms amount to the aggregate production/sink of HO₂ in the reactions referenced in the MECCA mechanism as G2100–G2112 and G3100–G3224, respectively (see Appendix A, Table A.1, p. 225). For CH₄, only the sink terms are shown. Other (not shown) photochemical CO sources refer to the CO produced from HCHO and CH₃O₂ stemming from dimethylsulphide, methyl halogens (Cl, Br), and their oxidation/intermediate products. The discrepancies between the total and component-wise budgets pertain to the latter as well. Annual tropospheric integrals are shown. Mind the broken axes for the OH and CH₄ plots.

Marginal changes to the photochemical turnover are noted in the ETSH. In particular, the unsubstantial increase in the surface sink of CO confirms that less than 6 Tg/yr of ΔCO are being eventually removed in the SH outside the tropics (*cf.* the overall ETSH sink term of ~ 230 Tg/yr). Likewise, the sink of CH_4 simulated in AE is some 0.5 Tg/yr (about 2.6%) smaller than that diagnosed in REF. This is equivalent to an increase in the tropospheric CH_4 lifetime by about 2.5 months (distributed into $+2.2^{+1.4}_{-0.9}\%$ with respect to $5.5^{+1.8}_{-0.9}$ yrs simulated in REF). In comparison, τ_{CO} increases by about two days, with a similar to τ_{CH_4} relative change in the ETSH and larger sensitivities elsewhere ($+3.4^{+8.8}_{-1.6}\%$ with respect to 34^{+71}_{-83} days in REF). The budgeting also concludes that the ETSH OH turnover is barely affected by the changes in the tropical/NH CO emissions. Instead, the primary OH production in the ETSH (negligibly decreased in AE) is more sensitive to the minute lowering of the $\text{O}(^1\text{D})$ abundances; the latter is caused by the slightly enhanced removal of CH_4 by $\text{O}(^1\text{D})$, as the sink of methane via OH gets inhibited. Similarly, the asymmetry in the primary OH production between the ETNH and ETSH (relating as $\sim 1.8:1$) results from the uneven hemispheric $\text{O}(^1\text{D})$ distribution, which, in turn, is governed by the photolysis of the unevenly distributed ozone. In addition to O_3 , the hemispheric asymmetries in NO and NO_3 abundances amplify this irregularity in the secondary OH production term to $\sim 2.6:1$.

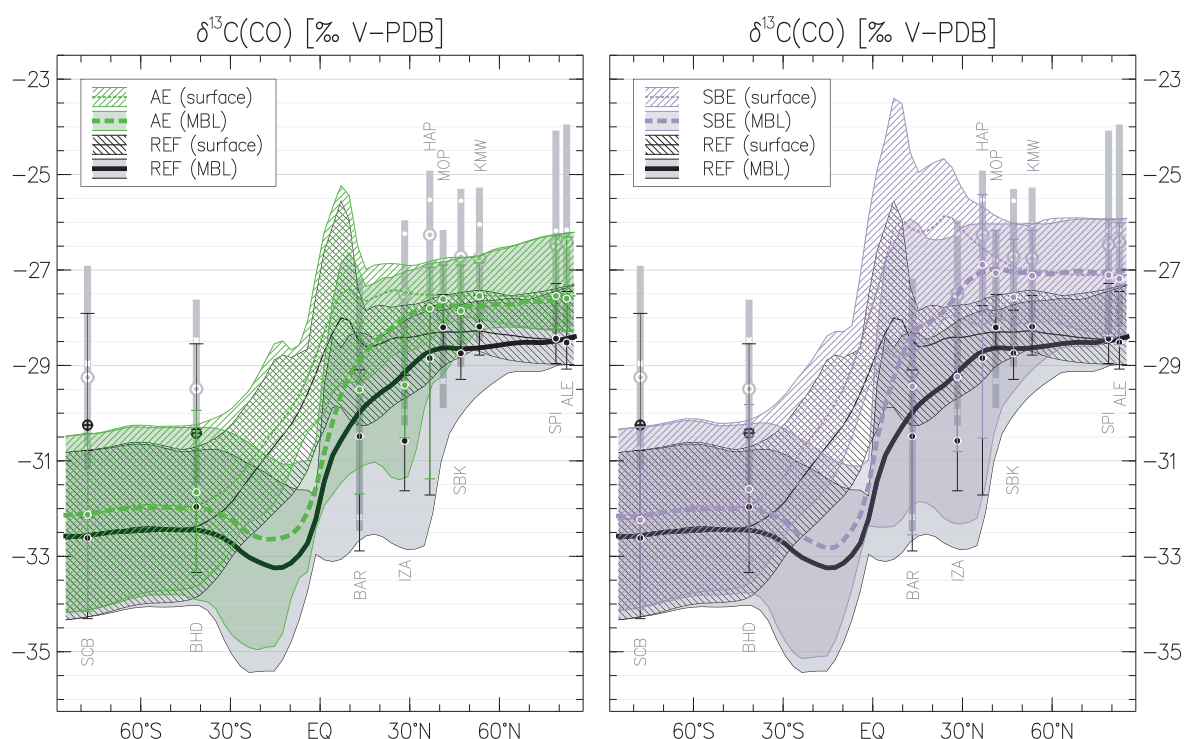


Figure 6.11 Zonal average $\delta^{13}\text{C}(\text{CO})$ simulated in the AE and SBE setups. Thin and thick lines refer to the averages in the surface layer and MBL, respectively. Grey symbols denote the station $\delta^{13}\text{C}(\text{CO})$ data (see Figure 6.5, p. 168, for references), black and coloured symbols denote the values simulated at the locations of the surface station data in the REF and respective sensitivity simulations.

The analysis of the AE simulation results is concluded by Figure 6.11 (left panel) showing the zonal profiles of the simulated $\delta^{13}\text{C}(\text{CO})$ in comparison with those obtained in REF. A perceptible improvement to the $\delta^{13}\text{C}(\text{CO})$ levels (compared to observations) is seen in the NH, with a uniform increase of at least $+1\%$ in the extratropical annual average and variation (mostly at the expense of the spring-summer maxima). In the tropics, the surface $\delta^{13}\text{C}(\text{CO})$ average north to the equator remains at -27.5% characteristic for the anthropogenic sources; the $\delta^{13}\text{C}(\text{CO})$ in the southern tropics is least sensitive to the extra emitted CO (*cf.* the curve for REF). The difference between the surface and MBL averages reaches $+2\%$ in the tropics and becomes extenuated only around 40°S/N , also much similar to what is seen in the reference simulation. A uniform annual MBL $\Delta\delta^{13}\text{C}$ of $+0.5\%$ is inferred for the entire ETSH, with a slight increase of the seasonal minima-to-maxima variation. Although a firm, non-negligible effect of the tropical CO emissions on the final ETSH $\delta^{13}\text{C}(\text{CO})$ is confirmed, it is obviously much lower than the observed SH discrepancy (about $1/5$ of the missing ^{13}C amount). The improvement in the NH is more significant, in particular for the seasonal $\delta^{13}\text{C}(\text{CO})$ minima; the NH averages and seasonal maxima are yet underestimated by as much as 1% and 2% , respectively. It is note-

worthy, however, that $[\text{CO}]$ simulated in the AE setup match the observed mixing ratios substantially better, as discussed above (p. 168, see also Figure 6.5).

6.2.3.2 Biofuel source $\delta^{13}\text{C}$ (SBE)

The right panel in Figure 6.11 presents the $\delta^{13}\text{C}(\text{CO})$ simulated in the SBE setup. The latter, in contrast to the AE setup, probes adjusting only the $\delta^{13}\text{C}$ signature of the CO/NMHCs surface emissions (see above), therefore introducing no perturbation to the simulated photochemical regime and embodying a rather $\delta^{13}\text{C}$ transport-sensitivity study.

The detailed distribution of $\Delta\delta^{13}\text{C}$ for SBE (the sensitivity of $\delta^{13}\text{C}(\text{CO})$ with respect to the values simulated in REF) is shown in Plate D.15 (p. 284), the results are discussed here. At first, the seasonal evolution of the $\Delta\delta^{13}\text{C}$ MBL/FT zonal averages (*ibid.*, panels (a)–(d)) shows less intertwined chemistry-transport effects as compared to that in the AE setup. Although a latitudinal transport pattern is noticed in the seasonal evolution of $\Delta\delta^{13}\text{C}$ in the FT, it is much less prominent than that seen in the AE simulation, owing to the unperturbed photochemistry. On the other hand, a nearly symmetric, anti-correlated seasonal development of the hemispheric $\Delta\delta^{13}\text{C}$ is seen, with sharper extrema (NH minima and SH maxima) occurring at the beginning of September. The alternating, less pronounced SH minima and tropical NH maxima extend throughout January–February, followed by the ETNH $\Delta\delta^{13}\text{C}$ peaking in March–April. As expected, the evolution of $\Delta\delta^{13}\text{C}$ correlates with the corresponding share of the surface CO component (CO_s, includes the CO from biofuel emissions) in the overall CO inventory, thus highlighting the augmented difference between the surface and in-situ sources' $\delta^{13}\text{C}$ signatures applied in the SBE setup. For instance, in September, the lowest CO_s share in the NH CO yields the minimum $\Delta\delta^{13}\text{C}$ at +0.6‰ (ETNH) and +1.3‰ (northern tropics), respectively. At this time, the SH inventory has collected the largest CO_s component, exhibiting the maximum $\Delta\delta^{13}\text{C}$ of +(0.6–0.7)‰, *i.e.* comparable to the ETNH minimum value. The situation reverses in the austral summer, when the photochemical processing of CO replaces CO_s with its in-situ components, decreasing the $\Delta\delta^{13}\text{C}$ value to a mere +0.1‰ in the remote SH. The corresponding NH MBL average $\Delta\delta^{13}\text{C}$ peaks at around +3‰ in the tropics and at +1.9‰ at the higher latitudes, respectively.

Secondly, substantially high $\Delta\delta^{13}\text{C}$ values are expected over CA and EA, associated with the largest emission influxes from biofuel-related sources. Thus, $\Delta\delta^{13}\text{C}$ above +5‰ and +3‰ are simulated year-round over India and China, respectively, as well as +(2–3)‰ over Central and South Africa and the northern Indian Ocean. In the boreal winter, ^{13}C -heavier biofuel sources are predicted to enrich the CO in the outflow region over the Northern Pacific at least by +(1.5–2)‰ and typically 0.5‰ less over the North Atlantic. The largest changes of +(7–8.5)‰ of the simulated $\delta^{13}\text{C}(\text{CO})$ are expected in the BL air over India throughout December–February. Taking the $\delta^{13}\text{C}(\text{CO})$ estimate of –26.5‰ obtained in REF, this implies that the CO with $\delta^{13}\text{C}$ above –20‰, a rather high value, should be typical for this area in winter. A few observations available for this case indicate that this is unlikely the case. The isotope composition of the biofuel-emitted aerosol can be used as an indirect measure of the $\delta^{13}\text{C}$ signature of the precursor carbon material from this source. Agnihotri *et al.*^[2011] observe a robust ^{13}C composition of the winter aerosol over India characterised with $\delta^{13}\text{C}$ of $-(25.3 \pm 0.6)\text{‰}$ ($\pm 1\sigma$ is given, data for February–March only), predominantly originating from the biomass and biofuel burning sources. This average corresponds to the authors' estimates of the biofuel source signature of –21.7‰ and the BB/BF ratio of the emission sources. The composition of the BB/BF emitted CO, too, is reckoned being close to that of the precursor burnt material, or slightly lower than that owing to the ^{13}C fractionation in the smouldering phase of the burning process, when most of CO is being released (see details in Sectss. 5.2.2 and 5.2.3). Therefore, similar $\delta^{13}\text{C}(\text{CO})$ of around –25‰ is expected from the combustion sources, much close to the $\delta^{13}\text{C}$ signatures used in REF and AE. A more direct evidence comes from the observations during the Indian Ocean Experiment (INDOEX, Mühle *et al.*^[2002]¹³³) in February–March 1999, when the CO mixing and isotope ratios were measured in the air masses encountered in the west and north-east of the Indian Ocean. Figure 6.12 presents the comparison of these data with the seasonal $\delta^{13}\text{C}(\text{CO})$ simulated in the AE (left panel) and SBE (right panel) setups, respectively. In the SBE results, the strongly enriched (exceeding –20‰ in $\delta^{13}\text{C}$) CO is pronounced over central and northern India. Rather large simulated $\delta^{13}\text{C}(\text{CO})$ values of $-(24 \pm 1)\text{‰}$ are seen over the north-west of the Indian Ocean, where the observed $\delta^{13}\text{C}(\text{CO})$ is at $(-27.4 \pm 0.9)\text{‰}$, *i.e.*, more than 3‰ lower than the results of SBE suggest. In contrast to that, the $\delta^{13}\text{C}(\text{CO})$ simulated in AE is found in good

¹³³The unpublished data on $\delta^{13}\text{C}(\text{CO})$ measured in INDOEX are kindly provided by C.A.M. Brenninkmeijer and P. Jöckel, MPI-C.

agreement (within $\pm 0.5\text{‰}$) with the observations. In addition, the Keeling-plot analysis of the INDOEX $\delta^{13}\text{C}(\text{CO})$ data¹³⁴ yields a $\delta^{13}\text{C}$ signature of the continental CO source of $(-24.8 \pm 0.5)\text{‰}$ (adj. $R^2 = 0.82$, $N = 15$), very close to the estimates for the aerosol source $\delta^{13}\text{C}$ quoted above. All this therefore confirms that the $\delta^{13}\text{C}$ of the BF source of CO is unlikely to be substantially higher than the value applied in the emission setup of REF, at least over India. Thus, the isotope mass-balance of the Indian sources suggests that the biofuel $\delta^{13}\text{C}$ signature matching those inferred from the INDOEX data must be on the order of $+(1 \pm 0.5)\text{‰}$ higher.

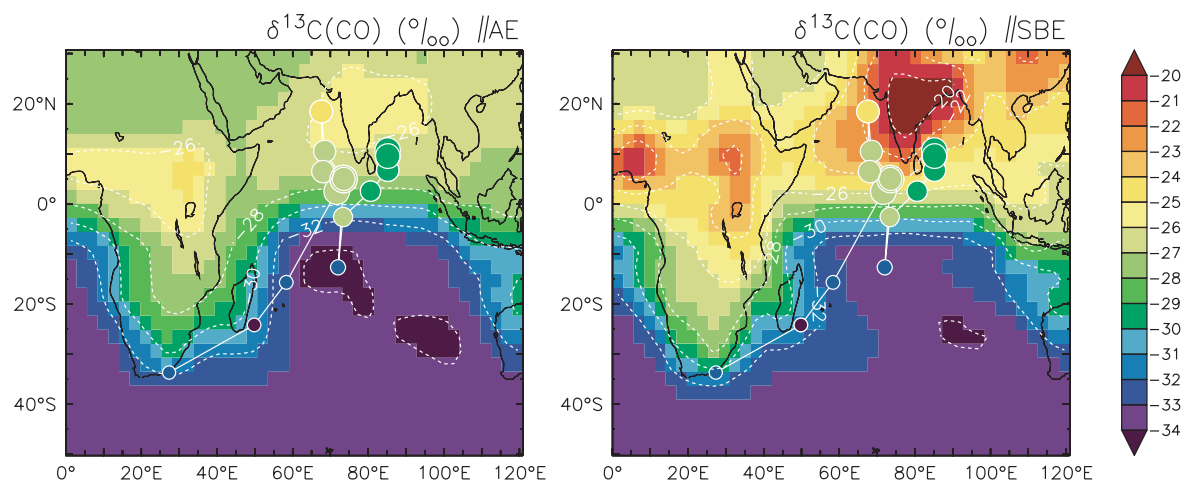


Figure 6.12 Comparison of the $\delta^{13}\text{C}(\text{CO})$ simulated in the AE (left panel) and SBE (right panel) setups versus the isotope CO observations from the INDOEX campaign¹³³ (denoted with symbols). Symbol sizes scale proportionally to the observed CO mixing ratio (45.7 to 197.8 ppb, respectively). Model averages for February–March are shown.

At last, one notes much similar effects of the adjustments considered in AE and SBE in Figure 6.11; these, however, correspond to the different $[\text{CO}]$ distributions simulated. When applied on top of the emission strengths considered in the AE setup, the BF emission $\delta^{13}\text{C}$ signatures from SBE are expected to yield largely unrealistic $\delta^{13}\text{C}(\text{CO})$, first of all over the India/China regions and northern (sub-)tropics in general. We note, however, that the ETNH $\delta^{13}\text{C}(\text{CO})$ simulated in the SBE setup shows larger, more realistic seasonal variations than that in the AE setup. Being a collateral result of a less reasonable hypothesis, this nevertheless suggests that the winter-spring CO arriving to the higher latitudes must bear a higher $^{13}\text{C}/^{12}\text{C}$ ratio. Regarding the SH CO composition, much similar results are achieved in both emission sensitivity setups. A slightly larger, but nonetheless minor increase of $+0.6\text{‰}$, in the ETSH average $\delta^{13}\text{C}(\text{CO})$ is estimated in SBE, despite the largely augmented African CO source $\delta^{13}\text{C}$ signature (see Table 6.6 above). Reusing the extended budgeting analysis for REF (whose photochemical turnover is identical to that simulated in SBE), the small sensitivity of the extratropical SH domain is explained in terms of short the tropical lifetime of CO. The diagnosed sink of CO_s in the ETNH is below $1/10$ of that in the tropics (or $1/15$ of the global term), which means that the largest part of the BF-emitted CO does not survive and cannot be transported to the ETSH.

Recapitulating, the emission-setup sensitivity studies presented here corroborate that: (1) A substantial improvement to the simulated CO mixing ratios in the NH is achieved with the AE setup using enhanced (by a factor of 2.9 for CO) anthropogenic emissions over East Asia (mostly India and China). The augmented surface component resolves around one-half of the discrepancy in the average NH $\delta^{13}\text{C}(\text{CO})$ (and $\sim 1/3$ in its variation) simulated in the REF setup. (2) A similar result is obtained for $\delta^{13}\text{C}(\text{CO})$, although not for $[\text{CO}]$, in the alternative SBE setup inquiring for the sensitivity of the simulated CO isotope composition to an ample increase in the ^{13}C content of the biofuel-derived sources. The comparison with the observational data suggests, however, that only a slight (about $+(1 \pm 0.5)\text{‰}$ vs. probed $+11\text{‰}$) adjustment to the BF $\delta^{13}\text{C}$ signature is required to match the $\delta^{13}\text{C}(\text{CO})$ measured over India, rendering the SBE hypothesis fairly implausible for the NH tropics. Unfortunately, no consistent comparison for the other large BF emission regions, particularly in Africa, is currently feasible. (3) Little improvement to the ETSH ^{13}CO abundance is achieved in both sensitivity studies. The de-

¹³⁴The mixing model approach is considered applicable here (see the discussion on p. 78): The data from the same season are regarded; the variations in the observed $\delta^{13}\text{C}(\text{CO})$ are assumed to ensue from the proportional mixing of the CO from the continental and oceanic (background) air masses, least (or equally) affected by the isotope fractionation in the atmospheric sink of CO. The quoted uncertainty range equals the 95% confidence interval for the intercept point value derived in the regression analysis.

tailed chemical turnover budgeting of the key species in EMAC attests that the discrepancy seen in the remote SH $\delta^{13}\text{C}(\text{CO})$ is clearly not related to the chosen emission setup, but rather to the atmospheric processing of CO and isotope effects escorting it. The latter are analysed next.

6.2.4 Removal effects

6.2.4.1 Sensitivity of the photochemical CO yield (SR2/SRU)

Two sensitivity simulations, abbreviated “SR2” and “SRU”, were conducted to assess the efficiency of the non-chemical removal processes (RPs, represented by the dry deposition and wet scavenging) simulated in EMAC. In particular, the sensitivity of the CO photochemical yield from methane, λ_{CH_4} , to the chosen parameters in the RPs implementation, was targeted for. As discussed above (in Sects. 6.1.1 and 6.2.2.1), a significantly lower λ_{CH_4} value (~ 0.8 or less of that simulated in REF) may resolve the inconsistencies in simulated $\delta^{13}\text{C}(\text{CO})$ related to the large share of the CH_4 -derived carbon monoxide component (CO_M) inferred in EMAC. Tersely, the RPs parameterisation in EMAC primarily operates with deposition velocities v_d (proportionating the species’ dry deposition fluxes to their atmospheric abundances) and Henry’s law coefficients k_H (defining the solubility of the species, hence their partitioning between the gas/aqueous phases, of which the latter is subject to scavenging by precipitation). Determined in the laboratory or derived from several assumptions, these parameters are usually associated with perceptible uncertainties. A case in point is formaldehyde, a key intermediate in the $\text{CO} \rightarrow \text{CH}_4$ chain: The range of reported k_H values for this compound spans from -50% to $+150\%$ about their average (Sander^[1999]). The v_d value for HCHO, alike for the majority of the dry deposited tracers considered in EMAC, is calculated with the resistance-based approach incorporating various assumptions, including the approximations based on the relatively well-known properties of ozone and SO_2 (see details in Sects. 0, 5.1.5). The deposition velocities of the latter, for example, vary within an order of magnitude in different environments. Regarding the uncertainty associated with the resistance-based approach itself, we note that in certain cases it does not realistically represent the dry deposition processes for SO_2 , because of poorly predicting the respective v_d values (Ganzeveld *et al.*^[1998]). It is therefore sensible to inquire into the potential of the large uncertainties in the RPs parameterisation to alter significantly the very important λ_{CH_4} value.

As a simple but robust concept, two modifications to the v_d and k_H values for the species directly or indirectly related to the CO production were considered here. In the first case (the SR2 setup), both, v_d and k_H , were doubled with respect to the original values used in the REF setup, which nonetheless preserved their values well within the uncertainty ranges. In the second case (the SRU setup), the upper-limit estimates of v_d and k_H were applied. The ensuing changes to the removal efficiency varied differently for different species, being calculated on-line during the model integration. For instance, the diagnosed dry deposition velocity for HCHO in the SRU setup has increased by around a factor of five. Overall, relative increments larger than a factor of ten were not diagnosed for all species regarded; being in essence irrelevant for the final results (see below), these are not detailed here.

The changes to the RPs parameterisation implemented in the SR2/SRU setups have minor effect on the simulated CO_M yields. Thus, a small reduction to the global λ_{CH_4} value, not exceeding 0.02 (SR2) and 0.05 (SRU), was simulated. Locally, these numbers may reach 0.03 and 0.06 in the extratropical winter, respectively, owing to the inhibited photochemistry, however with no tangible effect on the overall species turnover. The insignificant impact of a substantial change in the RPs efficiency is well explicable in the $\lambda_{\text{CH}_4}/\lambda_{\text{NMHCs}}/\lambda_{\text{isoprene}}$ framework outlined above in Sect. 6.2.2: The removal processes become largely outcompeted by the active photochemistry (for the shorter-lived compounds) and transport (mostly convective, for all species). This inference is furthermore corroborated by the results obtained in the AE setup: Despite the noticeable increase in the CO emissions, the resulting changes in simulated λ (shown with dashed lines in Figure 6.7, p. 170) are negligible. Conclusively, the rapid photochemistry and transport are the determining factors for the intermediates’ removal efficiency. From this standpoint, a proportionally small effect on λ_{NMHCs} and $\lambda_{\text{isoprene}}$ in the SR2/SRU setups are expected. Even in the extreme case of the SRU setup, only a little reduction (approximately 5%) to the CO_M component is expected. Projected onto the overall ^{13}CO budget simulated in REF, this implies a minute increase in the overall CO source $\delta^{13}\text{C}$ of around $+0.33^{+0.24}_{-0.38}\%$, respectively.¹³² This is an upper limit estimate, as the reductions in λ_{NMHCs} and $\lambda_{\text{isoprene}}$ are to shift the balance between the CO_M and other (photochemical) CO components closer to that reproduced in the REF setup.

6.2.4.2 Isotope effects in the removal of the intermediates (DEP)

Beyond this point, the analysis presented in this section will exclusively focus on the isotope effects escorting the atmospheric processing of CO and related species. It is important to outline which effects are regarded, and how they contribute to the isotope enrichment ϵ a given species acquires in the atmosphere. A case in point is CO. Disregarding the transport/mixing effects, the final isotope composition of the airborne CO is represented by the following relation:

$$\delta^{13}\text{C}(\text{CO}) = \delta^{13}\text{C}(\text{sources}) + {}^{13}\text{C}\epsilon_{\text{rem/chem}}(\text{intermediates}) + {}^{13}\text{C}\epsilon_{\text{sink}}(\text{CO}), \quad (6.1)$$

where the first member on the RHS denotes the contribution of the overall (both in-situ and direct) sources of CO. The second term stands for the additional modification of its photochemical precursors' isotope composition due to the kinetic isotope fractionation in either chemical reactions (${}^{13}\text{C}\epsilon_{\text{chem}}$) or RPs (${}^{13}\text{C}\epsilon_{\text{rem}}$). The third term denotes the modification induced by the isotope fractionation in the atmospheric sink of CO itself. In essence, Eq. (6.1) formulates the relationship depicted in Figure 6.1 (p. 141) in the beginning of this Chapter; it is applicable to any species regarded, however. Noteworthy, the comprehensive chemical mechanism employed in EMAC allows studying the fractionations ${}^{13}\text{C}\epsilon_{\text{rem}}$ in CO (and other species) associated with the RPs for the first time here. As discussed above in Sect. 6.1.4.2, ${}^{13}\text{C}\epsilon_{\text{sink}}(\text{CO})$ did not receive a thorough enough analysis in the previous modelling studies, too.

The simplified relation (6.1) does not embrace the effects that inevitably intervene in any atmosphere modelling study extending beyond a simplified well-mixed box. In particular, air transport and mixing convolute the individual contributions of each term, making it difficult to diagnose them separately.¹³⁵ Therefore, in order to estimate ${}^{13}\text{C}\epsilon_{\text{rem}}$, a separate sensitivity study implementing the DEP setup was devised. Such abbreviation was chosen because ${}^{13}\text{C}\epsilon_{\text{rem}}$ are found to be chiefly determined by the dry deposition effects. The DEP model setup mimics that of REF with the following modifications:

- All chemical isotope effects are switched off in order to single out the effects of the non-chemical removal processes (RPs),
- The isotope ratios of all emitted compounds and main photochemical sources (e.g., CH_4) are initialised to the reference standard ratio (i.e., equivalent to 0‰ in the $\delta^{13}\text{C}$ characteristic), in order to exclude the isotope variations caused by the differences/variations in the emission $\delta^{13}\text{C}$ signatures,
- The initial isotope ratios of all species are reset to 0‰.

Both of these modifications are used further in the set of Z setups studying $\epsilon_{\text{sink}}(\text{CO})$ for various isotopes individually (see next section). Simulated in DEP, the $\delta^{13}\text{C}$ of the given species reflects the isotope enrichment it acquires in the RPs (as well as the respective enrichment inherited from its precursors) ultimately modified by the atmospheric dynamics. Regarding CO, the objective of the DEP simulation is to quantify the ${}^{13}\text{C}\epsilon_{\text{rem}}(\text{CO})$ term and its potential contribution to the overall ${}^{13}\text{CO}$ atmospheric balance.

Figure 6.13 presents the resulting ${}^{13}\text{C}\epsilon_{\text{rem}}$ simulated in DEP for CO and its precursors in the $\text{CH}_4 \rightarrow \text{CO}$ chain, viz. formaldehyde, methanol and methyl hydroperoxide. Shown distributions refer to the model surface layer, where the largest enrichments were diagnosed. Except for CO, similar distributions are noted for each species. The largest enrichments are visible over the continents, where the source regions are located and dry deposition processes dominate. Owing mainly to the differences in the isotopologues' diffusivities, lighter species are preferentially taken up by soils and vegetation, resulting in positive enrichments for all compounds (see also Sect. 5.1.5, p. 114, for details). In the MBL, average ${}^{13}\text{C}\epsilon_{\text{rem}}$ values show a slight increase toward the poles, which is a mere transport effect seen in winter: The enriched intermediates (also from the isoprene/NMHCs oxidation sources) survive the latitudinal transport to be later broken down in summer.

A substantial enrichment (above +5‰ over its source $\delta^{13}\text{C}$ value) is simulated for methanol over Europe and North America; overall, enrichments in CH_3OH above +3‰ are characteristic over land, except for

¹³⁵To be precise, the isotope composition of an air parcel, in addition to the source-sink equilibration, is subject to the 'transport-mixing' equilibration in the atmosphere. That is, the terms in Eq. (6.1) are not additive linearly: A change in any of them is more likely to yield a non-linear response in the final $\delta^{13}\text{C}(\text{CO})$ value, because the atmospheric mixing intensity depends on the established chemical gradients of ${}^{12}\text{CO}$ and ${}^{13}\text{CO}$, for instance. Owing to the small (at most $\pm 5\%$ in $\delta^{13}\text{C}$) variations in isotope composition of tropospheric CO, however, this additive non-linearity in the simulated $\delta^{13}\text{C}(\text{CO})$ is negligible, as was purposely ascertained by the mass-balance of the sensitivity and control simulations. Nonetheless, mixing and transport play a substantial role in every term constituting the RHS of Eq. (6.1), such that the calculations of isotope equilibrium employing standard assumptions (e.g., well-mixed reservoirs and other simplifications) blunder when applied to atmospheric CO (see further Sect. 6.2.5.3, p. 190).

the deserts. Analogously, $^{13}\text{C}_{\text{rem}}$ values exceeding +2‰ are expected in these regions for HCHO. The latter is perceptibly affected by the composition of its closest precursor. A most prominent example is the continental outflow region in the east tropical Pacific, where co-located enhancements in $^{13}\text{C}_{\text{rem}}(\text{HCHO})$ and $^{13}\text{C}_{\text{rem}}(\text{CH}_3\text{OH})$ are seen. In contrast to formaldehyde, the methyl hydroperoxide is not derived from methanol, hence the distribution of $^{13}\text{C}_{\text{rem}}(\text{CH}_3\text{OOH})$ does not show this feature. All three intermediates show similar patterns over the Pacific and Atlantic, where the active photochemistry refills them with the non-enriched carbon from the CH_4 oxidation source.

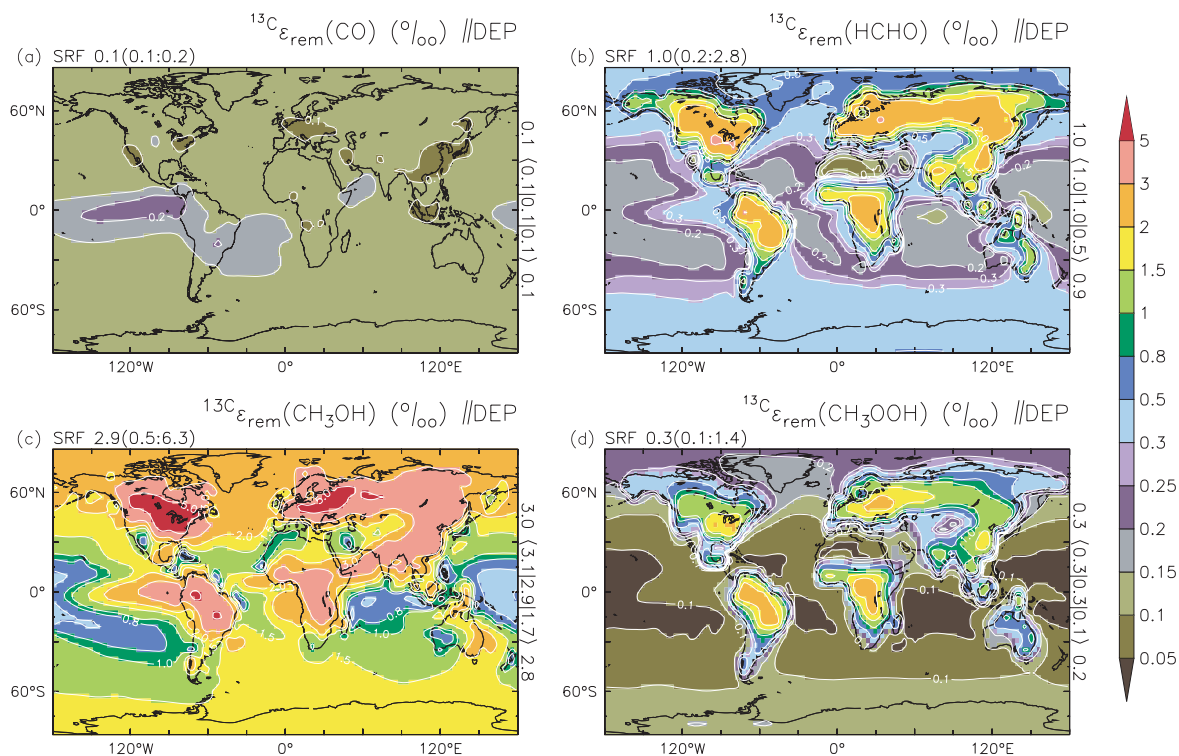


Figure 6.13 Distribution of the effective isotope enrichment $^{13}\text{C}_{\text{rem}}$ in CO and its precursors due to the isotope fractionation in the removal processes, simulated in the DEP setup. Annual averages for the surface layer are shown. See Figure D.1 (p. 255) for the legend.

A much different picture is seen for CO (panel (a) in Figure 6.13, *cf.* also the detailed distributions in Plate D.16, p. 286). The resulting global average $^{13}\text{C}_{\text{rem}}(\text{CO})$ of +0.15‰ is a small term in the overall ^{13}C mass-balance. The large surface emission component strongly dilutes this rather weak, purely photochemical signal. There is little more to be discussed on $^{13}\text{C}_{\text{rem}}(\text{CO})$. Its hemispheric distributions are rather homogeneous, owing to the relatively long CO lifetime. The maximum values of $^{13}\text{C}_{\text{rem}}(\text{CO})$ above +0.3‰ are found compact around the equator in the Pacific in July-August, influenced by the continental outflow region in the Eastern Pacific mentioned above. The average value and temporal variations of $^{13}\text{C}_{\text{rem}}(\text{CO})$ are about an order of magnitude smaller compared to the overall uncertainties associated with the $\delta^{13}\text{C}(\text{CO})$ simulated.

To recapitulate, results of the DEP simulation provide the first model estimate of the effective isotope fractionations escorting the dry deposition of carbonaceous species contributing to CO. Figure 6.14 presents the simulated vertical profiles of the average effective fractionations $^{13}\text{C}_{\text{rem}}$ for the most affected compounds. Omitting further details, effective fractionations below +0.5‰ denote little or insignificant impact of the dry deposition processes on the isotope composition of the majority of them. A few outliers, *viz.* formaldehyde, methanol, acetic acid and peroxyacetyl nitrate, exist, however. Despite the former two are the closest precursors of CO, their moderate BL effective enrichments are expected to have a negligible contribution to the final atmospheric $\delta^{13}\text{C}(\text{CO})$. The results inferred for the $^{13}\text{C}/^{12}\text{C}$ isotopologues may be scaled to obtain a rough projection of the effective enrichments in the respective $^{18}\text{O}/^{16}\text{O}$ isotopologues, owing to the diffusion-driven, hence merely mass-dependent, fractionation mechanism assumed. Alike with the $\text{CH}_4 \rightarrow \text{CO}$ chain, most of the intermediates in the non-methane chains are oxygenated, hence $^{18}\text{O}_{\text{rem}}$ values of a factor of two larger than that for $^{13}\text{C}_{\text{rem}}$ are expected. The respective $^{18}\text{O}_{\text{rem}}(\text{CO})$ reckoned at $\sim +0.3\text{‰}$ is negligible in the tropospheric $\delta^{18}\text{O}(\text{CO})$ balance as well. It is important to note that the inferred results substantially depend on the dry deposition parameterisation applied in EMAC (see details in Sect. 5.1.5, p. 114).

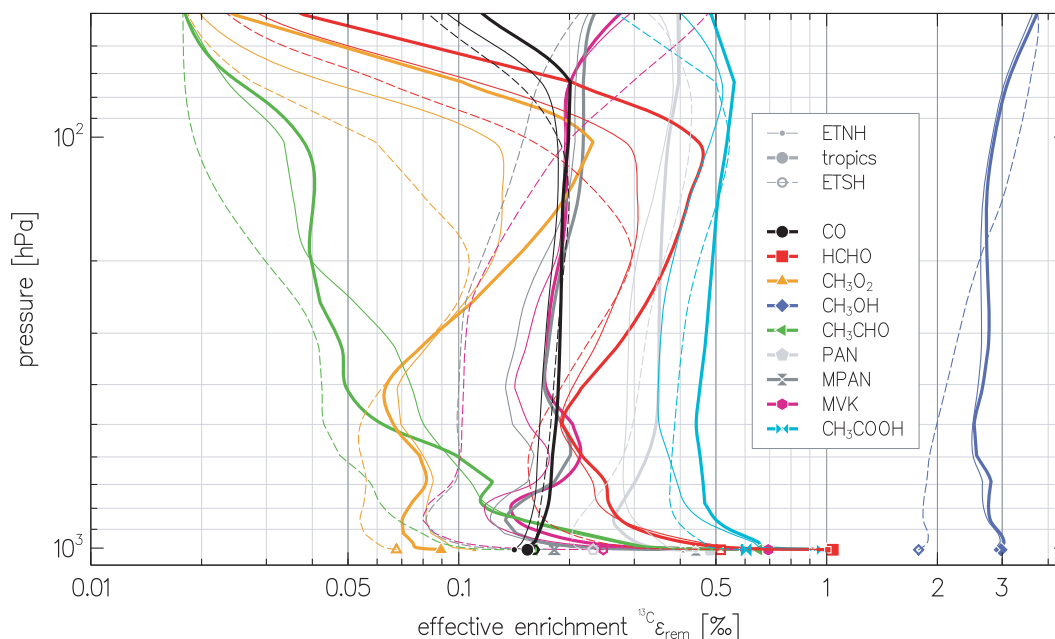


Figure 6.14 Vertical distribution of the effective isotope enrichments $^{13}\text{C} \epsilon_{\text{rem}}$ in selected carbonaceous compounds resulting from the isotope fractionation in the dry deposition processes and atmospheric transport, simulated in the DEP setup. Thick, thin solid and thin dashed lines refer to the topical, ETNH and ETSH annual averages, respectively.

6.2.5 Effective CO sink fractionation (Z)

The reader is foremost referred to Sects. 3.4.4 (p. 47) and 6.1.4.2 (p. 152) reviewing the aspects of the carbon monoxide atmospheric sink in the reaction of CO with the OH radical and kinetic isotope effects escorting it. A dedicated analysis of the resultant effective isotope fractionations appearing in CO was performed in the set of “ZERO” sensitivity simulations. The initial setup, designated “Z”, is based on the of REF setup with the following modifications:

- Except for the kinetic isotope effect (KIE) escorting the oxidation of CO by OH radical, all (chemical and non-chemical) isotope effects are switched off,
- The isotope ratios of all emitted compounds, as well as of the main photochemical sources (*e.g.*, CH_4 , O_2 , H_2O), are initialised to the reference standard ratios for $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, $^{17}\text{O}/^{16}\text{O}$ isotopes, yielding the emission signatures of 0‰ for all isotopologues, as well as for the respective $\Delta^{17}\text{O}$ characteristic,
- The initial isotope ratios of all species are reset to 0‰.

Such setting ensures that only the competition between the non-zero ϵ_{sink} term and zero-signature sources (see Eq. (6.1) above) determines the ultimate CO isotope ratios simulated in the model. That is, the KIEs in the CO+OH reaction solely contribute to the enhancement in the simulated ϵ_{sink} values, whilst the latter become attenuated upon the emission of CO from different sources, as well as during the atmospheric transport and mixing. Because of the latter, the numeric integration of the stable carbon and oxygen isotope tagging configurations in Z-setups was performed simultaneously, in order to study the correspondence between the effective enrichments of various isotopologues of CO under the same atmospheric dynamics. Some further modifications to the Z setup were made in order to account for the amendments introduced in this study, *viz.*:

- The adjusted, larger surface emission strengths of CO/NMHCs probed in the AE setup were implemented in the ZE setup. This allows studying the sensitivity of ϵ_{sink} to the increase in emissions and larger CO abundance.
- In the ZK setup, the conventional formulation of the KIE in the CO+OH reaction was replaced with the revisited parameterisation as proposed in this study.

The distributions of the effective $^{13}\text{C}/^{12}\text{C}$, $^{16}\text{O}/^{18}\text{O}$ and $\Delta^{17}\text{O}$ enrichments in tropospheric CO simulated in the Z setup are detailed in Plates D.17–D.19 (pp. 288–292), respectively. Because the C^{18}O sink KIE is inverse, it induces enrichments of the C^{16}O over C^{18}O isotopologues that are seen as negative $^{18}\text{O} \epsilon_{\text{sink}}$ values, correspondingly. The simulated ϵ_{sink} triad attests an adequately reproduced photochemical sink signal,

showing the lowest intensities over the regions subject to large emissions and enhanced enrichments in the remote areas. Thus, derived from a source with the same isotopic signature, summertime MBL and continental CO isotope compositions may differ by (2–5)% in the resulting $\delta^{13}\text{C}(\text{CO})$, and roughly twice as large in $\delta^{18}\text{O}(\text{CO})$, respectively. On the other hand, $^{13}\text{C}\epsilon_{\text{sink}}$ below +2‰ (for $^{18}\text{O}\epsilon_{\text{sink}}$, weaker than –5‰) are seen only in a few highly polluted regions (mostly CA and EA), therefore even the non-background air bears a perceptible, nonvoid isotope sink fractionation signal. Regarding the simulated $\Delta^{17}\text{O}$ enrichment, its variations in the BL are well comparable to those of ^{13}CO , particularly in the NH. Overall, the BL values of $^{18}\text{O}\epsilon_{\text{sink}}$, $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ and $^{13}\text{C}\epsilon_{\text{sink}}$ correlate tight hemispherically, scaling nearly linear as $\sim 1.7:1:0.9$ (NH) and $\sim 1.2:1:0.7$ (SH), respectively, in proportion to the magnitudes of their respective nominal sink fractionations in the lower troposphere and established hemispheric averages.¹³⁶

All three ϵ_{sink} signals display different vertical distributions, however. Owing to the strong pressure-dependence of the $^{13}\text{CO}+\text{OH}$ KIE, the respective ^{13}C enrichment rapidly weakens with height, turning into an effective depletion above 70–80 hPa in the tropics (180–120 hPa in the extratropics, seasonally varying, see panels (n)–(r) in Plate D.17, p. 288). At these altitudes, $\delta^{13}\text{C}(\text{CO})$ is expected to reflect the unmodified $\delta^{13}\text{C}$ signature of its sources, as the ^{12}CO enrichments escorting the sink in the LMS compensate the positive $^{13}\text{C}\epsilon_{\text{sink}}$ gained in the troposphere. Above 50 hPa, $^{13}\text{C}\epsilon_{\text{sink}}$ reaches the $^{13}\text{CO}+\text{OH}$ KIE low-pressure limit value of around –7‰. A moderate positive vertical gradient is simulated for $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ throughout the troposphere, despite the reducing $\Delta^{17}\text{O}$ nominal KIE magnitude with decreasing pressure. This suggests that the effect of the continuous sink fractionation during the atmospheric transport of CO outcompetes the photochemical production of the latter in the FT. The altitudes, above which $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ starts to rapidly decrease, are co-located with the zero- $^{13}\text{C}\epsilon_{\text{sink}}$ regions. Further into the stratosphere, the effective $\Delta^{17}\text{O}$ enrichment approaches the low-pressure KIE limit value of +1‰, respectively. Notably, together $^{18}\text{O}\epsilon_{\text{sink}}$ and $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ display homogeneous vertical distributions below 300 hPa in the efficaciously mixed CO inventory in the ETSH (see also above, p. 172). The effective C^{18}O depletion maximises at pressure altitudes between 100 and 50 hPa accommodating the CO with the longest lifetime (see Plate D.11, panels (q)–(w), p. 276). The perceptible vertical gradient in tropospheric $^{18}\text{O}\epsilon_{\text{sink}}$ resembles what one should see in the case of an invariable KIE of the CO sink; indeed, the $\text{C}^{18}\text{O}+\text{OH}$ KIE is least sensitive to the pressure variations (spanning –(9–11)‰ in the troposphere, see, *e.g.*, Figure 3.7, p. 54). Hence, contrasting the $^{18}\text{O}\epsilon_{\text{sink}}$ values of –9₁₁⁸‰¹³² at the surface, the continuously fractionated CO collected above the tropopause is strongly depleted (below –15‰) in ^{18}O . Beyond that point, the photochemical production in the stratosphere intensifies to dilute the low $^{18}\text{O}\epsilon_{\text{sink}}$ with the fresh CO from the methane oxidation source.

¹³⁶ In the BL, the relation between the ^{13}C and $\Delta^{17}\text{O}$ enrichments can be well approximated linearly as $\Delta^{17}\text{O}\epsilon_{\text{sink}} = \epsilon_0 + b_r \cdot ^{13}\text{C}\epsilon_{\text{sink}}$, where $\epsilon_0(b_r)$ equals 0.79(0.90) for the NH and 1.98(0.72) for the SH compositions, respectively. The accuracies of the fits (95% prediction interval, adj. $R^2 = 0.94$) are $\pm 0.44\%$ and $\pm 0.25\%$, respectively. The differences in $\epsilon_0(b_r)$ emphasise a substantial role of the mixing/transport processes in determining the hemispheric ϵ_{sink} values: Stronger SH average enrichments (larger ϵ_0) are less diluted by the surface emissions (lower b_r). An analogous relation between the ^{13}C and ^{18}O enrichments is inferred at $\epsilon_0(b_r)$ of –1.73(–2.15) for the NH and –1.16(–5.8) for the SH, with the respective accuracies of $\pm 0.96\%$ and $\pm 0.51\%$ ($R^2 = 0.92$), respectively.

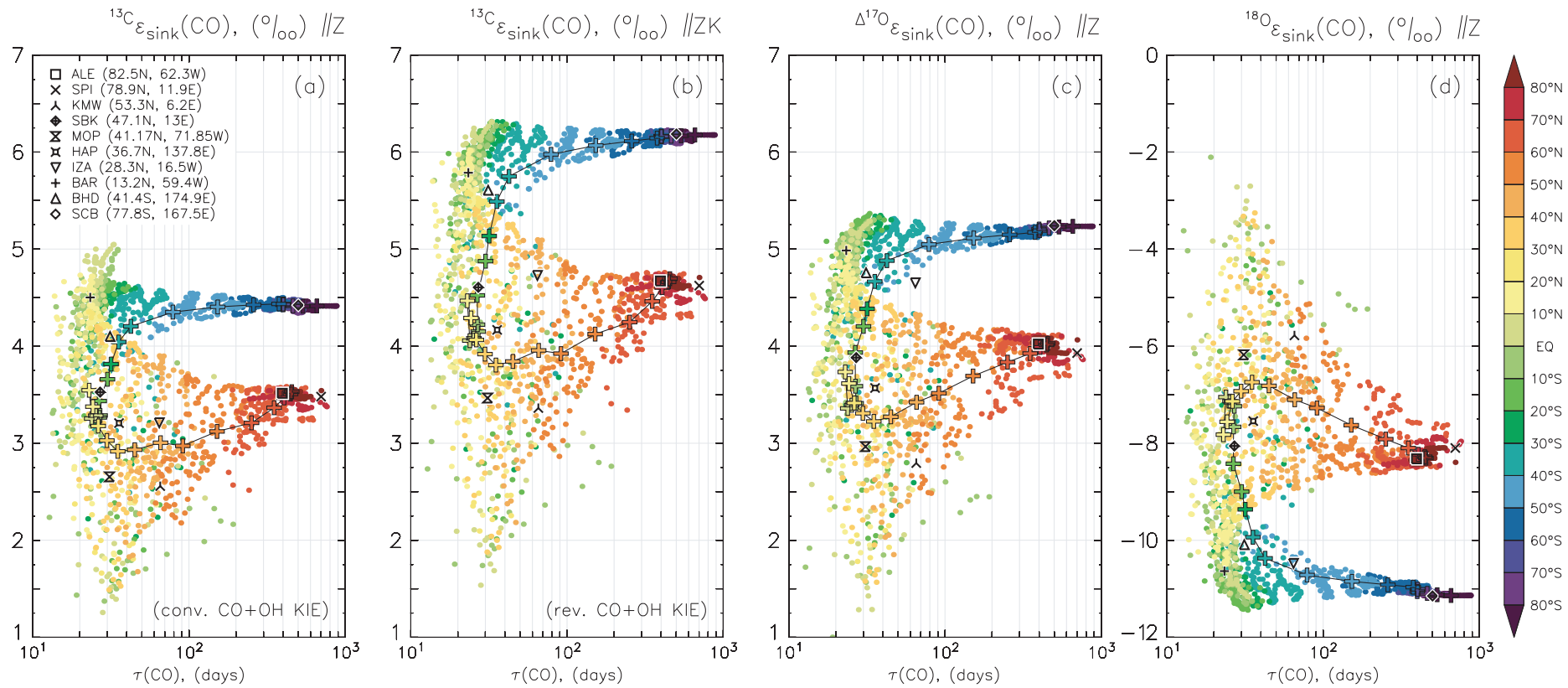


Figure 6.15 Simulated effective isotope enrichment in CO due to its sink fractionation in reaction with the OH radical, as a function of the CO lifetime. Panels (a) and (b) present the $^{13}\text{C}\epsilon_{\text{sink}}$ values obtained for the conventional and revisited $^{13}\text{CO}+\text{OH}$ KIE parameterisations (Z and ZK setups, respectively). Circles denote the values simulated in the BL model gridboxes positioned at the latitudes coded in colour. Large pluses (connected with solid line) denote the respective zonal averages. Black symbols denote the values simulated at the locations of the surface station data. Annual averages are shown.

Reverting to the lower troposphere, a conceptual relationship is seen in Figure 6.15 presenting the annual averages of ϵ_{sink} simulated in the BL, plotted as a function of the respective CO lifetime, τ_{CO} , and latitude (denoted with colour). The τ_{CO} values are calculated as the ratio of the annual average CO burden and integrated sink in a particular gridbox, respectively, and show similar hemispheric distributions, with maxima reaching about two years at the poles and minima below one month in the tropics. A conspicuously large longitudinal variability in the corresponding ϵ_{sink} values in the NH is brought by the much dissimilar values over ocean and land. Less frequent (than in the SH) NH MBL compositions are found close to the respective zonal averages of ϵ_{sink} that line up in the characteristic C-shape profiles (denoted with pluses). These emphasise the BL averages established in the extratropics (seen as the flat shoulders) and the hemispheric transition between them (seen in the vertical shift between weaker NH and stronger SH effective enrichments). Superimposed on the BL compositions, the averages of ϵ_{sink} simulated at the surface station data locations are shown with black symbols in Figure 6.15. Thus, ϵ_{sink} at the remote locations of ALE/SPI, and BHD/SCB are well comparable with the latitudinal averages. So are the values at IZA, SBK and HAP, however, these free tropospheric stations casually display the $\epsilon_{\text{sink}}/\tau_{\text{CO}}$ values not characteristic for the BL compositions at their respective latitudes, but stronger FT ϵ_{sink} signals. The shortest-lived CO is simulated at BAR, showing conformably strong effective sink enrichments. Regarding the remaining locations, ϵ_{sink} at KMW and MOP is diluted with the large surface CO component to roughly $5/6$ of the corresponding zonal averages.

6.2.5.1 Sensitivity to the revisited KIE parameterisation (ZK)

Panels (a) and (b) in Figure 6.15 contrast the effective ^{13}C enrichments simulated in Z and ZK setups implementing the conventional and revisited parameterisations of the $^{13}\text{CO}+\text{OH}$ KIE, respectively. Whereas the former approach considers the KIE nominal magnitude, $^{13}\text{C}\eta$, being merely pressure-dependent, the latter approach takes into account the small temperature-driven changes to the kinetics of the $\text{CO}+\text{OH}$ reaction (see details in Sect. 3.4.4, p. 47). In particular, it suggests concomitant alterations in $^{13}\text{C}\eta$ of about 0.5‰ (with respect to the ‘conventional’ values reckoned at 298K in the laboratory) per every 10K change in the ambient temperature, mostly effective at the high (above 100 hPa) pressures. Thus, the lower the temperatures at which CO sink proceeds, the higher the revisited $^{13}\text{C}\eta$ value, and therefore $^{13}\text{C}\epsilon_{\text{sink}}$. The opposite, *i.e.* lowering of $^{13}\text{C}\eta$ values at the temperatures above 298K, is valid as well. For a reference, the distributions of the nominal KIE magnitudes $^{13}\text{C}\eta$ calculated in the conventional and revisited parameterisations are compared in Figure 6.2a (p. 153, left panel). The resulting sensitivity of the effective enrichment to the chosen parameterisation, denoted $\Delta^{13}\text{C}\epsilon_{\text{sink}}$, is inferred as the difference between the $^{13}\text{C}\epsilon_{\text{sink}}$ values simulated in the ZK and Z setups, respectively, and presented in detail in Plate D.20 (p. 294).

As Figure 6.15 indicates, the revisited KIE parameterisation yields substantially larger effective ^{13}C enrichments ensuing from the CO sink fractionation: The perceptible zonal $\Delta^{13}\text{C}\epsilon_{\text{sink}}$ averages of $+0.90_{-1.4}^{+0.8}\text{‰}$ are simulated in the BL air, contrasted with the larger $^{13}\text{C}\epsilon_{\text{sink}}$ scatter in the NH and greater dissimilarity in the hemispheric averages. The enhanced NH variability results from the increased discrepancy between the $^{13}\text{C}\epsilon_{\text{sink}}$ levels over land and in the MBL, as the sink in the latter occurs at typically lower daytime temperatures. The ETSH variability remains nearly unchanged. The larger hemispheric difference in the BL $^{13}\text{C}\epsilon_{\text{sink}}$ arises partly from the increased overall effective fractionation magnitude; the latter is proportionally dampened in the NH by the larger surface emission term. The most influential factor, however, is the efficient mixing of the BL and FT inventories in the ETSH. Accounting for 81% of the overall SH CO sink, the reaction of CO with OH in the FT occurs at much lower temperatures, therefore yielding larger $\Delta^{13}\text{C}\epsilon_{\text{sink}}$ values that subsequently dilute the BL averages to a perceptibly higher value. This is also seen in the vertical profiles of $\Delta^{13}\text{C}\epsilon_{\text{sink}}$ presented in panels (u)–(w) of Plate D.20 (p. 295) as the homogeneous vertical distributions up to 500–400 hPa. The temperatures in the BL air are not expected to have a large influence on $\Delta^{13}\text{C}\epsilon_{\text{sink}}$ as in the FT. For instance, the annual average CO sink temperature¹³⁷ at the surface is lower by 8.4K/6.4K in the ETNH/ETSH, compared to 298.7K diagnosed in the tropics. This relation changes slightly (to 7.9K/6.6K lower compared to 292.9K, respectively) when the average BL average sink temperatures are considered, and correspond to the equivalent alteration in $^{13}\text{C}\eta$ of only $+(0.3\text{--}0.4)\text{‰}$. The average FT CO sink temperatures dramatically contrast those in the BL, being at least 40K lower (estimated at $257.1_{-23.7}^{+49.5}\text{K}$). Ultimately, through the mixing and transport, the largest changes in the $^{13}\text{C}\epsilon_{\text{sink}}$ BL inventory accumulate in the high latitudes, with augmented $+0.90\text{‰}$ and $+1.54\text{‰}$ diagnosed in

¹³⁷That is, the temperature is averaged using the $\text{CO}+\text{OH}$ reaction rate term as a weighting factor.

the Arctic and Antarctic, respectively. The seasonal variation in the BL $\Delta^{13}\text{C}_{\text{sink}}$ are indistinct in the tropics and small (about $\pm 0.25\text{‰}$) in the extratropical domains, nonetheless showing the distinct summer maxima (in both hemispheres) and minima (in the ETSH only). Exceptionally, the ETNH MBL values peak in June–July at $+1.4\text{‰}$ and even out by December to the minimum $+0.9\text{‰}$ seen until March (see Plate D.20, panels (i), (k) and (n), p. 295). That implies much perceptible changes to the seasonal variation (mostly through the enhanced maxima) in the Northern Pacific and Arctic, therefore to the $\delta^{13}\text{C}(\text{CO})$ simulated at ALE/SPI and HAP locations.

Overall, the revisited approach augments the tropospheric $\delta^{13}\text{C}(\text{CO})$ signature by non-negligible $+1.2\text{‰}$, with the hemispheric contributions to this number being unequal as $+1.0\text{‰}$ (NH) to $+1.6\text{‰}$ (SH) (see Table 6.7 on p. 195 listing the integrals of the ϵ_{sink} and $\Delta^{13}\text{C}_{\text{sink}}$ simulated in different Z-setups). On the other hand, the T -inclusive kinetics (used in the revisited KIE parameterisation), when implemented instead of the conventional $\text{CO}+\text{OH}$ reaction rate in EMAC, result in a corresponding increase of the tropospheric sink of CO by $\sim 2.6\%$ (comprised of 2.8% in the FT and 1.4% in the BL, respectively). This is small compared to the uncertainties associated with the reaction rate coefficient itself (15% in MECCA, see note³⁸ on p. 52) and the CO mixing ratio simulated (at least 40% , see Sect. 6.2.2). The largest sensitivity of $\delta^{13}\text{C}(\text{CO})$ to the changes in the sink KIE parameterisation are expected above the tropopause, where $\Delta^{13}\text{C}_{\text{sink}}$ is typically larger than $+1.4\text{‰}$ and exceeds $+2.4\text{‰}$ in the spring. Consequently, the zero- $^{13}\text{C}_{\text{sink}}$ regions simulated in ZE become lifted up by about 10 hPa inside, and by more noticeable 30–50 hPa outside the tropics, as compared to that in Z. Importantly, at the typical altitudes of the CARIBIC-1 observations in the ETNH (around 260 hPa, see Sect. 4.2), the $\Delta^{13}\text{C}_{\text{sink}}$ are still as large as $+(1-1.8)\text{‰}$, with the distinct seasonality similar to that in the FT. Together with the observations in the ETSH BL, the summer $\delta^{13}\text{C}(\text{CO})$ measured by CARIBIC in summer is to be the most indicative data for the revisited KIE hypothesis. Noteworthy, the $\delta^{13}\text{C}(\text{CO})$ simulated in these domains has a different sensitivity to the emission strengths (AE setup, see Sect. 6.2.3 above): The $\Delta\delta^{13}\text{C}(\text{CO})$ varies within $+(0.8-1.4)\text{‰}$ in the ETNH FT and only within $+(0.2-0.5)\text{‰}$ in the ETSH, respectively.

At last, Figure 6.16 (left panel) compares the BL zonal average and surface station $^{13}\text{C}_{\text{sink}}$ reckoned with both KIE approaches. In the tropics and ETNH, the increase in $^{13}\text{C}_{\text{sink}}$ is more pronounced in the MBL than at the surface, with a substantial enhancement (up to $+0.8\text{‰}$) in the NH MBL annual variation. The Arctic and ETSH variations are similarly enhanced by $+(0.6-0.8)\text{‰}$ at the expense of the higher seasonal maxima. These efficiently contribute to the $\delta^{13}\text{C}(\text{CO})$ variation, occurring simultaneously with the seasonal maxima in the latter, as opposed to the changes in the emission source strengths or signatures discussed above.¹³⁸ More importantly, unlike the other amendments considered in this study, only the revisited KIE parameterisation suggests a potent improvement to the $\delta^{13}\text{C}(\text{CO})$ in the ETSH: The average $^{13}\text{C}_{\text{sink}}$ value of $+6\text{‰}$ is expected (up to $+8\text{‰}$ in the austral summer) in contrast to the conventional value estimated at $\sim +4.4\text{‰}$. A proportional increase in $^{13}\text{C}_{\text{sink}}$ is simulated at both SH observational data locations, BHD and SCB. Disregarding the elevated seasonal minima, the $^{13}\text{C}_{\text{sink}}$ at BAR may be considered as representative for the MBL in the tropics. Noteworthy, since the temperature dependence of the $\text{CO}+\text{OH}$ KIE is assumed, the effective CO sink fractionation at this location is to be the most consistent with the KIEs measured in the laboratory, *i.e.* the fractionation magnitudes determined at around 298K. Regarding the ETNH, the average $\Delta^{13}\text{C}_{\text{sink}}$ vary within $+(1-1.5)\text{‰}$, depending on the CO source-sink equilibrium established at the particular location. Unfortunately, none of the observational sites between 20°N – 60°N appear to be subject to the large seasonal NH effective ^{13}C fractionations; situated in the MBL (northern Pacific and Atlantic), these may reach as high as $+6.2\text{‰}$ (conventional) and $+7.6\text{‰}$ (revisited approach) in summer. Exceptionally, the $\delta^{13}\text{C}(\text{CO})$ at SBK is expected to be more sensitive to the ϵ_{sink} input than other mid-latitude locations. The isotope composition of CO at higher latitudes, however, is reckoned to entirely reflect the MBL variations; the simulated $^{13}\text{C}_{\text{sink}}$ at SPI and ALE displays the largest variations in the BL over the globe, exceeding those in the Antarctic by at least a factor of $1/3$.

¹³⁸ For instance, the Arctic $\delta^{13}\text{C}(\text{CO})$ and $\Delta^{13}\text{C}_{\text{sink}}$ maximise in June, whereas the respective $\Delta\delta^{13}\text{C}(\text{CO})$ maxima simulated in the AE (increased emissions) and SBE (changed emission $\delta^{13}\text{C}$ signature) setups are in July and February, respectively. See also panels (i, k, n) in Plates D.14 and D.15 (pp. 283, 285).

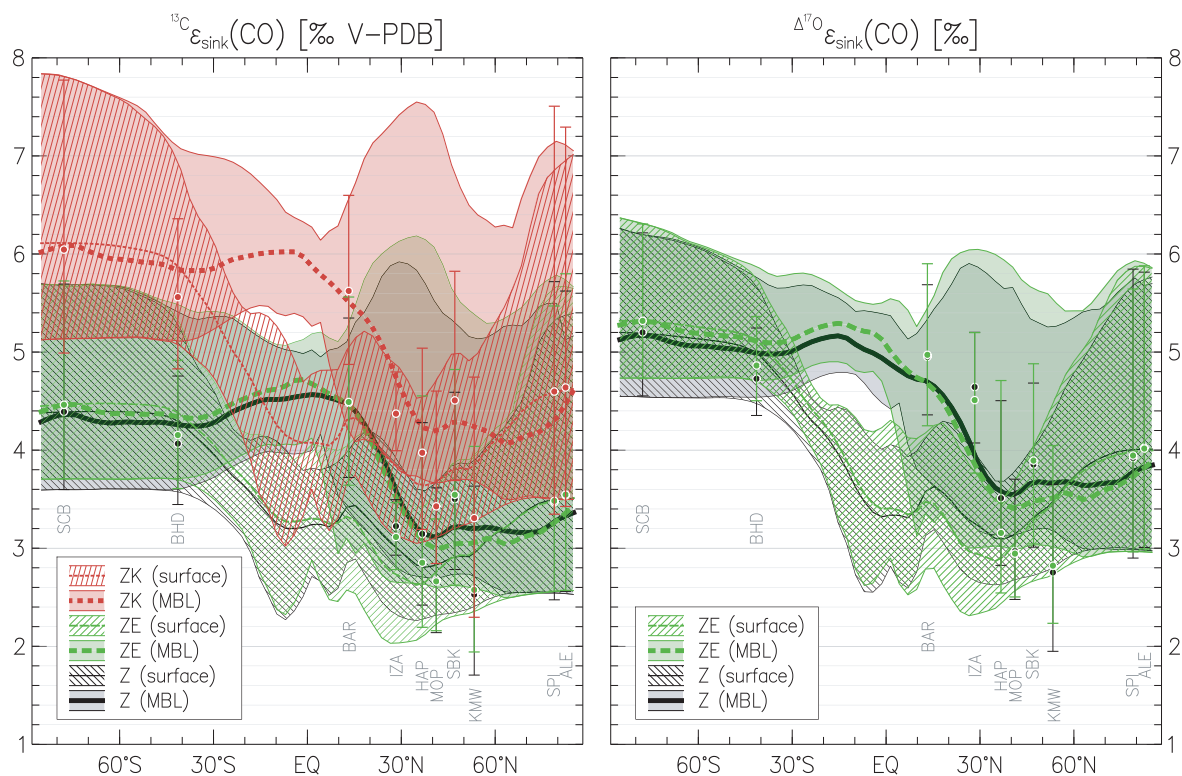


Figure 6.16 Zonal distribution of the BL ^{13}C and $\Delta^{17}\text{O}$ effective isotope enrichments in CO resulting from its sink and atmospheric transport/mixing processes, simulated in Z, ZE and ZK setups. Note that the concomitant CO mixing ratios in the ZE are larger (*i.e.* identical to those simulated in the AE setup), in contrast to the Z and ZE results corresponding to the [CO] from REF (see Figure 6.5, p. 168, for a reference). Black and coloured symbols denote the values simulated at the locations of the surface station data in the Z and respective sensitivity simulations. See Plates D.17–D.20 (pp. 288–294) for the detailed distributions.

6.2.5.2 Sensitivity to the emission strengths (ZE)

In addition to the $^{13}\text{C}\epsilon_{\text{sink}}$ profiles, Figure 6.16 further presents the zonal averages $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ simulated in Z/ZE setups (right panel). As discussed above, these sink fractionation signals correlate tightly, with their averages and variations being scaled by the respective sink KIE magnitudes. Owing to the greater CO abundances over land, the surface ϵ_{sink} averages in the tropics are similar to those of ETNH MBL, whereas the MBL values are comparable to those in the whole SH. The dashed lines in Figure 6.16 present the sensitivity of ϵ_{sink} to the amended surface emissions (implemented in the AE setup, see Sect. 6.2.3.1). Remarkably, a $\sim 9\%$ increase in the overall CO tropospheric source has a rather minor effect on the global ϵ_{sink} values. These changes are driven by two different factors, *viz.* photochemical turnover and transport. For example, the lowering of the $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ surface average by $(0.2\text{--}0.3)\text{‰}$ visible between 10°N – 40°N is a direct effect of the inhibited equilibrium between the sources and sinks of CO over the areas with the enhanced emissions. Transported towards the higher latitudes, these compositions further reappear in the MBL averages between 35°N – 70°N attenuated to $(0.1\text{--}0.2)\text{‰}$, and vanish upon entering the Arctic. The opposite is seen south of 10°N : The largest increase in $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ accumulates not at the surface but in the MBL inventory, with the largest enhancements of up to $+0.2\text{‰}$ around the equator. Surprisingly, contrariwise to that in the ETNH, the source-sink equilibrium in the tropics gets slightly enhanced upon adding extra CO, as explicated by the extended budgeting of the species photochemical turnover inferred in the REF/AE setups (discussed in Sect. 6.2.3 above). Indeed, seen in Figure 6.10 (p. 177), the overall CO photochemical production in the AE/ZE setups becomes shifted towards higher latitudes, being reduced in the tropics and the SH. Nonetheless, larger CO abundances consume larger amounts of a readily available hydroxyl radical in the tropics. Thus the transport and chemistry together favour the CO sink term that sets a marginally better (than in REF) equilibrium on average, therefore slightly higher ϵ_{sink} values. Exported from the tropics, the latter ultimately propagate into the ETSH.

Hereinbelow the sensitivities of the effective sink enrichments $\Delta\epsilon_{\text{sink}}$ (inferred as the difference between the ϵ_{sink} values simulated in the ZE and Z setups, respectively) are analysed only for the simulated $\Delta^{17}\text{O}$ enrichment in CO. In the BL, however, these results may be projected for the ^{13}C and ^{18}O effective enrichments employing the proportionality and firm correlation between all ϵ_{sink} signals (see note¹³⁶, p. 185). The spatiotemporal

BL distributions of $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ (detailed in Plate D.21, p. 296) expectedly highlight the regions associated with enhanced emissions over India and China and their continental outflow driven by the seasonal atmospheric transport in that area. For example, the large negative $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ values of $-(0.5-1)\%$ are pronounced over the tropical Indian ocean throughout November-March, whereas in summer this area is ventilated by air with $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ of $\sim 0\%$ arriving from the SH. In April, negative $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ values are simulated over the northern Pacific broad, however not exceeding -0.6% . These are followed by the short-lasting positive $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ values in the high-latitude Pacific and over the Arctic sea peaking at $+(0.6-0.8)\%$ in July. Apart from these events, the BL values are found scattered around their average of $+0.12\%$ with no conspicuous enhancements. The resulting ‘patchy’ $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ horizontal distributions are adequate, ensuing from the alternative transport/mixing dynamics established for the different CO isotopologues (as well as the other photochemically linked species) in the simulations with different emission setups. The increased East Asian CO emissions have various consequences for the ϵ_{sink} simulated at the locations of the observational data (shown with symbols in Figure 6.16). Thus, no effect is projected for BAR, MOP, SBK and ALE/SPI, apart from the small changes in the annual variation (of $\pm(0.2-0.4)\%$ for $\Delta^{17}\text{O}\epsilon_{\text{sink}}$). The only pronounced weakening of the average ϵ_{sink} value by $\sim 0.5\%$ is simulated at HAP, being seasonally subject to the compositions of the East China outflow; at the same time, however, the seasonal variation at this site increases by at least $+0.6\%$. The increase of the effective enrichments at BHD/SCB is identical to that seen in the SH MBL. It should be noted that analogous results were obtained for the ^{13}C effective enrichments simulated in the model setup incorporating the revisited KIE parameterisation (*i.e.*, the aggregate of ZE and ZK setups, not presented here).

The vertical distributions of $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ present some interesting features (see Plate D.21, p. 297). Thus, the tropical averages indicate disturbances to the enrichments only below ~ 800 hPa, *i.e.* merely in the BL, whereas virtually no changes are seen in the FT. There, the same equilibrium ϵ_{sink} values are established on top of the concomitant CO mixing ratios increased by ~ 8 ppb (see Plate D.13, p. 281, panel (v) for the identical results from AE). The vertical gradients in the extratropics are conspicuously different: In the ETNH, $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ enhances in the upper troposphere, which receives the largest share of the extra emitted CO/NMHCs. A small inverse gradient is seen in the ETSH, which points at the source effect ensuing from the export of the CO with higher $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ from the tropics. All vertical profiles show distinct minima at around 50 hPa altitude, accommodating the longest-lived, least-abundant CO. Surprisingly, the $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ of the latter may be affected by as much as -0.6% by the surface CO with negative $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ rapidly convected across the tropopause in the sub-tropics throughout the summer-fall period.

6.2.5.3 On the use as a measure of atmospheric OH (ZE/ZM)

As discussed above in Sect. 6.2.3.1 (p. 174), increasing the atmospheric CO source perturbs the photochemical turnover of the key related species, foremost of the hydroxyl radical as its chief reaction partner. Thus, the average tropospheric concentrations of OH simulated in the ZE (AE) setup experience a reduction by $0.37_{0.08}^{0.51}$ molec/cm³ (or equivalent $2.4_{1.3}^{6.4}\%$), in comparison to $15.3_{6.4}^{7.9}$ molec/cm³ simulated in Z (REF).¹³⁹ On the other hand, a definite response to the CO/OH perturbation is seen in the weakened global ϵ_{sink} values, ensuing from the different CO source-sink equilibrium established (see Table 6.7, p. 195). In contrast to the $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ signals (whose variations are determined by both, the effective sink enrichment and changes in the isotope composition of the sources), the $\Delta^{17}\text{O}(\text{CO})$ value is predominantly determined by the $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ alone (as all CO sources virtually equal 0% , see Sects. 3.5.2, 5.2.8, 4.1.3). It is therefore of practical interest to assess how $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ (and ultimately $\Delta^{17}\text{O}(\text{CO})$) quantitatively corresponds to the OH abundance, or its changes, respectively. First, however, we emphasise that the atmospheric lifetime of CO itself may be used as a relative measure for the abundance of OH it reacts with. By applying a quasi-steady state assumption (*i.e.*, assuming that the overall source and sinks of CO are balanced on a given temporal scale), the lifetime τ_{CO} is defined through the abundances (denoted with squared brackets) and a pseudo-reaction rate coefficient $^{\dagger}k_{\text{CO+OH}}$ of CO and OH as:

$$\tau_{\text{CO}} \equiv \frac{[\text{CO}]}{^{\dagger}k_{\text{CO+OH}}[\text{CO}][\text{OH}]} \propto [\text{OH}]^{-1}.$$

Here, it is implied that the sink through OH is the dominant CO removal process in the troposphere. Applied either to the entire troposphere or a selected domain (*e.g.*, MBL), τ_{CO} proportionates the inverse of the OH

¹³⁹ Except stated otherwise, the air mass-weighted tropospheric (or in a given domain) averages are implied for $[\text{OH}]$, τ_{CO} , $^{\dagger}k_{\text{CO+OH}}$, *etc.*

abundance, globally or locally, respectively. The pseudo-rate coefficient changes in conformity with the CO and OH atmospheric distributions, although it is more sensitive to the mean air pressure in the given domain (through the pressure-dependent actual rate coefficient). Aside from that, an estimate of $[\text{OH}]$ derived through the lifetime of CO is irrespective from the abundance (or emissions) of the latter. Analogously, the difference between the reciprocal CO lifetimes, $\Delta\tau_{\text{CO}}$, directly proportionates the changes in the $[\text{OH}]$ as

$$\Delta\tau_{\text{CO}} \equiv (\tau_{\text{CO}})_{\text{ZE}}^{-1} - (\tau_{\text{CO}})_{\text{Z}}^{-1} \propto \Delta[\text{OH}]_{\text{ZE-Z}}. \quad (6.2)$$

In this instance, the subscripts denote the values obtained in the Z and ZE simulations, respectively. The relationship (6.2) holds well in almost all tropospheric domains regarded, as seen in Figure 6.17a (left panel) presenting the correlation between the simulated $\Delta\tau_{\text{CO}}$ and $\Delta[\text{OH}]$. Thus, lowering of the OH concentration by $0.33 \cdot 10^5 \text{ molec cm}^{-3}$ in the ZE setup corresponds to an increased lifetime of CO by 2.1 days in the troposphere, providing the average sensitivity of $\Delta\tau_{\text{CO}}/\Delta[\text{OH}]$ of $2.57 \cdot 10^{-3} \text{ days}^{-1}$ per $10^5 \text{ molec cm}^{-3}$ OH. Very similar sensitivities are concluded for the tropics and most of the MBL averages, as opposed to the strongest reductions in the ETNH BL and FT mainly subject to the CO perturbation. In the NH, a larger disequilibrium establishes at the same reduction in τ_{CO} , as the lowered $[\text{OH}]$ shows. Markedly, the MBL OH and CO in the ETSH show hardly any sensitivity to the increased CO/NMHCs emissions over East Asia.

It is noteworthy that the intertwined photochemical turnover (*i.e.*, recycling of OH and HO_2) promotes disproportional changes in the integral CO/OH characteristics. For example, alteration in the total CO source of +8.6% yields a similar change in the sink of CO (+8.5%), a larger increase in the CO burden (+13.3%), a lower reduction in $\Delta\tau_{\text{CO}}$ (-4.3%), and the least disturbance to the OH abundance itself (-3.1%), respectively.¹⁴⁰ In absolute terms, about twenty additionally emitted CO molecules are needed to remove one OH available for reaction in the troposphere. This ratio evidently changes within each domain and with the initial CO abundance considered (*i.e.*, that of the unperturbed case), however unlikely significantly. Examined in the extended budgeting of the photochemical turnover in the Z and ZE simulations (see Sect. 6.2.3 above, also Figure 6.10 on p. 177), the enhancement in the OH production occurs by far through the secondary production reactions, *i.e.* involving HO_2 . The production of the latter is chiefly propelled by the increased CO sink through the atomic hydrogen stemming from the CO+OH reaction (*cf. ibid.* the increased HO_x chemistry source). Further, atomic H contributes to the OH production via reactions with ozone and HO_2 . Ultimately, the additional CO is responsible for the large fraction of the recycled OH, thus rendering the respective changes in the CO/OH abundances disproportional, but likely linearly correlated.

The situation with the $\Delta^{17}\text{O}\epsilon_{\text{sink}}(\text{CO})$ sensitivity to OH is more intricate. First of all, alike for any reservoir containing isotopically separated fractions, the equilibration between the sources and sinks is decisive for the resulting $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ established in CO. Unlike the lifetime, however, the $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ signal in CO is additionally subject to transport and mixing in the atmosphere that determine its relative distribution differently from that of $\Delta\tau_{\text{CO}}$. Secondly, because the changes in CO induced by the photochemistry and transport/mixing are comparable on the same timescale, they result in peculiar isotope composition equilibration dynamics. A somewhat counterintuitive outcome of this is, for example, that neither the domain nor the whole tropospheric averages of ϵ_{sink} can be approximated using the conventional simplified source-sink isotope models (*cf.* Mook^[2000], Chapter 4, p. 57–66). The underlying reason is the permanent perturbation of the initial conditions of the equilibrating reservoir, as well as irregular equilibration terms. Whilst the former is attributed to the transport/mixing processes, the latter are the inevitable due to the perceptible (spatial, seasonal) variations in surface emissions and photochemical processing of CO. At last, complex CO isotope composition equilibration dynamics in the atmosphere may not result in an unequivocal correspondence between the $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ and OH. A characteristic case is when a stable equilibrium between the sources and sinks of CO is reached in a particular domain, the same resulting $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ may be established on top of different CO and OH abundances (as exemplified by the zero $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ in the tropical FT discussed in the previous section).

Employing ϵ_{sink} as a measure of atmospheric OH is thus an arduous, nonetheless feasible, task when an appropriate chemistry-enabled GCM (alike in the current study with EMAC) is used, however, provided that a certain (or an assumed) distribution of the CO sources and sinks is known. In other words, different distributions of $[\text{CO}]$ are likely to yield different $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ averages corresponding to the same $[\text{OH}]$. Analogously, an

¹⁴⁰The discrepancy between the overall source and sink of CO accounts to the increased export to the stratosphere (which is proportional to the average CO abundance as $\sim 0.235 \text{ Tg/Tg yr}^{-1}$). For OH, a change of the tropospheric mass is quoted (as opposed to the mentioned above changes in the average mass-weighted concentrations).

identical (in amount) perturbation of the CO source at a different location/instant will yield a nonidentical, *i.e.* specific $\Delta^{17}\text{O}_{\text{sink}}$ *vs.* $\Delta[\text{OH}]$ sensitivity. This is exemplified by the results of the Z and ZE simulations presented in Figure 6.17a (right panel). The relationship between the simulated domain-averaged $\Delta[\text{OH}]$ and $\Delta^{17}\text{O}_{\text{sink}}$ differs distinctly from that of $\Delta\tau_{\text{CO}}$ and highlights the influence of transport and mixing processes on the compositions at high latitudes, where distinct changes in $\Delta^{17}\text{O}_{\text{sink}}$ are visible despite the least reductions to $[\text{OH}]$. In particular, the ETSH/Antarctic CO $\Delta^{17}\text{O}_{\text{sink}}$ averages exceed +0.1‰ on top of virtually unchanged CO and OH abundances. Contrasting the $\Delta^{17}\text{O}_{\text{sink}}$ reductions simulated in the Arctic, the effective sink enrichment in the ETSH CO is positively sensitive to the changes in the East Asian emissions. As discussed above in Sect. 6.2.3.1 (p. 174), this occurs at the expense of the extra emitted CO residue exported from the tropics. Similarly, the sensitivity of $\Delta^{17}\text{O}_{\text{sink}}$ to the $[\text{OH}]$ in the Arctic is enhanced, because of admixing of CO with more negative $\Delta^{17}\text{O}_{\text{sink}}$ from the lower NH latitudes. Notably, $\Delta[\text{OH}]$ is generally smaller in the MBL, where the source-sink equilibrium in CO is much less perturbed than over the continents. No sensitivity of $\Delta^{17}\text{O}_{\text{sink}}$ to $[\text{OH}]$ is seen in the global MBL and tropical FT averages. Whereas the FT compositions indeed remain unchanged due to the strong source-sink-transport equilibrium established in this domain, the MBL global average occasionally integrates the negative and positive $\Delta^{17}\text{O}_{\text{sink}}$ values simulated in the NH and SH, respectively. Finally, the sensitivity of the tropospheric average $\Delta^{17}\text{O}_{\text{sink}}$ is found to be similar to that of the ETNH BL, *i.e.* about 0.2‰ per $10^5 \text{ molec cm}^{-3}$ on average, which is concluded to be a characteristic sensitivity of $\Delta^{17}\text{O}_{\text{sink}}$ to $[\text{OH}]$ upon changes in the NH sub-tropical CO (East Asian) emissions. Being not large, this signal is however clearly nonzero, which is an important inference for the tropospheric CO as an isotope reservoir, whose sources and sinks remain (on the annual scale) in the equilibrium.

Probing a perturbation of the CO source in a particular region is a characteristic, although quite specific, sensitivity case study. It confirms that the atmospheric transport of CO isotopologues, and therefore the timing and location of the extra source, appear to be decisive for the resulting sensitivities established; moreover, the resulting alteration of the OH field is domain- and hemispherically asymmetric. But what happens if the $[\text{OH}]$ distribution is generally (*i.e.*, more homogeneously) altered throughout the troposphere? How should in this case the corresponding $\Delta^{17}\text{O}_{\text{sink}}$ values change? Again, it is not straightforward to inquire into such case because of the tight photochemical coupling of OH and CO. One could have decreased the OH levels in the model artificially (*e.g.*, by adding a fictitious sink term), however this will likely perturb the natural photochemical turnover, in particular the recycling of OH that is (as shown above) promoted in reactions of CO with OH. As a result, one may obtain a spurious $\Delta[\text{OH}]/\Delta\tau_{\text{CO}}/\Delta^{17}\text{O}_{\text{sink}}$ estimate. In this sense, the best suited solution is to change the overall CO abundance that in turn will globally alter the OH levels, however the relatively short lifetime of CO and the large spatial irregularity of its surface sources limit their application to such a problem. A more practical approach, implemented in the ancillary model setup abbreviated “ZM”, is followed here instead. It consists of augmenting the most homogenous (*i.e.*, CH_4 -derived) component of CO through the proportional elevation of the atmospheric methane abundance. In this case, a nearly uniform increase in $[\text{CO}]$ and decrease in $[\text{OH}]$ are expected, owing to the intensified CH_4 sink via OH. In order to introduce a common point in the simulated CO, the increase of the atmospheric CH_4 abundance was calculated at +27.1%, which yields the average tropospheric CO burden in ZM equal to that simulated in the ZE setup. Except for the amplified CH_4 levels, the setup of ZM reflects that of Z.

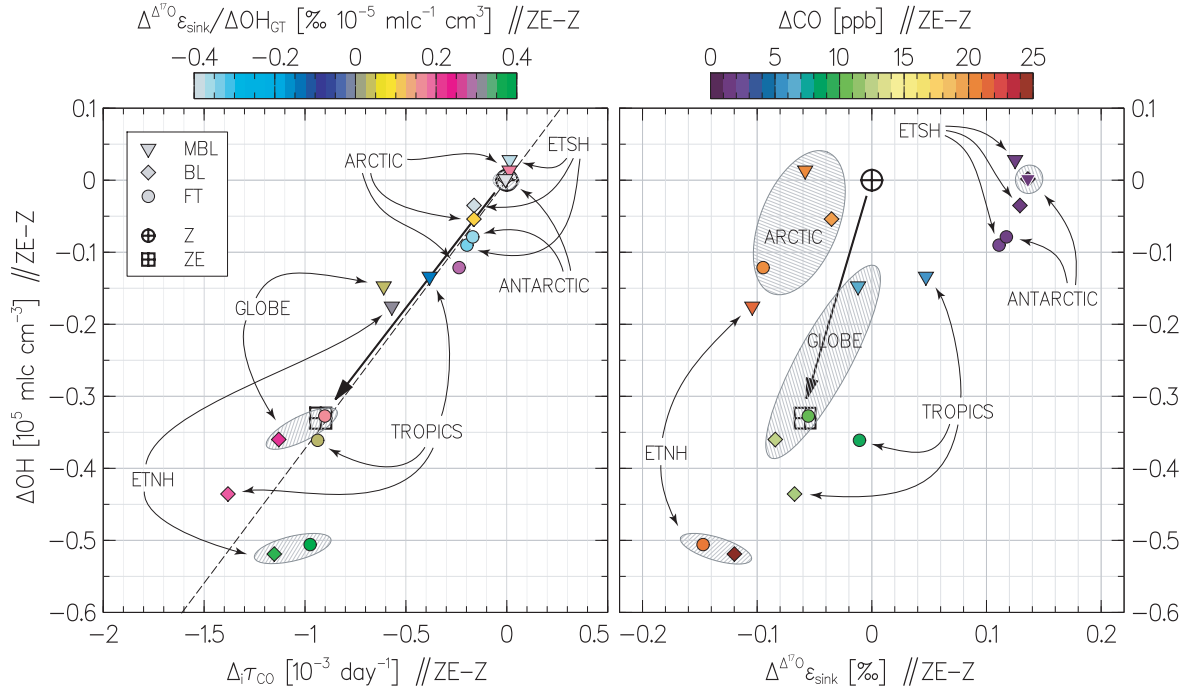


Figure 6.17a Sensitivity of the atmospheric CO lifetime, OH radical concentration and effective anomalous oxygen isotope enrichment $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ to the increase in surface CO emissions over East Asia (inferred from the Z and ZE setups). Symbols refer to the average sensitivities simulated in various zonal/vertical domains. Left: Domain-wise change in [OH] as a function of the change in reciprocal CO lifetime, $\Delta\tau_{\text{CO}}$; colours denote the sensitivity of $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ within the particular domain to the change in global tropospheric OH concentration, $\Delta\text{OH}_{\text{GT}}$. The dashed line shows the result of the linear regression through the values ($R^2 = 0.92$). Right: Domain-wise change in [OH] as a function of change in the effective $\Delta^{17}\text{O}$ sink enrichment in CO, $\Delta^{17}\text{O}\epsilon_{\text{sink}}$; colours denote the respective change in the simulated CO mixing ratio. Thick arrows identify the changes in the tropospheric averages (large black symbols). See text for details.

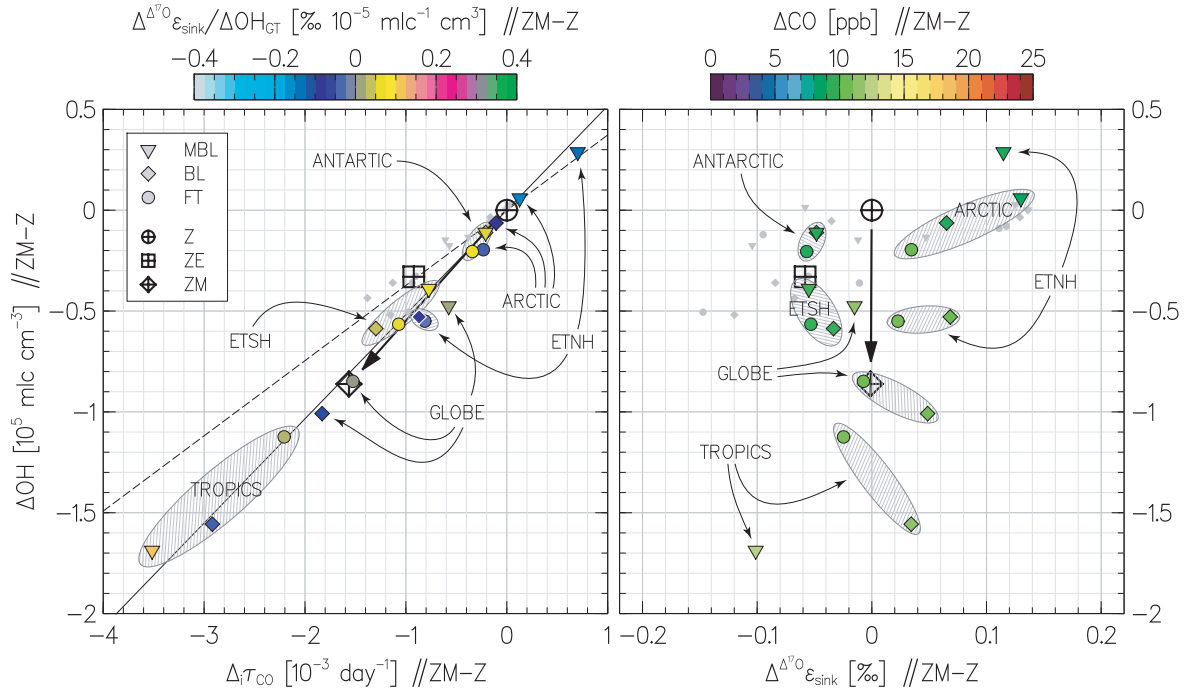


Figure 6.17b Same as in previous figure, but for the sensitivity to the increased CH_4 source of CO (inferred in the Z and ZM setups). Grey small symbols reproduce the values from the ZE setup (shown in Figure 6.17a) for comparison; mind the changed axes scales. Solid and dashed lines show the results of the linear regression through the ZM ($R^2 = 0.98$) and the ZE values, respectively. See text for details.

The resulting sensitivities inferred in the simulation with the ZM setup are presented in Figure 6.17b (left panel). A firm correspondence between the changes in OH and reciprocal CO lifetime is noted, with a $\Delta\tau_{\text{CO}}/\Delta[\text{OH}]$ sensitivity of $1.52 \cdot 10^{-3} \text{ days}^{-1}$ per $10^5 \text{ molec cm}^{-3}$, which is $\sim 1/3$ lower than that simulated in the case of increased East Asian emissions (ZE setup). This is because the methane chain intermediates (*viz.* methanol and formaldehyde), similarly to what occurs in the sink of CO, return an HO_2 molecule in their reactions with OH, thus the strengthened throughput of the $\text{CH}_4 \rightarrow \text{CO}$ chain contributes to the increasing HO_2 turnover. In contrast to the conditions established in the ZE (AE) setup, the latter in ZM becomes amplified by one-third more ($\sim +300$ *vs.* $\sim +200 \text{ Tg}(\text{HO}_2)/\text{yr}$, respectively¹⁴¹), which in turn, as described above, eventually catalyses the recycling of OH (increased turnover of $\sim +150$ *vs.* $\sim +80 \text{ Tg}(\text{OH})/\text{yr}$, respectively). Subsequently, a similar increase of the CO burden (+13.3%) is accompanied in ZM by the different changes of the OH burden (−7.3%), sinks of CO (+5.1%) and CH_4 (+17.2%) and a reduction of $\Delta\tau_{\text{CO}}$ (−7.3%). The larger change in the tropospheric OH is by far due to methane, whose efficiency in reducing the available atmospheric OH is about three times higher than that of CO. Ultimately, only five CO and six-and-a-half CH_4 extra molecules remove one available OH molecule in ZM (*cf.* twenty CO in ZE), therefore smaller changes to the reciprocal CO lifetime per same $\Delta[\text{OH}]$ are simulated. Being additionally reinforced by the larger NO_x/NO_3 burden in the NH, the intensified $\text{CH}_4 \rightarrow \text{CO}$ chain turnover even leads to an increased [OH] and shorter-lived CO in the ETNH and Arctic MBL. The resulting domain-wise changes to CO and OH are, nonetheless, much dependent on the competition between the rates of the temperature-sensitive $\text{CH}_4 + \text{OH}$ reaction and the mostly pressure-sensitive reaction between CO and OH. This is confirmed by the largest tropical $\Delta\tau_{\text{CO}}$ and $\Delta[\text{OH}]$ averages, with the latter showing a perceptible decrease in the MBL of $1.7 \cdot 10^5 \text{ molec cm}^{-3}$, *i.e.*, threefold the largest $\Delta[\text{OH}]$ diagnosed in the ZE setup. We note furthermore that the correlation between $\Delta[\text{OH}]$ and $\Delta\tau_{\text{CO}}$ is tighter in the ZM setup, as the $\Delta\tau_{\text{CO}}$ is chiefly formulated in the photochemistry terms, and the perturbations induced in CO and OH are mostly homogeneous. The contrasting inhomogeneity in the ZE setup results in different $\Delta\tau_{\text{CO}}/\Delta[\text{OH}]$ sensitivities in variously affected domains (*e.g.*, in the ETNH and Arctic).

The distribution of the simulated $\Delta[\text{OH}]$ sensitivities (seen best in the right panel of Figure 6.17b) is in agreement with these arguments, as confirmed by the similar averages diagnosed in the NH and SH extratropics. Interestingly, the concomitant changes in the $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ are of the opposite courses, built on top of the comparable increases in [CO] of 8–12 ppb. In contrast to the ZE setup, the ETNH compositions show an enhancement in the effective sink fractionation owing to the better CO source-sink equilibrium established in spring and summer, and a reversed situation (*i.e.*, inhibited equilibrium) in the ETSH. Likewise seen in all simulations with EMAC, the intensive mixing of the tropospheric CO inventory strongly evens out the differences between the domain averages in the ETSH. As the perturbation to the CO mixing ratio is close to being homogeneous, only small contribution from the interhemispheric transport (*e.g.*, an increased export of CO from the tropics to the ETSH) is expected in the simulated $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ values. Nonetheless, the effect of the latitudinal transport/mixing is seen in a progressive enhancement of $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ at the higher latitudes. Moreover, higher $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ values are generally found in the regions subject to large surface emissions, where a larger relative increase in HO_2 and OH turnover is diagnosed. The remoteness from the BL similarly explicates the systematically lower $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ values simulated in the FT. At last, the important result of the sensitivity study with the ZM setup is the negligible change to the average tropospheric effective sink enrichment in CO, despite the substantial changes established in the sources, sinks and burden of the latter. This singular result is an occasional superposition of the key factors decisive for the resulting $\Delta^{17}\text{O}\epsilon_{\text{sink}}$, mostly of the established transport-mixing patterns and the spatial variations in the CO sink fractionation magnitude caused by the peculiar pressure dependence of the CO sink KIE. A proof of that are the jointly simulated ^{13}C and ^{18}O effective enrichments, which show nonvoid changes in the ZM setup, however, also very small. In particular, the tropospheric averages of $\Delta\epsilon_{\text{sink}}$ in the ZE/ZM setups relate as +0.125‰:−0.022‰ (for ^{18}O) and −0.048‰:−0.017‰ (for ^{13}C), respectively, concluding larger changes in the ZE setup and pointing to the smallest effect for the least pressure-dependent ^{18}O KIE in the ZM. Therefore, the hemispheric asymmetry in the perturbed CO source is surmised to be the most influential driver for the changes in the tropospheric average of ϵ_{sink} .

¹⁴¹The extended budgeting of the species turnover simulated in Z (REF) and ZM setups is detailed in Plate D.22 on p. 298.

Table 6.7 Simulated effective sink isotope enrichment in CO in the Z, ZE and ZK model setups

Domains	TR ^{ETNH} _{ETSH}	AR(AQ)	Globe	TR ^{ETNH} _{ETSH}	AR(AQ)	Globe	TR ^{ETNH} _{ETSH}	AR(AQ)	Globe
	¹³ C ϵ_{sink} [‰] //Z			¹⁸ O ϵ_{sink} [‰] //Z			$\Delta^{17}\text{O}\epsilon_{\text{sink}}$ [‰] //Z		
SRF	+3.31 ^{3.00} _{4.26}	+3.36(+4.39)	+3.34	-7.52 ^{7.08} _{10.55}	-8.09(-10.94)	-7.80	+3.56 ^{3.41} _{4.97}	+3.92(+5.16)	+3.71
BL	+3.52 ^{3.03} _{4.20}	+3.25(+4.30)	+3.45	-8.06 ^{7.24} _{10.50}	-7.89(-10.85)	-8.13	+3.81 ^{3.47} _{4.93}	+3.82(+5.10)	+3.85
MBL	+4.37 ^{3.22} _{4.28}	+3.20(+4.30)	+4.00	-10.19 ^{7.68} _{10.72}	-7.71(-10.85)	-9.62	+4.82 ^{3.67} _{5.03}	+3.70(+5.10)	+4.54
FT	+3.31 ^{3.24} _{3.88}	+3.35(+4.14)	+3.39	-9.87 ^{8.69} _{10.95}	-8.47(-11.06)	-9.66	+4.41 ^{4.04} _{5.01}	+4.02(+5.13)	+4.38
T	+3.33 ^{3.22} _{3.91}	+3.34(+4.15)	+3.40	-9.71 ^{8.53} _{10.91}	-8.42(-11.05)	-9.52	+4.36 ^{3.98} _{5.00}	+4.01(+5.13)	+4.33
TP	+1.55 ^{3.43} _{3.37}	+2.88(+3.11)	+2.21	-12.98 ^{10.56} _{12.31}	-9.61(-12.02)	-11.75	+5.04 ^{4.50} _{3.16}	+4.30(+5.22)	+4.84
	¹³ C ϵ_{sink} [‰] //ZK			Δ^a ¹³ C ϵ_{sink} [‰] //ZE-Z			Δ^a $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ [‰] //ZE-Z		
SRF	+4.11 ^{3.80} _{3.72}	+4.28(+5.95)	+4.23	-0.65 ^{-0.95} _{+0.11}	-0.09(+1.09)	-0.78	-0.65 ^{-1.11} _{+1.29}	-0.27(+1.22)	-0.81
BL	+4.38 ^{3.86} _{3.63}	+4.15(+5.84)	+4.38	-0.67 ^{-1.06} _{+1.19}	-0.18(+1.29)	-0.82	-0.67 ^{-1.20} _{+1.29}	-0.35(+1.36)	-0.84
MBL	+5.54 ^{4.17} _{3.75}	+4.10(+5.84)	+5.20	+0.47 ^{-0.99} _{+1.16}	-0.37(+1.29)	-0.15	+0.47 ^{-1.04} _{+1.25}	-0.58(+1.36)	-0.12
FT	+4.53 ^{4.32} _{3.44}	+4.37(+5.74)	+4.61	+0.04 ^{-1.22} _{+0.96}	-0.75(+1.05)	-0.44	-0.11 ^{-1.47} _{+1.11}	-0.95(+1.17)	-0.55
T	+4.52 ^{4.27} _{3.46}	+4.36(+5.75)	+4.59	-0.10 ^{-1.20} _{+0.98}	-0.71(+1.06)	-0.48	-0.16 ^{-1.44} _{+1.13}	-0.90(+1.19)	-0.58
TP	+3.41 ^{3.99} _{4.53}	+4.26(+5.04)	+3.97	-0.34 ^{-1.05} _{+0.67}	-1.15(+0.98)	-0.44	+0.05 ^{-1.83} _{+0.73}	-1.43(+0.97)	-0.81

Notes:

Air mass- and [CO]-weighted annual averages over the given vertical/zonal domains are shown; the planetary boundary layer and tropopause heights are diagnosed.

The vertical domains are abbreviated as: SRF – surface (lowermost model) layer, BL – boundary layer (spanning from the surface to the planetary BL height), MBL – marine BL (BL excluding continents and regions subject to large pollution), FT – free troposphere (below the tropopause and above the BL), T – troposphere (below the tropopause), TP – at the tropopause.

The zonal domains are abbreviated as: TR – tropics, ETNH/ETSH – extratropical SH/NH, AR – Arctic (north of 66°N), AQ – Antarctic (south of 60°S).

^{a)} Denotes sensitivities, *i.e.* changes to the effective fractionations simulated in the ZE and Z setups are quoted. Mind the per ten thousand units (1‰ is equivalent to 0.1‰).

Recapitulating, the set of dedicated “ZERO” model setups performed in this study allowed simulating the effective CO sink fractionation, ϵ_{sink} , for all stable isotope signals (including the $\Delta^{17}\text{O}$) simultaneously, *i.e.* subject to the same atmospheric dynamics. The analysis of atmospheric ϵ_{sink} is presented here for the first time, and at a sufficiently detailed level. Thus, the simulated large spatiotemporal variations in ϵ_{sink} are adequate and attributed to various factors, *e.g.* admixing of the freshly emitted CO, zonal and vertical transport and the continuous fractionation processes escorting it. Being well proportional in the BL, the ¹³C, ¹⁸O and $\Delta^{17}\text{O}$ effective sink fractionations have characteristically different vertical distributions, owing to the dissimilar pressure dependence of the rates of CO isotopologues reactions with OH. A prominent example is the absent ¹³C effective enrichment expected above the tropopause.

Further, three relevant aspects have been investigated. At first, a revisited, pressure- and temperature-sensitive parameterisation for the ¹³C KIE in the CO+OH reaction has been probed in the ZK setup of EMAC. The resulting revisited tropospheric ¹³C ϵ_{sink} average value is appreciably larger than that ensuing from the conventional approaches. The effect is equally well pronounced in both, NH and SH compositions, as opposed to the cases of adjusting the surface sources strengths/signatures. Importantly, the revisited KIE approach appears to be an unparalleled amendment that is capable of alleviating the discrepancies unresolved for the ETSH $\delta^{13}\text{C}(\text{CO})$ so far. Secondly, in view of the amended trace gas emission proposed in this study (AE setup), the effect of increasing the East Asian emissions on the atmospheric CO effective enrichments was investigated in the ZE setup. As a result, surprisingly low sensitivities of ϵ_{sink} are inferred, with a projected negligible outcome for the simulated $\delta^{13}\text{C}(\text{CO})$ in comparison to its large uncertainty and variations in the troposphere (*cf.* Table 6.7 below and Sect. 6.2.2 above). Third, the mutual relationship between the variations in the atmospheric OH, CO, its reciprocal lifetime $\Delta\tau_{\text{CO}}$ and effective $\Delta^{17}\text{O}$ enrichment is scrutinised using the results of the ZE and ZM setups. Being more of a virtual (model) characteristic, τ_{CO} is shown to change unambiguously with atmospheric [OH], with a moderately varying sensitivity due to the complex photochemical kinetics interwoven with CO and OH in the troposphere. The more practical $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ characteristic presents itself as a more complex tracer, being subject to the transport effects and variable CO+OH KIE magnitude in the atmosphere. In particular, $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ may be locally sensitive to changes in global OH and CO (*e.g.*, the signal from the increased East Asian emissions’ may be picked up in the Arctic BL), as well as insensitive to the increase in the CO source (in case of a well established source-sink equilibrium, *e.g.* in the tropical free troposphere). The model results also affirm an essential conclusion drawn here for the equilibrium kinetics of the atmospheric CO

as an isotope reservoir: Being moderately short-lived, this species is comparably altered by the photochemical and transport/mixing processes, which makes the application of the simplified models (like, for example, that used by Tans^[1997] for the long-lived CH₄) unfeasible. It is shown that a similar change to the overall CO and OH tropospheric burdens may yield opposite changes in $\Delta^{17}\text{O}\epsilon_{\text{sink}}$ in a given atmospheric domain. Whereas that provides a powerful insight into the processes inducing changes in the atmospheric CO and OH, the complexity of the ϵ_{sink} signal and its quite low sensitivity are the drawbacks of exploiting this tracer. For example, it may be much less sensitive to homogenous changes in the atmospheric CO sources or sinks. Furthermore, the sink of CO itself is found to substantially recycle atmospheric OH, that is, about three times more efficiently than methane when calculated per emitted molecule. This, however, reduces the ultimate sensitivity of CO mixing (though not isotope) ratios to changing atmospheric OH levels.

6.2.6 Kinetic chemistry effects (AK, SMK)

This section completes the enumeration of the sensitivity studies on $\delta^{13}\text{C}(\text{CO})$ performed with EMAC in this study with two model setups/simulations analysed. Abbreviated “AK”, the first setup incorporates the revisited, amended CO+OH reaction KIE parameterisation and is otherwise identical to the base REF setup of EMAC. The details on the analogous modification introduced in the ZK setup are given above in Sect. [373] (p. 187). Complementing the objectives of the ZK setup, the purpose of AK is to provide an estimate of the atmospheric $\delta^{13}\text{C}(\text{CO})$ on top of the realistic surface sources’ isotope signatures, and with all initially considered isotope effects included. This additionally allows checking (*e.g.*, by the isotope mass-balance) whether the nonlinearities introduced by the atmospheric mixing do not significantly affect the individual estimates of $\delta^{13}\text{C}(\text{CO})$ constituents. Enumerated in Eq. (6.1) (p. 182), these terms are all non-zero in AK, in contrast to that in the DEP or Z setups.

The second setup, abbreviated “SMK”, is devised to probe the sensitivity of $\delta^{13}\text{C}(\text{CO})$ to the inclusion of the kinetic isotope effect in the reaction of methanol with OH. As detailed in Sect. 3.4.1.2 (p. 40), some of the laboratory measurements of the ¹³C KIEs appear unreliable, hence some of them were discarded already at the initial stage of creating the isotope chemistry parameterisation in this study. In particular, the HCHO KIEs, assayed in box-model simulations, produced unrealistic ¹³C/¹²C ratios in HCHO and CO and thus were rejected in the reference setup of EMAC (REF). So is the KIE in the CH₃OH+OH reaction that was derived at $^{13}\text{C}\eta_{\text{CH}_3\text{OH}+\text{OH}} = +(31\pm 21)\%$ in the laboratory approach analogous to that used for HCHO KIEs. Being, however, not as strong as the KIEs for HCHO, the methanol KIE did not unambiguously indicate its unreliability in the box-model tests. In order to estimate its potential influence on the $\delta^{13}\text{C}(\text{CO})$ in a 3D model study, it was included in the SMK setup that otherwise does not diverge from REF.

Figure 6.18 (left panel) below presents the zonal averages of $\delta^{13}\text{C}(\text{CO})$ simulated in REF, AK and AEK simulations (the setup of the latter aggregates the improvements introduced for ¹³CO in this study, see Sect. 6.2.2 and Table 6.5 on pp. 165–167). The resulting $\delta^{13}\text{C}(\text{CO})$ in AK shows, similar to ZK and Z, enhancements on top of the meridional variation ensuing from the realistic ¹³C/¹²C compositions of CO sources. The isotope mass balance of ¹³CO/¹²CO confirms that the changes between the whole-tropospheric and domain averages of $\delta^{13}\text{C}(\text{CO})$ simulated in AK and REF equal those obtained in the Z and ZK setups to within $\pm 0.01\%$ (for the domain averages, under same atmospheric dynamics). That is, the decoupled estimates of the CO sink effective enrichments ϵ_{sink} obtained in the simulations with the Z setups are adequate and are not significantly affected by the nonlinear effects of atmospheric mixing (see the discussion on p. 182, also note¹³⁵ there). Analogously, the estimate of the effective fractionations in the removal effects (DEP setup) was found to contribute linearly to the overall ¹³CO budget, so that the closure of the global isotope mass-balance of CO is susceptible to such a small term (equivalent to $+0.15\%$ in $\delta^{13}\text{C}$).

Applying the new KIE parameterisation, however, has a distinctly different effect on the seasonal variations in the effective sink enrichment ($^{13}\text{C}\epsilon_{\text{sink}}$) and in the resulting $\delta^{13}\text{C}(\text{CO})$, owing to the variations in the ¹³C/¹²C ratio of the underlying overall CO source. For instance, the minimum-to-maximum span in the ETSH $^{13}\text{C}\epsilon_{\text{sink}}$ enhances from 2.1‰ to 2.7‰ (see Figure 6.16, p. 189). However, because the maxima of $^{13}\text{C}\epsilon_{\text{sink}}$ occur timely with the lowest in $\delta^{13}\text{C}$ sources of CO in summer (from to the largest fraction of the ¹³C-depleted CH₄-derived component of CO), the resulting seasonal $\delta^{13}\text{C}(\text{CO})$ amplitude actually slightly decreases (from 3.5‰ to 3.4‰, nevertheless retaining the higher annual average). The variations in the SH lose another (0.1–0.2)‰ when the amended surface emissions are applied (*cf.* Figure 6.18, the AEK curves). Quite the opposite is seen in the ETNH zonal averages. The increase in the $^{13}\text{C}\epsilon_{\text{sink}}$ span (from 2.9‰ to 3.5‰) proportionally augments the

$\delta^{13}\text{C}(\text{CO})$ variation (1.6‰ to 2.3‰, respectively), whilst the improved emissions add another 0.1‰. These differences are caused by the dissimilar hemispheric temporal dynamics of the mixing and isotope ratios of CO. As detailed above in Sect. 4.1.2 (see also Figure 4.9, p. 87), the phase shift between the $\delta^{13}\text{C}(\text{CO})$ and $[\text{CO}]$ seasonal variations in the ETNH may be as large as 4 months in contrast to 1–1.5 months in the ETS, promoted by the latitudinal transport of fresh CO in the former and efficacious mixing of the tropospheric inventory in the latter. As a result, the seasonal drop in the high-latitude NH CO source $\delta^{13}\text{C}$ signature occurs perceptibly later than the intensification of the photochemistry in late spring, thus giving more time for the OH sink to enrich CO in ^{13}C before the methane starts to refill it with the ^{13}C -depleted carbon. On the other hand, $\delta^{13}\text{C}(\text{CO})$ variations in the ETNH change similarly in all three amended setups, *i.e.* AK and AE and their aggregate AEK, which contrasts the peculiar asynchronous seasonal development in the components determining the final atmospheric $\delta^{13}\text{C}(\text{CO})$ (see Eq. (6.1), p. 182) in the NH. In the ETS, however, their relationship is less tangled. For instance, the improved surface emissions yield small but clearly larger $\delta^{13}\text{C}(\text{CO})$ variations (*cf.* Figure 6.11 on p. 178, left panel), whereas the revisited CO+OH KIE has the opposite consequences by counterbalancing the growing share of the CH_4 -derived CO. Ultimately, the contribution of the revisited KIE is marked in the SH $\delta^{13}\text{C}(\text{CO})$ average but not in its variation.

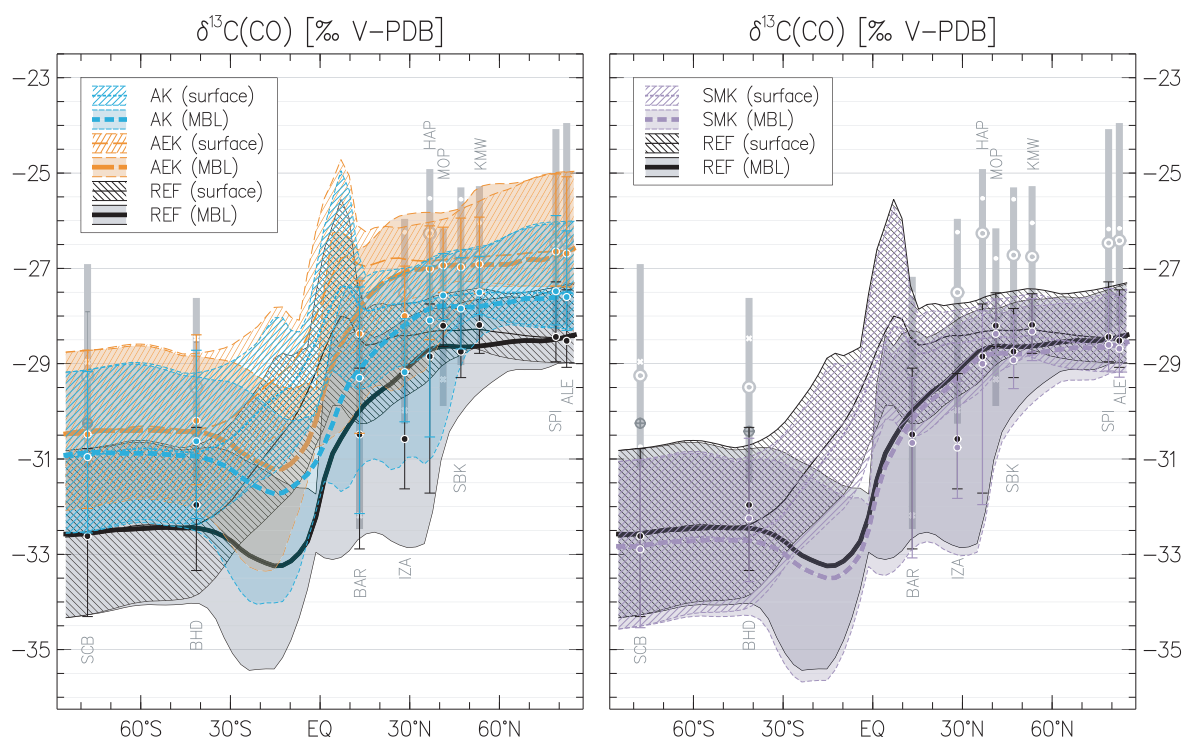


Figure 6.18 Zonal average $\delta^{13}\text{C}(\text{CO})$ simulated in REF, AK and AEK (left panel) and SMK (right panel) setups. Thin and thick lines refer to the averages in the surface layer and MBL, respectively. Grey symbols denote the station $\delta^{13}\text{C}(\text{CO})$ data, black and coloured symbols denote the values simulated at the locations of the surface station data in the REF and respective sensitivity simulations. Note that the concomitant CO mixing ratios in the AEK are larger than those simulated in the other setups. See Figure 6.5, p. 168, for reference.

The effects of the AK/AEK setups improvements on the $\delta^{13}\text{C}(\text{CO})$ values simulated at the surface locations are found to be much similar to that seen in the BL averages. A slightly larger contribution of the new CO sink KIE parameterisation is noticed at IZA and BAR, where the photochemical processing of CO dominates. The seasonal $\delta^{13}\text{C}(\text{CO})$ variation simulated at BAR distinctly increases in the AK setup, yielding the best-matching simulated $^{13}\text{C}/^{12}\text{C}$ isotope ratios. The best-matching mixing ratios simulated at BAR in the AE setup (*cf.* Figure 6.5 on p. 168, left panel), on the contrary, do not fit the underestimated $\delta^{13}\text{C}(\text{CO})$ variation. A similar inconsistency is seen for $\delta^{13}\text{C}(\text{CO})$ at HAP, where its span is initially overestimated by about 1‰ in REF. A clear improvement for the isotope CO simulated at this site is concluded with much better mixing ratios reproduced in the AEK setup. Overall, adjusting the surface emissions ameliorates the compositions at all NH stations as much as applying the revisited CO sink KIE parameterisation.

6.2.6.1 Sensitivity to the methanol oxidation KIE (SMK)

The inclusion of the methanol oxidation KIE is found to have a minor effect on the simulated $\delta^{13}\text{C}(\text{CO})$. As expected, the CO produced in the photochemical chains involving CH_3OH becomes affected, in particular, the positive $\text{CH}_3\text{OH}+\text{OH}$ KIE favours the production of the ^{12}C isotopologues of the intermediate HCHO, and subsequently leads to the production of the more ^{13}C -depleted CO. Propagating essentially through the same chemical pathways, this signal is very similar to that inferred for the effective removal fractionation in CO in the DEP setup ($^{13}\text{C}\epsilon_{\text{rem}}$, cf. Plate D.16, p. 286) caused predominantly by the fractionations in the dry deposition of CH_3OH and HCHO. In comparison to $^{13}\text{C}\epsilon_{\text{rem}}$, the sensitivity $\Delta\delta^{13}\text{C}(\text{CO})$ to the methanol KIE (inferred as the difference between the $\delta^{13}\text{C}(\text{CO})$ simulated in the SMK and REF setups) is negative, and larger by a factor of 1.2 (NH) to 1.6 (SH) than the $^{13}\text{C}\epsilon_{\text{rem}}$ magnitudes simulated in the BL. The vertical distribution and temporal evolution of $\Delta\delta^{13}\text{C}(\text{CO})$ is featureless, with the average of $-0.24_{-0.26}^{+0.17}\text{‰}$ ¹³² being characteristic for both, BL and FT; the only pronounced variations of about 0.1‰ are simulated in the ETNH, with the maxima and minima in February and August, respectively. The largest $\Delta\delta^{13}\text{C}(\text{CO})$ values of $-(0.4\text{--}0.5)\text{‰}$ are found in the tropics over the Eastern Pacific, Oceania and Southern America, and are associated with the regions of large seasonal methanol emissions (mostly biogenic sources, see Sect. 5.2.5, p. 131).

In contrast to the weak signal in CO, the resulting changes to the methanol $\delta^{13}\text{C}$ signature are more pronounced. The intensive sink of CH_3OH (corresponding to a lifetime of about 5 days, Millet *et al.*^[2008]) together with the large concomitant KIE magnitude promote strong spatial $\Delta\delta^{13}\text{C}(\text{CH}_3\text{OH})$ gradients. For example, the continental and MBL values establish at $+(5\text{--}10)\text{‰}$ and $+(25\text{--}35)\text{‰}$, respectively. In the FT, $\Delta\delta^{13}\text{C}(\text{CH}_3\text{OH})$ is generally above $+20\text{‰}$ ($+30\text{‰}$ in the MBL) and seasonally exceeds $+40\text{‰}$ in the tropical Pacific. Because of the slow in-situ production of methanol in the FT, the continuous sink fractionation leads to the average $\Delta\delta^{13}\text{C}(\text{CH}_3\text{OH})$ values of $+35\text{‰}$ established at the tropopause. Overall, the strong sensitivity of $\delta^{13}\text{C}(\text{CH}_3\text{OH})$ suggests that observations of the methanol isotope composition in the MBL or FT may provide certainty about the existence of the large $\text{CH}_3\text{OH}+\text{OH}$ KIE. For example, taking the only available measurement of ambient $\delta^{13}\text{C}(\text{CH}_3\text{OH})$ of $-(36.3\pm 3.7)\text{‰}$ (Giebel *et al.*^[2010], South Florida, 25.3°N , 80.9°W) as a reference, methanol $\delta^{13}\text{C}$ in the East Pacific is expected to be above -10‰ in case the $\text{CH}_3\text{OH}+\text{OH}$ KIE is present, as suggested by the SMK setup results. To compare, the annual averages and span of $\delta^{13}\text{C}(\text{CH}_3\text{OH})$ simulated at these locations in REF are $-(23.5\pm 0.4)\text{‰}$ and $-(36.6\pm 10.8)\text{‰}$, respectively, with the conspicuously large variations highlighting the MBL conditions. Without sufficient observational data it is therefore not feasible to corroborate the adequacy of the CH_3OH emissions $\delta^{13}\text{C}$ signatures and isotope chemistry parameterisation implemented in EMAC.

As discussed above, tropospheric $\delta^{13}\text{C}(\text{CO})$ is little sensitive to large changes in the isotope composition (or sink KIE) of CH_3OH . The resulting $\delta^{13}\text{C}(\text{CO})$ BL zonal averages simulated in SMK are further shown in Figure 6.18 (right panel) and present a small homogenous ^{13}C depletion in CO corresponding to the weak $\Delta\delta^{13}\text{C}(\text{CO})$ photochemical signal. Comparable changes to $\delta^{13}\text{C}(\text{CO})$ are noted at the locations of the observational data, *i.e.* none of the sites in the model are subject to CO, which bears an enhanced share of the CH_3OH -derived component. Overall, the inclusion of the methanol oxidation KIE favouring more ^{13}C -depleted tropospheric CO is not in line with the discrepancies seen in $\delta^{13}\text{C}(\text{CO})$.

To recapitulate, probing the alternative KIEs in the isotope chemistry parameterisation of this study provides different outcomes for the final $\delta^{13}\text{C}(\text{CO})$: (1) The inclusion of the uncertain $\text{CH}_3\text{OH}+\text{OH}$ KIE in the model (SMK setup) forces a minor decrease in the global $\delta^{13}\text{C}(\text{CO})$, not exceeding -0.5‰ at a few tropical locations that do not include the available observational sites. The concomitant effect on the isotope composition of methanol is large and thus detectable, provided that more observational data would be available. (2) Applying the revisited $\text{CO}+\text{OH}$ KIE parameterisation (AK setup) yields a substantial augmentation of $\delta^{13}\text{C}(\text{CO})$ globally, giving a more realistic result in view of the missing ^{13}CO simulated in REF. It is shown that the asynchronous variations in the source $\delta^{13}\text{C}$ and sink effective enrichment of CO, when superposed, result in distinctly larger NH and slightly smaller SH seasonal $\delta^{13}\text{C}(\text{CO})$ variations, as compared to that in REF, retaining the augmented global average, however. In the NH, the increase in $\delta^{13}\text{C}(\text{CO})$ in the AK setup is much similar to that simulated in AE (amended surface emissions) and much larger (as $\sim 4:1$) in the SH, respectively. The isotope mass-balance of CO in the different model simulations confirms the applicability of the decoupled sensitivity studies, that is, for instance, the principal components of $\delta^{13}\text{C}(\text{CO})$ can be simulated/estimated separately and linearly superposed.

6.2.7 Comparison with observational data

The following section details the comparison of the CO mixing and $^{13}\text{C}/^{12}\text{C}$ isotope ratios simulated with EMAC in four principal model setups (*i.e.*, REF, AE, AK and AEK, see Sect. 6.2.1) with the available observational data. The reader is referred to Sect. 4 (p. 67) for the overview and analysis of the latter, as well as to Sect. 6.2.1 (p. 167) for the details on the simulated characteristics compared (*i.e.*, monthly averages and IMVs). The BL (surface station) and UTLS (aircraft observations) data are considered consecutively.

6.2.7.1 Surface station data

Shown in Figure 6.19 are the scatter plots of the observed (abscissa) *vs.* simulated (ordinate) CO mixing ratio and $\delta^{13}\text{C}(\text{CO})$ monthly averages. Panels (a) and (c) refer to the results of the initial EMAC setup (REF). Further, the panels are arranged in an order emphasising the effect of each improvement introduced in the model. For instance, the upper and lower panels differentiate merely the impact of applying the original and amended surface emissions, respectively. Thus, as seen in the panels (a) and (b), the underestimated (in REF) winter-spring [CO] at the ETNH stations becomes improved in the AE setup, with the maxima gaining some missing 30 ppb at SPI/ALE to 50 ppb at KMW, SBK and HAP. A general improvement is seen for the compositions in the tropics at IZA (except for the seasonal minima) and the seasonal extrema simulated at BAR. The CO mixing ratios at this site are on average 10 ppb lower than the observed, however. The increased emissions also yield a substantially better agreement for the austral winter CO abundances simulated at BHD and SCB. There, the seasonal maxima become augmented by 5 ppb, or perceptible (7–8)% of the seasonal inventory. Overall, the July–November values at the SH sites are simulated in a very close correspondence with the observations in the AE setup.

A few systematic discrepancies are noted in both setups, nonetheless. First, an underestimated seasonal variation is seen at SPI, ALE and SBK, which points to either the underestimated seasonal variation in the surface emissions, or to the insufficient seasonal sink of CO simulated in the ETNH by the model. The former is not corroborated by the improved [CO] variations at HAP, IZA and BAR in the AE setup, and, although these tropical locations are less representative for the mid-latitude emissions, the augmented East Asian emissions do indeed improve both, the low-latitude averages and the high-latitude maxima of [CO]. The missing sink hypothesis, however, suits better the concomitantly overestimated $\delta^{13}\text{C}(\text{CO})$ minima marked at all NH stations (*ibid.*, panels (c)–(d)): If more OH is required to increase the CO sink, it implies lowering of the $\delta^{13}\text{C}(\text{CO})$ due to the simultaneously increasing share of the CH_4 -derived source. Second, poorly matching [CO] in both setups is seen at the locations subject to large surface emissions, hence larger bottom-up uncertainties in the reproduced mixing ratios. Such is seen at KMW and MOP, however, whereas the improved emissions lead to a generally more realistic seasonality at MOP, merely the averages become improved at KMW. Quantitatively this is expressed by the statistics on the temporal correspondence between the simulated and observed seasonal cycles of CO presented in Figure 6.20 (panels (a)–(b)). Shown are the Taylor diagrams (Taylor^[2001]) accommodating the correlation coefficients ρ between the observed and simulated series (angular coordinate) and the ratio between their standard deviations ($\sigma_n = \sigma_{\text{obs}}/\sigma_{\text{sim}}$, radial coordinate), respectively, for [CO] or $\delta^{13}\text{C}(\text{CO})$ at each station. A seasonal cycle with the variations perfectly matching the observations is to be found to the right of the origin point at $\sigma_n = 1$. The respective biases between the simulated and observed annual averages (which may be non-zero in the case of a perfectly correlating variations) are listed besides and additionally colour-coded. Thus, applying the improved emissions proportionally ameliorates ρ (0.39 to 0.65) and σ_n (0.41 to 0.73) at MOP, but has no effect on ρ (0.73 *vs.* 0.75) and worsens the variations (σ_n changes from 0.97 to 1.67) on top of the improved bias at KMW, respectively. This result, however, does not contradict the regular (non-isotope inclusive) [CO] data at KMW representing the unfiltered (*i.e.*, unaffected by the local pollution) compositions observed (see the discussion on p. 78).

Overall, applying the amended emissions improves the seasonal cycles and reduced biases of [CO], as concluded in Figure 6.20, panel (b). It is noteworthy that [CO] correlates well (ρ above 0.85) at six of ten regarded locations in REF (eight in the AE setup). This is in line with the findings of Pozzer *et al.*^[2007], who obtained generally high ρ values in comparison of [CO] simulated with EMAC1 with the NOAA/CDML observations (average 0.67, median ~ 0.8 over 32 stations), similar to the high REF correlations (above 0.9) in the ETSH and the low correlations (ρ below 0.7) in the regions subject to large surface emissions. Much more realistic seasonal cycles are reproduced at SBK (ρ of 0.91 *vs.* 0.62) and MOP (ρ of 0.65 *vs.* 0.39), in comparison to

the moderate corrections at BAR (ρ of 0.88 *vs.* 0.76). In all three cases the improvement is due to the winter-spring seasonality (*i.e.*, enhanced [CO] throughout December-May), with the case of SBK exemplifying a high sensitivity of the European FT CO to the East Asian sources. At last, moderate biases (12–15 ppb) are still evident for the [CO] simulated in the AE setup at MOP, BAR and HAP. Related to the average abundances simulated at these locations, however, these are low (*i.e.*, 7%, 9% and 15%, respectively) in comparison to the overall simulated [CO] uncertainty of at least 40% (see Sect. 6.2.1, p. 169), and are contrasted by the improved variations at BAR and HAP.

The concomitantly observed/simulated $\delta^{13}\text{C}(\text{CO})$ are presented in panels (c)–(f) of Figures 6.19 and 6.2, respectively, with left and right panels discerning the effect of applying the new CO+OH KIE parameterisation on top of the reference and amended emission setups (upper and lower panels), respectively. Except for the summertime minima at SBK, KMW and BAR, the $\delta^{13}\text{C}(\text{CO})$ simulated in REF is systematically too low. Marked discrepancies (exceeding 3‰) are seen in the ETNH in winter-spring, and generally at IZA and both ETSH sites. Whereas the simulated $\delta^{13}\text{C}(\text{CO})$ variations at BHD/SCB are moderately underestimated (σ_n of 0.81 and 0.87, respectively), in the ETNH they account for less than a half of that observed (σ_n is typically 0.4 in REF). Except for $\delta^{13}\text{C}(\text{CO})$ at MOP (whose value is chiefly determined by $\delta^{13}\text{C}$ of the local sources), negative biases larger than 1‰ are calculated for all sites, with discrepancies at ALE, HAP, IZA, BHD exceeding 2‰ and utterly low simulated $\delta^{13}\text{C}(\text{CO})$ at SCB (bias of –3.4‰).

Comparing that to the AE setup results (panels (d)), the amended emissions ameliorate the simulated ETNH $\delta^{13}\text{C}(\text{CO})$ but have little or no effect at the tropical and ETSH locations. Apart from the substantially reduced NH biases, the statistics on $\delta^{13}\text{C}(\text{CO})$ in the AE setup is virtually the same as in REF. This contrasts the improvement to the seasonality of [CO], and is explained by the similar $\delta^{13}\text{C}$ signatures of the augmented surface sources, that do not yield a proportionally large increase in the winter-spring $\delta^{13}\text{C}(\text{CO})$. A similar effect on the ETNH $\delta^{13}\text{C}(\text{CO})$ and a substantially larger impact on the tropical and ETSH compositions is seen when the revisited CO+OH KIE parameterisation is applied (AK setup, panels (e)). In particular, this is the only factor that yields a much more realistically simulated seasonal cycle of $\delta^{13}\text{C}(\text{CO})$ in the Antarctic (at SCB). The statistics suggests very similar changes to the NH $\delta^{13}\text{C}(\text{CO})$ in the AE and AK setups based on much different mixing ratios. This confirms that the high-latitude NH CO is chiefly determined by the $\delta^{13}\text{C}$ of CO entering the domain from the lower latitudes. The slightly improved variation (σ_n) is seen for $\delta^{13}\text{C}(\text{CO})$ at BAR and HAP, however, the effect for the latter is rather unsystematic, owing to the location of this site in the vicinity of regions with large surface emissions. Thus, the average $\delta^{13}\text{C}(\text{CO})$ at HAP remains the most underestimated in the AE/AK setups.

The peculiar phase shifts in the simulated $\delta^{13}\text{C}(\text{CO})$ are further noteworthy at BAR, IZA and SCB, with smaller but evidently similar discrepancies in the respective [CO] seasonalities visible at the tropical locations. At BAR, the model anticipates the observed seasonal dynamics of $\delta^{13}\text{C}(\text{CO})$ precisely by one month, thus the values simulated in AE taken one month earlier yield a very tight correlation (ρ of 0.97 *vs.* 0.78) with the observed series. The same is not true for [CO] whose highest ρ corresponds the lag of approximately two weeks and improves only slightly (+0.07). At IZA, more realistic seasonalities of both, $\delta^{13}\text{C}(\text{CO})$ and [CO], are obtained when the simulated series are shifted by about two weeks, however in this case the observations forestall the model and the improvement is small. The same analysis for SCB clearly suggests a lag in $\delta^{13}\text{C}(\text{CO})$ similar to that at BAR at the concomitantly synchronous [CO]. Whereas the phase shift at BAR is the result of a too early onset of the seasonal CO emissions (likely the biomass burning in the SH), the lag seen at SCB is a $\delta^{13}\text{C}$ source effect echoing through the well-mixed ETSH in the Arctic. To note, the CO simulated at the other ETSH location, BHD, does not witness asynchronous dynamics, thus being rather subject to the regional emissions with a better resolved seasonality.

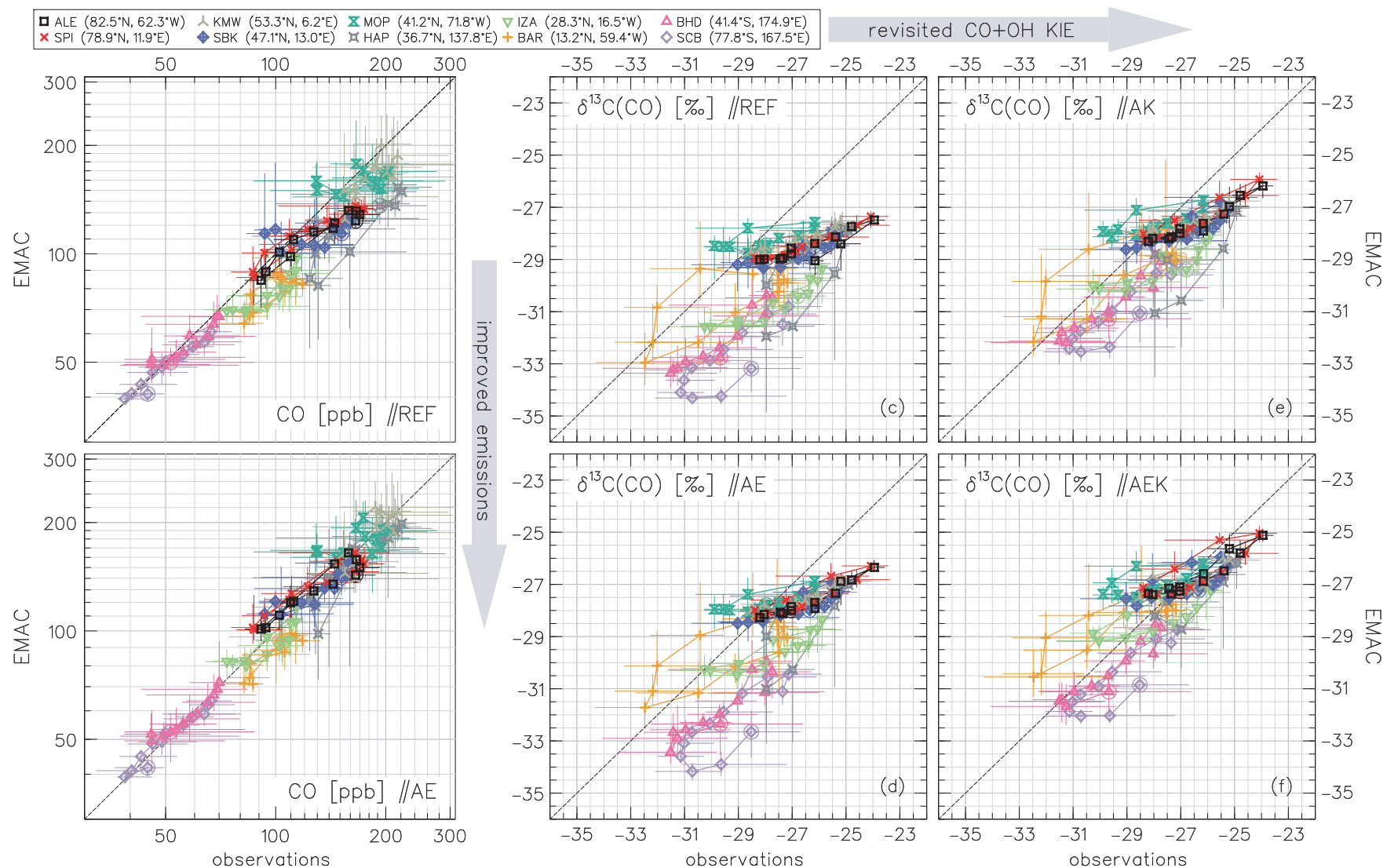


Figure 6.19 Observed and simulated surface station CO mixing and $^{13}\text{C}/^{12}\text{C}$ isotope ratios. Upper and lower panels contrast the changes upon applying the amended emissions (AE/AEK setups), middle and right panels highlight the changes upon applying the revisited CO+OH KIE parameterisation (AK/AEK setups), respectively. Error bars denote the IQRs of the shown monthly data. The encircled points denote the January values, thin lines connect the monthly averages from January throughout December. See text for details.

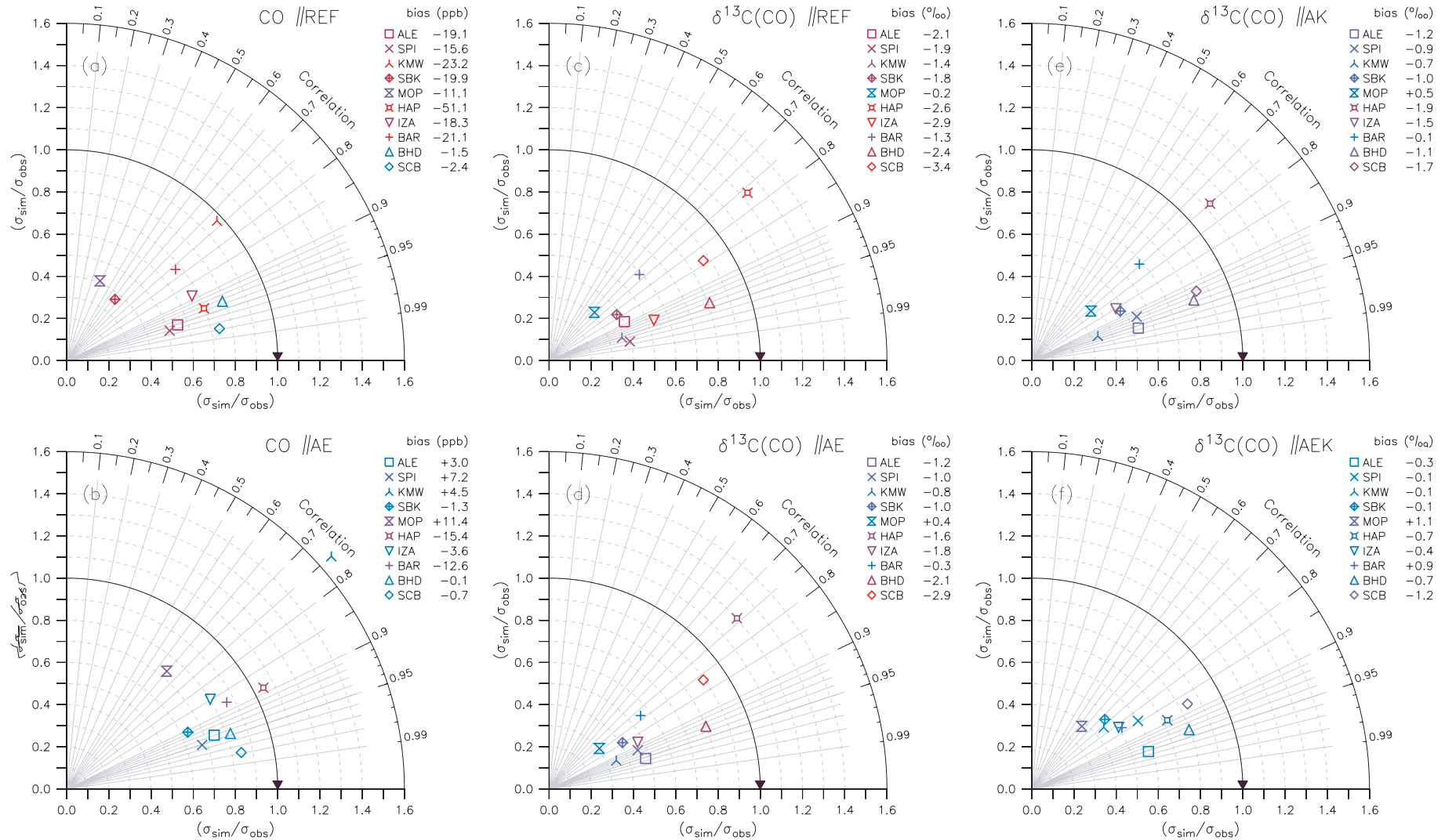


Figure 6.20 (complements Figure 6.19) Statistics on the temporal correspondence between the observed and simulated station data summarised in Taylor diagrams. Symbol colours vary with the absolute biases calculated, *i.e.* from highest (red) to lowest (blue) values. Black triangles denote the perfectly matching correspondence. In the panel (b), the $\sigma_{\text{sim}}/\sigma_{\text{obs}}$ value for KMW is found at 1.67 (off the diagram). The layout of the panels follows that in Figure 6.19. See text for details.

Finally, the comparison of $\delta^{13}\text{C}(\text{CO})$ simulated in the AEK setup is presented in panels (f) of Figures 6.19–6.2. Being the best-matching result obtained for isotope CO in this study, it nonetheless highlights some unresolved systematic discrepancies. Thus, except for the HAP, BHD and SCB sites, no adequate $\delta^{13}\text{C}(\text{CO})$ variations are simulated (*i.e.*, σ_n typically does not exceed 0.6), with the problematic point being to a various degree underestimated $\delta^{13}\text{C}(\text{CO})$ and $[\text{CO}]$ in the summer-fall season at all NH stations. It appears that larger photochemical throughput of CO (*e.g.*, the OH-driven sink and production from CH_4) may alleviate this seasonal discrepancy, however this surmise cannot be further quantified here. It is noted, however, that more realistic CO abundances simulated in AEK (in particular, at IZA and the ETNH locations in fall-spring) confirm that the East Asian CO source is likely missing in REF. The statistics on $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ (in particular, σ_n) show that the seasonality of the (likely biomass-burning) emissions in the SH is not well resolved by the applied emission inventory, as exemplified by the apparent phase shifts in the $\delta^{13}\text{C}(\text{CO})$ at BAR and, noteworthy, SCB. Among all locations, MOP is largely subject to the emissions in the model, which makes it least sensitive to the improvements introduced, as well as least comparable to the observational data. Overall, we emphasise a substantial reduction of the biases in simulated $\delta^{13}\text{C}(\text{CO})$ (below 1‰, excluding SCB) and generally improved statistics for the most difficult high-latitude locations seen in the AEK.

6.2.7.2 Observations from CARIBIC-1

The simulated CO and $\delta^{13}\text{C}(\text{CO})$ were further compared with the UTLS observations from the CARIBIC project (abbreviated “C1”, see in Sect. 4.2, p. 96). It is noted that the simulations presented here do not entirely cover the observational period of C1, *i.e.* the years 1997 and 1998 (the latter was used for the model spin-up, see above, p. 167) are not represented by the model. Therefore, the respective simulated daily climatological means were used to substitute the absent model data for the comparison. This substitution is considered appropriate, as it was found not to significantly alter the comparison statistics and allowed obtaining a more accurate estimate of the model biases. Furthermore, only the tropospheric compositions are compared.

The results are summarised in Figure 6.21 below. Panels (a) and (b) present the observed and simulated $\delta^{13}\text{C}(\text{CO})$ as a function of its reciprocal mixing ratio, which roughly denotes the transition between more fresh (*i.e.*, containing a larger share of the surface-emitted component) and more aged (*i.e.*, underwent atmospheric mixing and photochemistry) CO compositions, respectively. As discussed above in Sect. 4.2, the $\delta^{13}\text{C}(\text{CO})$ in the UTLS is determined by various factors, *viz.* admixing of the rapidly elevated CO freshly emitted at from surface, its continuous photochemical production (mostly from the ^{13}C -depleted $\text{CH}_4 + \text{OH}$ source) and sink fractionation (about +6.5‰ at the surface, +(1–2)‰ in the upper troposphere). The resulting distribution of C1 $\delta^{13}\text{C}(\text{CO})$ seen in Figure 6.21 is a complex superposition of these factors. In particular, the winter-spring values (denoted by colour) line up in a more mixing-like relationship, as opposed to the summer-fall $\delta^{13}\text{C}(\text{CO})$ that decrease substantially faster with reduced $[\text{CO}]$ owing to the active photochemistry. Furthermore, C1 observes large variations in $\delta^{13}\text{C}(\text{CO})$ that increase from $\pm 1\text{‰}$ to $\pm 2\text{‰}$ within 7 to 12 ppm^{-1} of $[\text{CO}]^{-1}$, respectively, denoting likely larger sampling-mixing effects in $\delta^{13}\text{C}(\text{CO})$ expected at the lower CO mixing ratios (see below).

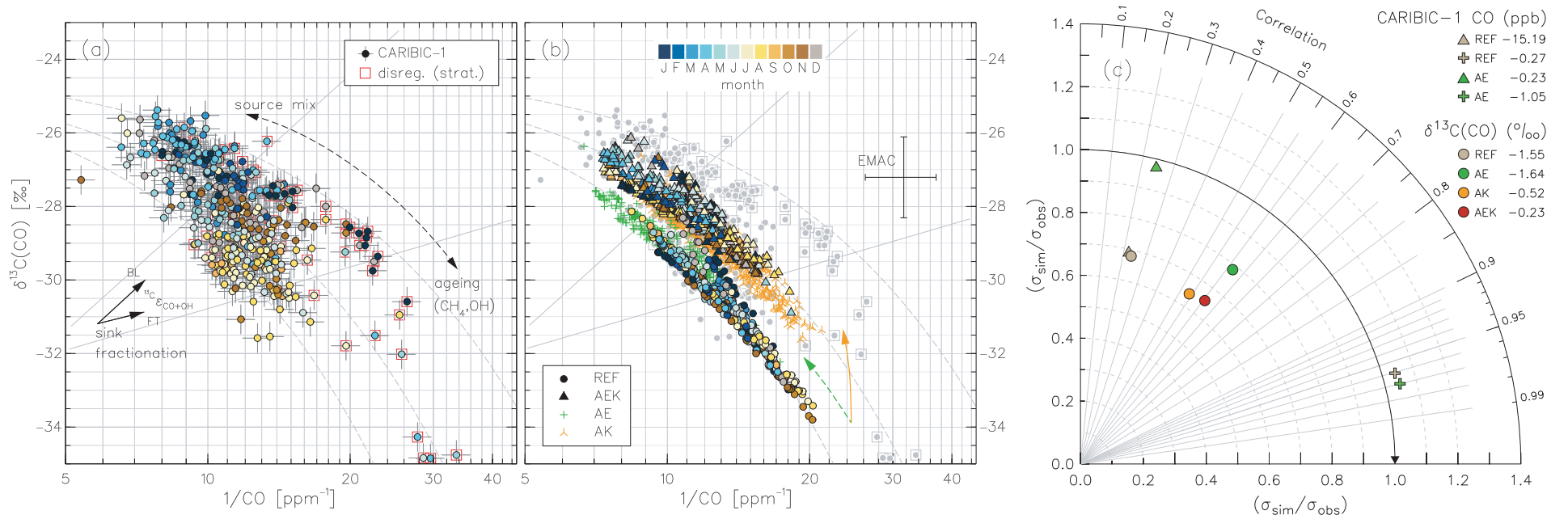


Figure 6.21 CO mixing and isotope ratios observed by CARIBIC-1 and simulated by EMAC. Panels (a) and (b): Observed and simulated $\delta^{13}\text{C}(\text{CO})$ as a function of reciprocal CO mixing ratio, respectively. Symbol colours refer to the season, frames denote the disregarded stratospheric C1 data. Dashed lines exemplify the evolution of the composition upon admixing the CO from the surface ($\delta^{13}\text{C}$ of -24‰) into the atmospheric reservoir, reckoned for the different average $\delta^{13}\text{C}(\text{CO})$ (viz., -31‰, -29‰ and -27‰, respectively) and an abundance of 70 ppb of the latter. Panel (b): Coloured arrows denote the approximate evolution of the simulated compositions upon applying the amended emissions (AE setup, green dashed) and revisited CO+OH KIE (AK setup, solid orange), respectively. The error bars denote the approximate bottom-up uncertainties in [CO] and $\delta^{13}\text{C}(\text{CO})$ simulated in EMAC. Panel (c): Statistics on the temporal correspondence between the observed and simulated CO and $\delta^{13}\text{C}(\text{CO})$ at the CARIBIC-1 routes summarised in a Taylor diagram. Triangles denote the results derived for the entire dataset, pluses and circles refer to the simulated compositions with [CO] equating the observed mixing ratios within their uncertainty. See text for details.

A clear mixing-like relationship is evident in the corresponding simulated CO (*cf.* panel (b)), however, the characteristic $\delta^{13}\text{C}(\text{CO})$ variation is much smaller (for example, it reaches a maximum of $\pm 0.8\text{‰}$ at $[\text{CO}]^{-1}$ of $\sim 13 \text{ ppm}^{-1}$ in REF). Moreover, a less apparent seasonality is seen in the model results, with the spring-summer compositions more often found with large $[\text{CO}]$. In contrast, the June–September compositions (spanning the entire range of simulated mixing ratios in EMAC) are rarely encountered in C1 at $[\text{CO}]^{-1}$ lower than $\sim 10 \text{ ppm}^{-1}$. This suggests that the model picks up rather different air masses than those seen by C1, or the same air masses, but more often diluted by the surface sources. We note, however, that evident (although less pronounced) seasonal variations in the UTLS $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ are reproduced in EMAC. Whereas the ranges of the simulated CO mixing and isotope ratios are comparable to that observed by C1, it is not entirely clear what causes their more compact correlation in the model. Variations of $[\text{CO}]$ in the UTLS simulated in the evaluation study with EMAC2 were found often underestimated and vertically more uniform in comparison with the observations (see Jöckel *et al.*^[2005], Supplement material, Sect. 3.7). Being similar to what is seen for the summer–spring CO in this study, this hints at the potential (rather vertical) over-mixing in the model, which likely originates from a problematic convective transport (*e.g.*, overestimated de- and entrainment rates).¹⁴² For instance, in a sensitivity study with EMAC1, Tost *et al.*^[2006] show that the convective transport into the UTLS region is particularly sensitive to the chosen convective parameterisation. What implications their inference has for the variations of a chemical tracer like CO in the UTLS is, however, unknown.

At the same time, the sample-mixing effects in C1 most likely lead to a peculiar disproportional change in $[\text{CO}]$ *vs.* $\delta^{13}\text{C}(\text{CO})$ (see details in Appendix C) that result in the larger observed variability. For example, admixing of a portion of LMS air (bearing a substantially ^{13}C -depleted CO with only moderately lower mixing ratio) to the tropospheric air shifts the average sample composition away from the typical tropospheric mixing line expected. Each observation in C1 represents an average of the compositions sampled throughout ~ 20 minutes, or along a ~ 250 km path that is very probable to cross much different air masses, *e.g.* stratospheric filaments. Such sample averaging is thus a substantially different kind of mixing compared to the processes implemented in the model. It is important to note that the production simulations with EMAC in this study were integrated with a time step of 1200 s (see Sect. 5.1.1, p. 107, comparable to the C1 sampling time), *i.e.* it is not possible to resolve the sample-mixing effects in the model without involving assumptions on the evolution of the simulated compositions within one model time step. This concludes that comparing the observed and simulated UTLS $\delta^{13}\text{C}(\text{CO})/\text{CO}$ variations (as opposed to the ranges/averages though) is not entirely consistent, as the spatiotemporally averaged compositions in C1 are confronted with the simulated instantaneous values representing the average compositions in a particular model gridbox.

Recurring to the model results, one notes that different amendments cause distinctly different changes in the simulated $\delta^{13}\text{C}(\text{CO})$ *vs.* $[\text{CO}]^{-1}$ distributions. Thus, the increased emissions in the AE setup shift the compositions strictly in a mixing-like relationship (*cf.* green symbols in panel (b) of Figure 6.21), *i.e.* larger $\delta^{13}\text{C}(\text{CO})$ are not attainable in the model by merely adjusting the CO surface sources' strengths. In this sense, the UTLS compositions provide a vigorous indication that either higher $\delta^{13}\text{C}$ of the CO source or larger ^{13}C effective enrichment of atmospheric CO is required. Indeed, applying the revisited CO+OH KIE (AK setup, *cf. ibid.* orange symbols) yields a different $\delta^{13}\text{C}(\text{CO})$ *vs.* $[\text{CO}]^{-1}$ distribution, with average $\delta^{13}\text{C}(\text{CO})$ increasing from $+1\text{‰}$ to $+2.5\text{‰}$ throughout the range of respective $1/[\text{CO}]$ values. The latter in this case, however, are not found below $\sim 9 \text{ ppm}^{-1}$, indicating that the largest mixing ratios are underestimated. A relationship between the $\delta^{13}\text{C}(\text{CO})$ and $[\text{CO}]^{-1}$ much similar to tropospheric observations from C1 is ultimately obtained in the AEK setup, which incorporates both improvements.

The statistics on the seasonal correspondence between the observed and simulated C1 data are further summarised in the Taylor diagram shown in Figure 6.21 (panel (c)). Note that the entire simulated series were not found to correlate with the observations, thus ρ of 0.2–0.3 at σ_n of ~ 0.7 are inferred for both, $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$, in REF (for $[\text{CO}]$, the statistics on the entire series are shown with triangles). This is attributed to the above mentioned less apparent seasonality in the simulated data. Picked up at the locations corresponding to the C1 observations, the simulated series represent either different air masses or compositions much diluted by the surface sources. Despite the uncorrelated seasonal (or spatial) mixing ratios, the simulated $[\text{CO}]$ variations

¹⁴²It should be noted that the semi-Lagrangian advection schemes employed in GCMs also have the disadvantage of smoothing the species' spatial gradients (see, *e.g.*, Reithmeier and Sausen^[2002]). The flux-form advection scheme used in EMAC (from Lin and Rood^[1996], see also Sect. 5.1.1, p. 107), however, has moderate capabilities to keep steep gradients; the convective transport thus might be more crucial for the over-mixing in vertical direction (Jöckel *et al.*^[2001]).

become substantially improved in the AE setup (σ_n is 0.98 *vs.* 0.67 in REF), also the [CO] bias is reduced. In order to infer a consistent comparison of the simulated $\delta^{13}\text{C}(\text{CO})$, only those pairs of the simulated/observed compositions which agreed in [CO] within the uncertainty of the C1 observations were selected.¹⁴³ The resulting values are shown with circles (*ibid.*) and suggest that the amended setups yield clearly a more realistic $\delta^{13}\text{C}(\text{CO})$ seasonality than that simulated in REF (ρ of 0.24). In particular, the augmented East Asian emissions result in an improvement of the timing and variation of $\delta^{13}\text{C}(\text{CO})$ ($\rho=0.62$, $\sigma_n=0.79$ in AE), as compared to the case of applying the revisited CO+OH KIE ($\rho=0.54$, $\sigma_n=0.64$ in AK, respectively). The opposite result is seen for the simulated biases, however, which are about three times smaller in AK than that in AE/REF. The superposed improvements (AEK setup) result in lowest biases and statistics comparable to that of AK with $\rho=0.61$ and $\sigma_n=0.65$. Noteworthy, smaller $\delta^{13}\text{C}(\text{CO})$ variations in the model (which are expected to contribute to the low resulting σ_n values inferred here) are mostly the result of the inconsistencies in sampling of the EMAC data and C1 observations.

Last but not least, the best-matching results from AEK still witness a characteristic discrepancy of the CO compositions observed in summer. The latter are found at $[\text{CO}]^{-1}$ of $(12.5 \pm 2) \text{ ppm}^{-1}$ and $\delta^{13}\text{C}(\text{CO})$ of $-(29.5 \pm 1)\text{‰}$, or about 1.5‰ lower than the isotope ratios observed in other seasons, and clearly appear to be of photochemical nature. The comparable $\delta^{13}\text{C}(\text{CO})$ values are found in EMAC at significantly lower mixing ratios ($[\text{CO}]^{-1}$ of $(16.5 \pm 2) \text{ ppm}^{-1}$), *i.e.* the simulated photochemical CO component equilibrates with the surface sources at substantially lower abundances in summer. Oppositely, the observations suggest a larger photochemical CO turnover, in particular a greater share of the CH_4 -derived CO. Whereas the C1 distribution is unlikely to arise from the seasonal sampling specifics (less than 1/6 of all summertime compositions is estimated to be significantly influenced by stratospheric input, as the concomitant N_2O data confirms, see details in Sect. 4.2, p. 96), the most plausible explanation for the model disagreement is the underestimated summertime OH, which corroborates the conclusions for the simulated station data. The estimated bias in the summertime mixing ratios (at the same average $\delta^{13}\text{C}(\text{CO})$) amounts to ~15 ppb, which is a substantial term in comparison to the observed [CO] of ~80 ppb. We note also that alike for the station data, this discrepancy is pronounced in the simulated NH compositions.

6.2.7.3 UTLS observations in the ETSH

The model results obtained in this study with EMAC are subsequently compared with the unparalleled observations of the isotope composition of CO and CH_4 in the UTLS conducted between New Zealand and Antarctic by Brenninkmeijer *et al.*^[1996] (hereinafter referred to as “B96”). The air samples were collected in October 1993, during the austral spring “ozone hole” conditions characterised with elevated SH stratospheric atomic Cl abundances (Solomon^[1999]). The observations (shown below in Figure 6.22) witness a compact distribution of tropospheric $\delta^{13}\text{C}(\text{CO})$ values and a rapid decrease in stratospheric $^{13}\text{CO}/^{12}\text{CO}$ ratios as [CO] drops below 30 ppb, with the rate of decline exceeding 2‰ per ppb CO. As B96 infer, in order to produce such a strong $\delta^{13}\text{C}$ gradient, a local *in situ* CO production from a very ^{13}C -depleted source, *e.g.* in the CH_4+Cl reaction, is required. The authors elucidate that the mutual relationship of $[\text{CH}_4]$ and $\delta^{13}\text{C}(\text{CO})$ rules out the transport of the ^{13}C -depleted CO from lower latitudes of the middle stratosphere and appoints the observed depleted compositions to higher latitudes and the polar vortex origin. In the companion modelling study, Müller *et al.*^[1996] (“M96”) corroborate this inference by simulating $\delta^{13}\text{C}(\text{CO})$ in the parcel circulating in the polar vortex. They confirm the strong fractionations escorting the sink of CH_4 and fit the observations to yield the range of Cl estimates. To note, later laboratory studies reported different ^{13}C KIE for reactions of CH_4 with $\text{O}(^1\text{D})$ and OH, updating them to +13‰ and +3.9‰, respectively (Saueressig *et al.*^[2001]). Modelling studies prior to that (*e.g.*, Bergamaschi *et al.*^[1996] and M96) employed significantly different values of +1‰ and +5.4‰ (see Sect. 3.4.1.1, p. 39), respectively, *i.e.* likely underestimating the contribution of $\text{O}(^1\text{D})$ to the overall CH_4 sink fractionation, and overestimating it for OH. Whereas this does not alter the interpretation given by B96 and M96, the most recent KIEs are likely to suggest the different partitioning between the OH-, $\text{O}(^1\text{D})$ - and Cl-driven sink of CH_4 in the lower stratosphere, hence the inferred concomitant abundances of these reactants.

Figure 6.22 further presents the distributions of the typical isotope compositions of CO, CH_4 and of a set of additionally diagnosed related characteristics, simulated in EMAC at the location and period correspond-

¹⁴³The selected sample sizes amount to 64 (REF), 83 (AE), 68 (AK) and 70 (AEK), respectively, as compared to the initial series of 344 samples (tropospheric C1 compositions).

ing the observations from the surface to the pressure altitude of 50 hPa. Note, all characteristics in Figure 6.22 are plotted as a function of [CO], simulated or observed. That is, CO mixing ratio resembles a vertical coordinate, denoting the transition between the stratospheric and tropospheric compositions confined at $\sim(31\pm2)$ ppb (*cf.* the variations in the B96 and ETSH station data). At first, markedly different observed and simulated distributions of CO isotopes are seen: The model reproduces a continuous mixing relationship of $\delta^{13}\text{C}(\text{CO})$ along [CO], whereas B96 observes rather a bimodal mixing behaviour. This appears to be the case of the vertical over-mixing of the simulated [CO]/ $\delta^{13}\text{C}(\text{CO})$ values, analogous to that mentioned above in the comparison of the CARIBIC-1 observations with EMAC. By matching the results of the REF and AEK setups (black and green symbols, respectively), one sees that the differences in the simulated tropospheric $\delta^{13}\text{C}(\text{CO})$ propagate up to [CO] of (22–25) ppb in the model, not clarifying, however, whether the deeper stratospheric compositions exhibit the mixing artefact as well. To probe for that, a simple exposure model (EM) assuming the continuous sink and production of CO in an ascending isolated air parcel was used to fit the B96 stratospheric data. The dashed red line exemplifies the result of the EM obtained for the parcel with an initial [CO] of 30 ppb and $\delta^{13}\text{C}(\text{CO})$ of -31‰ subjected to continuous refilling by the CO with $\delta^{13}\text{C}$ of $-(60\text{--}65)\text{‰}$ (diagnosed signature of the CH_4 source of CO in EMAC, *cf. ibid.* orange symbols) and sink fractionation. The EM suggests steeper $\delta^{13}\text{C}(\text{CO})$ /[CO] evolution slopes in an isolated parcel than those seen in the simulated data down to ~ 16 ppb of [CO], where both, the EM and EMAC compositions, coincide at a quasi-steady state established in CO between its sink and the CH_4 source (~ 13 ppb). Ultimately, alike for the CARIBIC data, the model adequately represents the ranges of [CO] and $\delta^{13}\text{C}(\text{CO})$, however with much smaller variations and smoothened gradients of $\delta^{13}\text{C}(\text{CO})$ along [CO]. To note, analogous over-mixing artefacts are seen in the simulated isotope CH_4 in EMAC in comparison with the observations by B96, with the largest discrepancy in $\delta^{13}\text{C}(\text{CH}_4)$ of $+0.4\text{‰}$ coinciding with that for $\delta^{13}\text{C}(\text{CO})$ at [CO] of around 30 ppb.

The tagging of the chemical mechanism in EMAC allows additionally inferring the photochemical and surface-derived components of CO, their isotope composition and the effective sink fractionation $^{13}\text{C}\epsilon_{\text{eff}}$ a particular species experiences. Thus, red and blue arrows in Figure 6.22 exemplify how the latter in CO and CH_4 changes with [CO], or altitude. Equating the difference between the overall source $\delta^{13}\text{C}$ (grey symbols) and the resulting $\delta^{13}\text{C}(\text{CO})$ value, $^{13}\text{C}\epsilon_{\text{eff}}(\text{CO})$ is found adequately traversing from the positive tropospheric to negative stratospheric values through zero fractionations at [CO] of ~ 33 ppb in REF and ~ 28 ppb in AEK, respectively. It is unclear whether this result is coherent with the most compact $\delta^{13}\text{C}(\text{CO})$ observed by B96 at around 30 ppb, however, the rapidly increasing sink effective ^{13}C depletions simulated in the model below that boundary result in a substantial lowering of the final $\delta^{13}\text{C}(\text{CO})$. That is, for example, about 4‰ depletion with respect to the source $\delta^{13}\text{C}$ are simulated at the lowest [CO] of 23.7 ppb observed by B96. The sink effective fractionation in CH_4 is also expected to be much variable in the LMS, according to EMAC. Thus, the characteristic tropospheric $^{13}\text{C}\epsilon_{\text{eff}}(\text{CH}_4)$ value of $\sim +4\text{‰}$ (enrichment in the leftover CH_4) quadruples by [CO] of ~ 25 ppb, with the main cause for this being the increasing sink of CH_4 via the atomic Cl. The lower panel of Figure 6.22 presents the partitioning of the overall methane sink into the separate channels, averaged per simulated CO mixing ratio (1 ppb bins are used). Above 60 ppb, the OH channel is dominating in the troposphere; overall, it accounts for 86.1% of the total CH_4 sink simulated (*i.e.*, at the pressure altitudes below 50 hPa). Below 60 ppb (above ~ 200 hPa), however, only 64.4% of CH_4 is oxidised by OH, with the remainder being shared between Cl and $\text{O}(^1\text{D})$ as 31.0% and 4.6%, respectively. The overall contribution of these channels (below 50 hPa) is estimated at 6.4% and 1.0%, respectively, which is in good agreement with the estimate of B96 for the CH_4 +Cl sink contribution ($\sim 5.2\%$)¹⁴⁴. Further, below 25 ppb of [CO], the $\text{O}(^1\text{D})$ channel starts to enhance and reaches a comparable (to Cl) loss rate at [CO] of 15 ppb.

The results obtained with EMAC here importantly suggest a different explanation for the large ^{13}C depletion in the ETSH LMS than that given by M96. In particular, there is no evidence that large atomic chlorine abundances are required to produce similarly low $\delta^{13}\text{C}(\text{CO})$ at [CO] below 30 ppb: The inferred by M96 Cl concentrations of $(2\text{--}8)\cdot 10^5$ molec cm^3 are by an order of magnitude larger than those simulated in EMAC ([Cl] of $(0.6\text{--}6.4)\cdot 10^4$ molec cm^3 , average of $1.25\cdot 10^4$ molec cm^3). This discrepancy is attributed to the missing ^{13}C fractionations in several reactions related to CO, that were compensated by the fractionation in the reaction of CH_4 +Cl, hence by larger [Cl] in M96. In particular, they used a different set of methane oxidation KIEs (some are to date obsolete). Of these, the CH_4 + $\text{O}(^1\text{D})$ KIE has changed drastically ($+1\text{‰}$ *vs.* the current estimate of $+13\text{‰}$), although since the CH_4 sink via $\text{O}(^1\text{D})$ is minor (below 5% at [CO] lower than 60 ppb), this

¹⁴⁴The reported value of 9% is updated according to the new methane KIE laboratory data.

brings only a minor underestimation to the CH_4 -derived $\delta^{13}\text{C}(\text{CO})$ of about 0.6‰. Two other used KIEs, *viz.* for the OH and Cl reactions with CH_4 , were actually larger than those used here in EMAC: +5‰ *vs.* +3.9‰ (for OH), and +75‰ *vs.* +(68–72)% (for Cl; the difference is due to the neglected temperature dependence by M96), respectively, which actually implies even larger Cl concentrations than those derived by M96. The most influential factor is, however, the KIE in the CO+OH reaction, that is more than by a factor of two larger in EMAC. The value of –3‰ assumed by M96 is appropriate for the pressure altitude of 200 hPa, but it is underestimated for 100 hPa they used as the initial height of the descending air parcel (the equilibrated starting $\delta^{13}\text{C}(\text{CO})$ was thus overestimated). In contrast, as Figure 6.22 shows, $^{13}\text{C}_{\text{eff}}(\text{CO})$ can be as large as –7.5‰ at $[\text{CO}]$ of ~16 ppb, which, as the exposure model corroborates, does not disagree with the B96 data.

Recapitulating, the comparison of the simulated compositions with the comprehensive observations by B96 yields a new piece of information on the LMS ^{13}CO . Despite the large over-mixing effects seen in EMAC, it provides an adequate estimate of the lower-end $\delta^{13}\text{C}(\text{CO})$ value in the ETSH LMS (–62‰ at ~16 ppb of $[\text{CO}]$, respectively) in the regarded domain/season. Expected at around 50 hPa, these are the largest ^{13}CO depletions simulated: Deeper into the stratosphere the increasing share of the methane sink via $\text{O}(^1\text{D})$ and photolysis of CO_2 start to further enrich atmospheric CO in ^{13}C with height. We further note the robust estimate of the CH_4 +Cl sink term by B96, which is established merely from the observed $\delta^{13}\text{C}(\text{CH}_4)$ and laboratory data, and is confirmed by EMAC. The model study by M96 focuses on more intricate $\delta^{13}\text{C}(\text{CO})$, which requires careful treatment of the sources, sinks, their concomitant isotope ratios and fractionations associated with this complex tracer. The results of M96 offer an explanation for the observed $\delta^{13}\text{C}(\text{CO})$ at substantially larger Cl abundances, owing to the most likely erroneous assumptions on CO+OH KIE, hence the initial conditions for the simulated $\delta^{13}\text{C}(\text{CO})$. Simulations with EMAC suggest that the rapid depletion of CO in ^{13}C with height is largely driven by the strengthening effective ^{13}C depletion in the CO sink, which does not require as much enhanced Cl levels in the LMS as M96 suggest.

Regarding the comparison of all observational data given in this section, the following aspects are worth summarising. (1) The proposed model amendments yield a distinct improvement to the simulated CO mixing and isotope ratios, as confirmed by both, surface and UTLS observations. Applying the revisited CO+OH KIE parameterisation is crucial for the simulated tropospheric ETSH $\delta^{13}\text{C}(\text{CO})$, whereas the more realistic CO mixing ratios and $\delta^{13}\text{C}$ in the ETNH are obtained with additionally increased surface emissions of CO. The statistics on the correspondence between the simulated and observed CO/ $\delta^{13}\text{C}(\text{CO})$ seasonal cycles confirm much similar effects of each model improvement on the $\delta^{13}\text{C}(\text{CO})$ in the ETNH, suggesting that the isotope composition of CO entering higher latitudes is decisive for the seasonalities established there. The station data further confirm a forestalling model $\delta^{13}\text{C}(\text{CO})$ development seen at the tropical and Antarctic sites, which is likely related to the mistiming of the emissions in the SH. (2) An unambiguous indication that both, the increased emissions and effective ^{13}C enrichments, are initially missing in the EMAC-simulated UTLS CO isotopes is given by the CARIBIC data. The large vertical over-mixing artefacts are marked in the simulated $[\text{CO}]$ *vs.* $\delta^{13}\text{C}(\text{CO})$ in comparison with the two sets of observations in the UTLS. Whereas the averages and ranges and averages of the simulated characteristics appear to be adequate, the mixing character (mostly continuous over the tropopause, as opposed to the observed isolated bimodal distribution) and local variations of $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ are not well represented by the model. (3) Finally, both surface station and CARIBIC data indicate the likely underestimated NH OH abundances in the model that yield characteristic discrepancies in the simulated $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ in the summer.

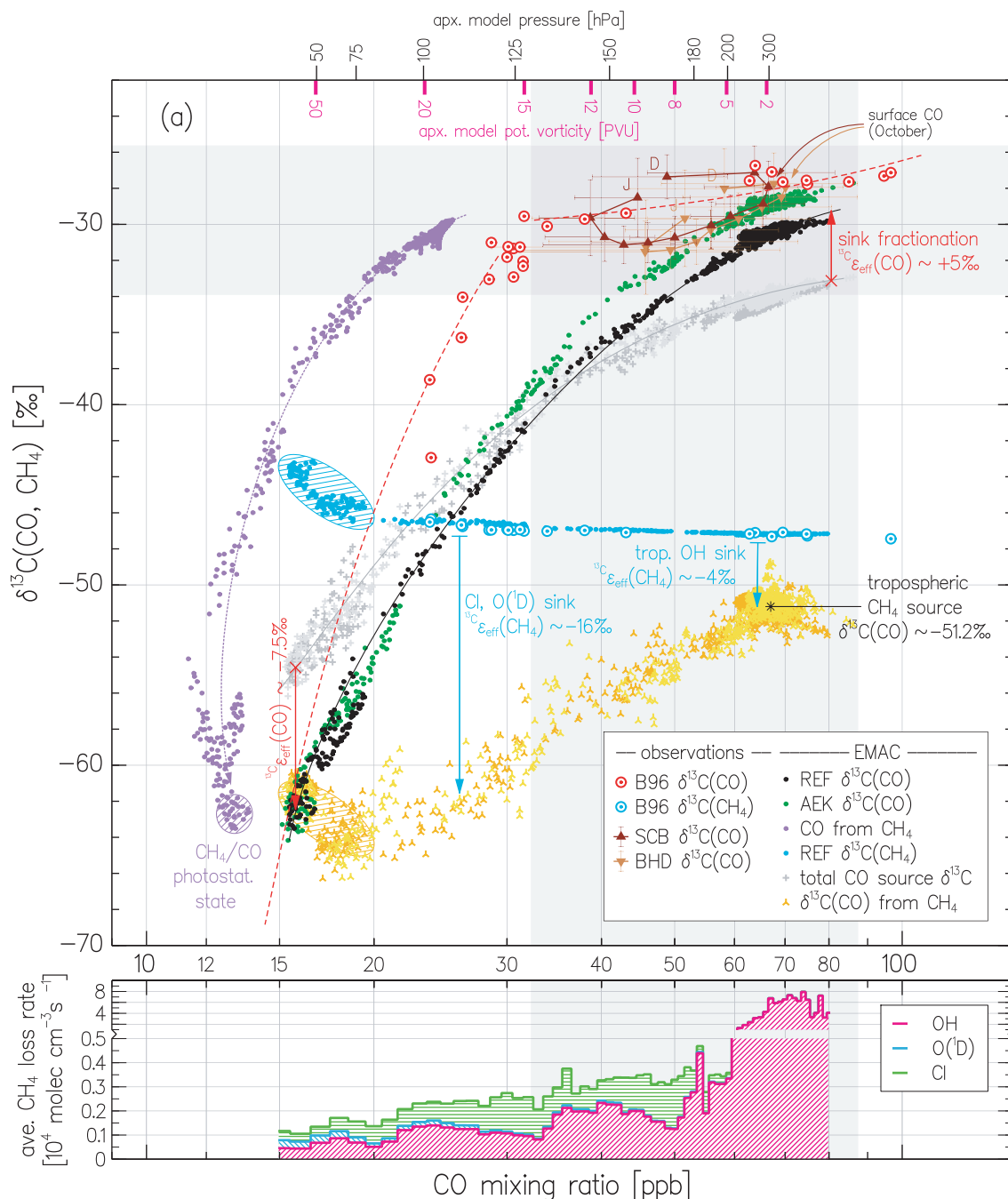


Figure 6.22 Observed and simulated mixing and isotope ratios of CO and CH₄ in the UTLS between New Zealand and Antarctic. All values are plotted using the CO mixing ratio as abscissa. Upper axes refer to the approximate pressure height and potential vorticity (PV) diagnosed in EMAC with respect to the simulated [CO]. Panel (a): Large symbols refer to the observations from Brenninkmeijer *et al.*^[1996]. Note that these refer to the different pressure altitudes and PV and are shown to highlight the discrepancy between the observed and simulated [CO] *vs.* $\delta^{13}\text{C}(\text{CO})$ relationship. Triangles denote the seasonal cycles of [CO] and $\delta^{13}\text{C}(\text{CO})$ observed at the surface stations in the ETSH (BHD and SCB, letters identify the January and December values, respectively). Dashed lines show the fits through the observed CO compositions; below 30 ppb, the results of the exposure model are used. The model data represent the climatological compositions simulated in the second half of October within (160–180)°E and (40–80)°S. Only the values below 50 hPa pressure altitude are shown. The CH₄-derived CO component is plotted against the simulated $\delta^{13}\text{C}$ of the overall CO. Thin lines navigate through the selected characteristics; arrows exemplify the CO and CH₄ sink effective enrichments. Hatched ellipses denote the rapid increase in the LMS $\delta^{13}\text{C}(\text{CH}_4)$ and the respective $\delta^{13}\text{C}$ of the CO source due to the shift of the CH₄ sink from the OH to O(¹D)/Cl channels. The hatched circle identifies the compositions at which the sink CO is in equilibrium with its sources (*i.e.*, methane oxidation and CO transport from the lower altitudes). Shaded areas denote the seasonal variations of the tropospheric [CO] and $\delta^{13}\text{C}(\text{CO})$ in the ETSH derived from the surface station data. Panel (b): Simulated CH₄ sink rates (daily averages) via different channels as a function of [CO]. Note that the shown terms are stacked, *i.e.* OH and Cl sink are comparable at [CO] of 30 ppb. Mind the broken ordinate axis.

6.2.8 Simulated atmospheric $\Delta^{17}\text{O}(\text{CO})$

We conclude the analysis of the model simulations performed in this study with the results on the anomalous (mass-independently fractionated, MIF) oxygen isotope composition of CO, $\Delta^{17}\text{O}(\text{CO})$. The reader is referred to Sects. 3.2, 3.3.2 and 3.4.3 for a review the on notation and specifics of MIF in the atmospheric chemistry, and to Sect. 5.2.8 for the information on the MIF composition of the oxygen reservoirs and surface sources implemented in EMAC. In analogy to the ^{13}C case, the control and sensitivity simulations were used to infer the atmospheric distributions of $\Delta^{17}\text{O}(\text{CO})$ and its main constituents. The relation between the former and the latter can be expressed as

$$\Delta^{17}\text{O}(\text{CO}) = \Delta^{17}\text{O}_{\text{src}} + \Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO}) + \Delta^{17}\text{O}_{\text{sink}}(\text{CO}), \quad (6.3)$$

which is analogous to the expression (6.1) (p. 182) used to describe $\delta^{13}\text{C}(\text{CO})$, however with some different principal components. Here the first member on the RHS similarly denotes the contribution of the overall (both in-situ and direct) sources of CO bearing the mass-dependently fractionated (MDF) compositions. Exceptionally, all in-situ produced CO that incorporates the oxygen atoms originating from ozone (be it a direct production in the VOC ozonolysis reactions or the oxygen chemically transferred via any set of intermediates) is singled out in the second term. Conventionally, the last term denotes the modification induced by the isotope fractionation in the atmospheric sink of CO itself.

The $\Delta^{17}\text{O}$ of the MDF sources is usually assumed equal to 0‰ in the atmospheric studies employing MIF. Strictly speaking, however, the compositions of the terrestrial MDF reservoirs differ by tenths of permil owing to the various nature of the fractionation kinetics escorting the oxygen exchange in/between them. Being recalculated using the formulation employed in this study (that is, using Eq. (3.5) and the unified slope coefficient β , see Sect. 3.2, p. 31), their $\Delta^{17}\text{O}$ signatures appear slightly negative (see details in Sect. 5.2.8 (p. 137). For CO, this implies a slightly negative first term in Eq. (6.3), which reduces the overall $\Delta^{17}\text{O}(\text{CO})$ (see below). The second and third terms are the principal matter of investigation in this study. Tersely, ozone possesses an extremely high MIF signal in the atmosphere owing to the peculiar isotope effects escorting its gas-phase formation (see details in Sect. 3.4.3, p. 45). Being transferred to CO, the oxygen atoms from O_3 contribute with an individual signal to the final $\Delta^{17}\text{O}(\text{CO})$. In the simulations with a simplified box-model employed in this study (see Sect. 3.5.2), it is estimated at $\sim +1\text{‰}$, however, this inference by no means reflects the actual atmospheric situation, *i.e.* transport/mixing effects, distribution of the sources and sinks and changes to the MIF in O_3 itself. The sensitivity simulations with EMAC here are used to obtain a more consistent estimate of $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ and ultimately compare it to the presumably principal driver of $\Delta^{17}\text{O}(\text{CO})$, the anomalous oxygen fractionation induced by the KIE in the $\text{CO} + \text{OH}$ reaction.

The outline of the sensitivity simulations for stable oxygen isotopes principally follows that used for the $^{13}\text{C}/^{12}\text{C}$ (see Sect. 6.2.1, p. 164) and uses the same abbreviations. That is, the reference setup (REF) incorporates the base EMAC setup (described in Sect. 5.1), with all considered oxygen isotope kinetics (Sects. 3.3 and 3.4) and trace gas emissions (Sects. 5.2 and 5.2.8). Furthermore, these modifications were made to REF in the sensitivity setups:

- Z setup: Except for the KIE escorting the oxidation of CO by OH, all (chemical and non-chemical) isotope effects are switched off. As opposed to the stable isotope configuration, two modifications with the original (REF) and zeroed isotope signatures of the emitted compounds were made in order to infer all three terms of Eq. (6.3).
- AE setup: The adjusted, larger surface emission strengths of CO/NMHCs are implemented (see details in Sect. 6.2.3), no changes are made to the photochemistry. This allows studying the integral effect of increased East Asian surface emissions on $\Delta^{17}\text{O}(\text{CO})$.
- ZE setup: The amended emissions from AE are used in the otherwise identical to Z setup. This allows additionally studying the sensitivity of all $\Delta^{17}\text{O}(\text{CO})$ components.

The simulated averages of atmospheric $\Delta^{17}\text{O}(\text{CO})$ and its components are presented in Table 6.8 below, except for the $\Delta^{17}\text{O}_{\text{sink}}(\text{CO})$ already analysed in Sect. 6.2.5 and listed separately in Table 6.7 (p. 195). As it is seen, on the global scale the input of the surface sources and O_3 to $\Delta^{17}\text{O}(\text{CO})$ is minor compared to $\Delta^{17}\text{O}_{\text{sink}}(\text{CO})$. The magnitude of the $\Delta^{17}\text{O}_{\text{src}}$ signal is stronger in the SH denoting the larger fraction of the O_2 -derived oxygen in CO (-0.455‰ , propagating mostly via the $\text{CH}_4 \rightarrow \text{CO}$ chain), whereas the NH CO receives more of the oxygen from H_2O (with $\Delta^{17}\text{O}$ very close to 0‰) through the larger NMHC oxidation source. Overall, the vertical distribution of $\Delta^{17}\text{O}_{\text{src}}$ is nearly uniform, with small differences pertaining to the variations

in the surface/photochemical sources ratio in CO. The input of ozone oxygen to $\Delta^{17}\text{O}(\text{CO})$, in turn, is positive, and a factor of ~ 2.5 larger than that of $\Delta^{17}\text{O}_{\text{src}}$. Importantly, these two signals compensate each other, reducing the average non- $\Delta^{17}\text{O}_{\text{sink}}$ MIF in CO to $(0.23\text{--}0.43)\text{‰}$ in various domains, with the ETNH/ETSH averages relating as $\sim 1:2$. The lower part of Table 6.8 presents the sensitivities of the final $\Delta^{17}\text{O}(\text{CO})$ to the adjusted emissions in the model, which equate those for $\Delta^{17}\text{O}_{\text{sink}}$ (cf. $\Delta^{17}\text{O}_{\text{sink}}$ in Table 6.7) to the aggregate of the changes in $\Delta^{17}\text{O}_{\text{src}}$ and $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$. The latter (*ibid.*, right column) is by an order of magnitude smaller, except for the tropical and Arctic MBL, where the sensitivity of $\Delta^{17}\text{O}(\text{CO})$ to the changes in CO/OH becomes reduced. Overall, however, the results confirm that the aggregate sensitivity of the non- $\Delta^{17}\text{O}_{\text{sink}}$ terms constituting $\Delta^{17}\text{O}(\text{CO})$ to the increased emissions is very small (below 0.01‰).

Table 6.8 Simulated $\Delta^{17}\text{O}(\text{CO})$ and its constituents inferred in the REF, AE and Z setups ^a

Domains	TR ^{ETNH} _{ETSH}	AR(AQ)	Globe	TR ^{ETNH} _{ETSH}	AR(AQ)	Globe	TR ^{ETNH} _{ETSH}	AR(AQ)	Globe
	$\Delta^{17}\text{O}(\text{CO}) [\text{‰}] \quad //\text{REF}$			$\Delta^{17}\text{O}_{\text{src}} [\text{‰}] \quad //\text{REF-Z}$			$\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO}) [\text{‰}] \quad //\text{REF}$		
SRF	+3.92 ^{3.68} _{-3.39}	+4.18(+5.55)	+4.05	-0.23 ^{0.16} _{-0.31}	-0.16(-0.32)	-0.22	+0.59 ^{0.41} _{-0.73}	+0.42(+0.72)	+0.55
BL	+4.17 ^{3.76} _{-3.36}	+4.07(+5.50)	+4.20	-0.24 ^{0.16} _{-0.31}	-0.15(-0.32)	-0.22	+0.60 ^{0.45} _{-0.75}	+0.40(+0.73)	+0.57
MBL	+5.07 ^{3.92} _{-3.44}	+3.93(+5.50)	+4.85	-0.29 ^{0.17} _{-0.32}	-0.13(-0.32)	-0.27	+0.54 ^{0.42} _{-0.72}	+0.36(+0.73)	+0.57
FT	+4.78 ^{3.34} _{-3.43}	+4.30(+5.55)	+4.75	-0.26 ^{0.19} _{-0.31}	-0.17(-0.31)	-0.24	+0.63 ^{0.50} _{-0.73}	+0.45(+0.73)	+0.61
T	+4.73 ^{4.28} _{-3.58}	+4.28(+5.54)	+4.70	-0.26 ^{0.19} _{-0.31}	-0.17(-0.31)	-0.24	+0.63 ^{0.49} _{-0.73}	+0.44(+0.73)	+0.60
TP	+5.27 ^{4.81} _{-3.58}	+4.61(+5.65)	+5.16	-0.26 ^{0.23} _{-0.28}	-0.19(-0.29)	-0.25	+0.48 ^{0.54} _{-0.69}	+0.50(+0.72)	+0.59
	$\Delta^b \Delta^{17}\text{O}(\text{CO}) [\text{‰}] \quad //\text{AE-REF}$			$\Delta^b (\Delta^{17}\text{O}_{\text{src}} + \Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})) [\text{‰}] \quad //\text{AE-REF}$					
SRF	-0.55 ^{-1.20} _{+1.09}	-0.41(+1.16)	-0.85	+0.11 ^{-0.09} _{-0.20}	-0.14(-0.05)	-0.04			
BL	-0.59 ^{-1.27} _{+1.11}	-0.35(+1.16)	-0.89	+0.08 ^{-0.07} _{-0.18}	+0.00(-0.20)	-0.05			
MBL	+0.96 ^{-1.03} _{+1.14}	-0.13(+1.16)	-0.13	+0.49 ^{-0.01} _{-0.11}	+0.45(-0.20)	-0.01			
FT	-0.06 ^{-1.59} _{+1.07}	-1.04(+1.13)	-0.63	+0.05 ^{-0.12} _{-0.04}	-0.09(-0.04)	-0.08			
T	-0.11 ^{-1.55} _{+1.07}	-0.98(+1.13)	-0.66	+0.05 ^{-0.11} _{-0.06}	-0.08(-0.05)	-0.08			
TP	+0.31 ^{-2.16} _{+1.09}	-2.01(+1.18)	-0.87	+0.26 ^{-0.34} _{+0.36}	-0.58(+0.21)	-0.06			

Notes:

Air mass- and [CO]-weighted annual averages over the given vertical/zonal domains are shown; the diagnosed planetary boundary layer and tropopause heights are used.

Following vertical domains are abbreviated as: SRF – surface (lowermost model) layer, BL – boundary layer (spanning from the surface to the planetary BL height), MBL – marine BL (BL excluding continents and regions subject to large pollution), FT – free troposphere (below the tropopause and above the BL), T – troposphere (below the tropopause), TP – at the tropopause.

Following zonal domains are abbreviated as: TR – tropics, ETNH/ETSH – extratropical SH/NH, AR – Arctic (north of 66°N), AQ – Antarctic (south of 60°S).

^a) See also Table 6.7 (p. 195) listing the averages of the simulated sink effective fractionation ($\Delta^{17}\text{O}_{\text{sink}}$) in CO.

^b) Shown are the sensitivities, *i.e.* the difference between the values simulated in the AE and REF setups. Mind the per ten thousand units (1‰ is equivalent to 0.1‰).

6.2.8.1 Sensitivity of $\Delta^{17}\text{O}(\text{CO})$ to the input from ozone

The detailed distribution of $\Delta^{17}\text{O}(\text{CO})$ simulated in REF setup is presented in Plate D.23 (p. 300) and, being generally determined by the sink effective fractionation in CO, follows that of $\Delta^{17}\text{O}_{\text{sink}}$ (see the analysis in Sect. 6.2.5 and Plate D.19, p. 292), on top of the slightly larger integrals due to the O_3 input. The latter, despite the moderate domain averages, shows perceptible spatiotemporal variations (detailed in Plate D.24, p. 302). Thus, typically large $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ values of up to 1.8‰ are found in the MBL areas subject to outflow from the regions subject to large VOC emissions, predominantly in the SH. The rapid ozonolysis of the alkenes (the main pathway of transferring O_3 oxygen to CO) promotes strong, much localised enhancements of $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ that are transported and further dilute in the hemispheric inventories. This way the outflow from Australia is expected to produce a $(0.1\text{--}0.2)\text{‰}$ larger ozone signal in $\Delta^{17}\text{O}(\text{CO})$ at BHD as compared to that expected at SCB, for example (the simulated $\Delta^{17}\text{O}(\text{CO})$ and $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ at these sites are detailed below in Sect. 6.2.8.3). In the more abundant NH CO, the ozone signal generally spans $(0.2\text{--}0.5)\text{‰}$, except for the continental compositions at mid-latitudes that may exceed $+1\text{‰}$ in summer. The tropospheric vertical distribution of $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ is rather featureless, showing seasonal excursions of $\pm 0.1\text{‰}$ around the averages of $0.7\text{‰}/0.5\text{‰}$ in the ETNH/ETSH, respectively. A conspicuous increase in the ozone input is seen above

150 hPa, which is mediated by the alternative photochemical pathway between O_3 and CO through the $O(^1D)$ radical activating in the stratosphere. Inheriting its $\Delta^{17}O$ from O_3 , $O(^1D)$ reacts with methane and transfers ozone MIF to HCHO and subsequently to CO. At the 50 hPa pressure altitude, this adds about $+2.5\text{‰}^{145}$ to $\Delta^{17}O(CO)$, hence outcompeting the sink effective fractionation signal weakening with height.

It is necessary to emphasise that the estimates of $\Delta^{17}O(O_3 \rightarrow CO)$ crucially depend on three factors. The first factor is relevant for the tropospheric results and is related to the amount of CO produced in the alkene ozonolysis reactions. The uncertainty associated with this source is difficult to quantify and appears to be large, comprised of the uncertainties in the reaction rates (typically of 15%–25%, see refs. in Appendix A, Table A.3, p. 236), emission strengths (at least $\pm 50\%$, see details in Sect. 5.2.7, Table 5.11, p. 137) and potentially under-represented alkene chemistry in the condensed kinetic mechanism used here (*e.g.*, missing butene and alkenes higher than isoprene in MIM, see Sect. 3.1, unquantifiable uncertainty). The direct production of CO in ozonolysis reactions in EMAC amounts to $3.87_{0.68}^{1.14}$ Tg(CO) yr⁻¹, or an equivalent of $0.16_{0.05}^{0.08}$ ppb compared to the average tropospheric CO concentration of 86_{56}^{125} ppb.¹³² This tiny term accounts for $\sim 1/8$ of all O_3 oxygen arriving to CO, whereas the large remainder is transferred through the various intermediates of the isoprene, NMHC and methane chains. The total production of CO bearing the ozone-derived oxygen is thus simulated to be 42 Tg(CO) yr⁻¹, or less than 2% of the overall tropospheric CO source. Unfortunately, no commensurate estimate is available in the literature to date.¹⁴⁶

The second, more important factor, is related to the uncertainties in the transfer of the O_3 -derived oxygen isotopes to CO and other compounds in the course of the complex ozonolysis reactions. As the laboratory experiments of Röckmann *et al.*^[1998a] (“R98”) witness, in the presence of water vapour not all CO produced during alkene ozonolysis inherits the $\Delta^{17}O$ signature of ozone, accompanied by the side production of CO incorporating the MDF oxygen. The resulting $\Delta^{17}O(CO)$ becomes diluted to a various degree for different reactants. Furthermore, in all experiments simpler educts (bearing smaller number of carbon atoms, *e.g.*, ethene) yielded the CO with systematically higher $\Delta^{17}O$, possibly suggesting that the intermediates from the more complex alkene molecules are more likely to produce additional CO using O_2 . The chemical mechanism of EMAC to a certain degree accounts for this peculiarity by redistributing the O_3 and O_2 oxygen among the multiple products¹⁴⁷, so that eventually CO with both, MIF and MDF, signatures is produced from either of the multiple intermediates. It is not feasible, however, to compare the simulated $\Delta^{17}O$ dilution effects with the laboratory measurements of R98, owing to the different ambient conditions and species represented in the model (either a box or 3D). On the other hand, the yields of CO (per reacted O_3) in alkene ozonolysis reactions were diagnosed in EMAC and amount to (18–28)% (averages in the regarded tropospheric domains, see notes to Table 6.8), which is in a very good agreement with the yields of (6–30)% obtained by R98 in the laboratory. We reiterate that only about one of eight CO molecules carrying the ozone $\Delta^{17}O$ signature is produced directly in the ozonolysis reactions in the troposphere, as the simulations suggest.

In addition to the dilution effects, the matter of isotope transfer between ozone and CO is complicated by the peculiar intramolecular distribution of isotope enrichments in the former. In particular, O_3 terminal atoms (TA) carry a larger MIF signal, with $\Delta^{17}O$ being of about 1.5 times larger than that of the bulk $\Delta^{17}O(O_3)$ (see Vicars^[2013] and refs. therein). Observing $\Delta^{17}O(CO)$ larger than the bulk $\Delta^{17}O(O_3)$ in their experiments, R98 conjecture that in specific alkene ozonolysis reactions, CO more readily acquires the TA from ozone. Without accurately quantifying the concomitant MDF-dilution effects (see above), however, the contribution of the TA to $\Delta^{17}O(CO)$ is rather imponderable. A re-analysis of R98 results suggests, nonetheless, that the presence of water vapour likely mediates the dilution effects, but not the selectivity of the channels transferring the terminal ozone oxygen to CO.¹⁴⁸ At the same time, the predominant share of CO produced in atmospheric alkene ozo-

¹⁴⁵ Noteworthy, this estimate is subject to $\pm 50\%$ uncertainty associated with the yield of the channel producing formaldehyde in the $CH_4 + O(^1D)$ reaction (Sander *et al.*^[2006]), disregarding the uncertainties in other factors, *i.e.* simulated mixing ratios, *etc.*

¹⁴⁶ The estimate of (10–15)% by Röckmann *et al.*^[1998a] assuming the MDF in the sink of CO is inapplicable here.

¹⁴⁷ See the oxygen isotope transfer in alkene ozonolysis reactions listed in Appendix A, Table A.1 (p. 225, labelled G4201, G4301, G4405 and G4500, respectively).

¹⁴⁸ An attempt to estimate the share of ozone TA in CO can be undertaken by revisiting the results of R98 in light of the posterior laboratory experiments by Bhattacharya *et al.*^[2008] (“B08”), who inferred the distributions of $\delta^{18}O$ and $\Delta^{17}O$ over the central and terminal O_3 atoms as a function of bulk $\delta^{18}O(O_3)$. Applying the results of B08 to the experimental conditions of R98 (*i.e.*, generation of ozone by the UV photolysis of oxygen with initial $\delta^{18}O = 12.9\text{‰}$ and $\delta^{17}O = 6.5\text{‰}$) yields the expected composition of the terminal O_3 oxygen of $\delta^{18}O_{TA} = (88.3\text{–}98.5)\text{‰}$ and $\Delta^{17}O_{TA} = (40.6\text{–}43.4)\text{‰}$ that correspond to the bulk $\delta^{18}O(O_3)$ of (84–92)‰ obtained by R98. From this, the shares of the terminal and central O_3 atoms proportionate as $\sim 5:1$ in ethene-, $\sim 2:1$ (*i.e.*, bulk) in isoprene- and $\sim 1:0$ (likely all oxygen is

(continued on next page)

olysis stems likely from isoprene (*cf.* the emissions of C_5H_8 that are an order of magnitude larger than the aggregate of other alkenes in EMAC, see Table 5.11, p. 137). In the experiments of R98, the latter firmly yielded $\Delta^{17}\text{O}(\text{CO})$ characteristic for the bulk $\Delta^{17}\text{O}(\text{O}_3)$, further diluted by the additional (15–35)% of O_2 oxygen. The upper limit of this range (corresponding to the “wet” isoprene ozonolysis conditions) is well comparable to the MDF-dilution factor of ~40% in EMAC, reckoned from the difference between the simulated yields of CO: A production of 1.6 CO molecules is diagnosed per one reacted alkene in the troposphere, as compared to the average yield of 2.7 molecules from isoprene and other NMHCs (see Sect. 6.2.2.1, p. 171). Conclusively, $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ is likely to be determined by the bulk isotope composition of O_3 , provided that isoprene is the major source of CO in atmospheric alkene ozonolysis.

6.2.8.2 Ozone isotope composition

The last decisive factor determining the $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ is the isotope composition of ozone itself. Being more extensively measured in the stratosphere, it is hitherto ambiguously quantified in the troposphere, as well as in the atmospheric models. A thorough review on this problem is given by Morin *et al.*^[2007], who carefully revisited the scant observational data and analyses and conclude that the perceptible variability seen in the tropospheric $\Delta^{17}\text{O}(\text{O}_3)$ can neither be unequivocally attributed to the measurement artefacts nor be explained in light of current (enough extensive) knowledge on O_3 isotope kinetics (see details in Sect. 3.4.3, p. 45). Whereas the variations in $\delta^{18}\text{O}(\text{O}_3)$ can be explicated by a combination of various (perhaps underestimated, but summing up to the observed values) MDF KIEs in the atmospheric (re)cycling of O_3 , attempts to reconcile the concomitant MIF without involving additional mass-independent effects (*i.e.*, to the only unequivocally confirmed MIF in the formation of O_3) are to date futile. In particular, employing the laboratory data in a kinetic framework (*e.g.*, a photochemical box-model) shows that at typical tropospheric conditions ozone should exhibit a robust $\Delta^{17}\text{O}$ signature of around +34‰, with small sensitivities to temperature and pressure changes through the O_3 isotopologues’ production rates (Vicars^[2013]). Most of the laboratory studies corroborate this value, *e.g.* R98 as well see the production of O_3 with similar $\Delta^{17}\text{O}$ of $+(33.2 \pm 1.1)\%$ ¹⁴⁹. On the other hand, the ambient measurements of $\Delta^{17}\text{O}(\text{O}_3)$ put this value at the upper end of the observed variability of $+(20\text{--}35)\%$ (see Figure 6.23 below). The kinetics dictate that in order to produce ozone with a 1‰ lower $\Delta^{17}\text{O}$ signature at a pressure of one atm., a drop of about 12 K in the ambient air temperature is required, which suggests that the observed 15‰ variability in $\Delta^{17}\text{O}(\text{O}_3)$, if realistic, is driven by other factors that do not manifest themselves in the laboratory. The observations also likely do not attest to the effects of dilution by the MDF compositions, as the concomitant $\delta^{18}\text{O}(\text{O}_3)$ data suggest. Further ingenious laboratory experiments may provide insights into the riddle of the tropospheric $\Delta^{17}\text{O}(\text{O}_3)$. A most recent study by Feilberg *et al.*^[2013], for example, delivers a new piece of information on the isotope selectivity in the ozone formation process, probing it in bathing gases with different quenching efficiencies. It could be that the stabilisation process of the O_3 formation intermediates is peculiarly sensitive to the ambient atmospheric conditions/composition. To note, unresolved questions remain on the $\text{CO}+\text{OH}$ KIE quenching effects, which appear to be much more intricate than the theory predicts (see details in Sect. 3.4.4, p. 49). Furthermore, additional observational data of a better quality than that available to date should help. A case in point is the recently developed measurement technique by Vicars *et al.*^[2012] that offers several advantages over the previous approaches and confirms rather moderate ozone $\Delta^{17}\text{O}$ variability in the troposphere (see below).

In the meanwhile, atmospheric modelling studies employing ozone MIF conventionally resort to using a constant value for tropospheric $\Delta^{17}\text{O}(\text{O}_3)$, optionally examining the sensitivity of the inferred results, within the range of $+(25\text{--}35)\%$ (see, *e.g.*, a review by Savarino and Morin^[2012]). An attempt to explicitly simulate the (tropospheric) ozone isotope composition is undertaken in this study with EMAC. Thus, the parameterisation of the oxygen isotope effects and exchange kinetics relevant to ozone is proposed (see details Sects. 3.3.3, 3.4.2 and 3.4.3). It is noteworthy that due to the specifics of the kinetic chemistry implementation in EMAC, only bulk O_3 isotope compositions are simulated (*i.e.*, the intramolecular distributions of $\Delta^{17}\text{O}$ over the terminal and

from TA) in β -pinene-derived CO, respectively. The mutual variations of $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ confirm that these ratios persist in the CO diluted by the MDF oxygen, too: Changes to the selectivity in the channels leading to the TA incorporation should have caused steeper slopes in the three-isotope ($\delta^{17}\text{O}$ or $\Delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$) plot for CO, as compared to those that R98 found. These, in turn, firmly suggest that except for the “dry” ethene ozonolysis, all produced CO becomes to a various degree diluted by the oxygen from O_2 .

¹⁴⁹Quoted is the average and span of two $\Delta^{17}\text{O}(\text{O}_3)$ measurements; the span is augmented with the uncertainty in $\Delta^{17}\text{O}$ determination ($\pm 0.3\%$). Values are recalculated to comply the $\Delta^{17}\text{O}$ formulation used in this study (see Sect. 3.2).

central oxygen atoms are not resolved). This, however, is likely irrelevant for the estimates of $\Delta^{17}\text{O}(\text{CO})$ (see above, p. 213) and does not impede the analysis of the results for $\Delta^{17}\text{O}(\text{O}_3)$ inferred here. The latter generally reiterate the synopsis given above. The simulated tropospheric $\Delta^{17}\text{O}(\text{O}_3)$ distribution (detailed in Plate D.25 on p. 304) presents much moderate variations within $+(27\text{--}32)\text{‰}$ around the tropospheric average of $+30.4\text{‰}$, with the spatiotemporal dynamics being chiefly determined by the changes in ambient temperature and vertical transport. For instance, no expected temperature-driven seasonal variation is seen around the tropopause in the subtropics due to the subsidence of the stratospheric air carrying more enriched ozone. Higher average temperatures result in about 1‰ higher BL $\Delta^{17}\text{O}(\text{O}_3)$ in the tropics over the continents, as compared to the MBL values. In the elevated regions, the effect of lowered pressures overcompensates that of the decreasing temperatures with height, promoting larger MIF in ozone formation and hence highest simulated values in the BL. The peculiar double annual minima in $\Delta^{17}\text{O}(\text{O}_3)$ are simulated in the Arctic and Antarctic BL (*cf. ibid.*, panels (a)–(b)). These manifest the enhanced input of the low- $\Delta^{17}\text{O}$ stratospheric O_3 in spring, followed by the drop in the ambient temperatures while ozone is still being photochemically produced in fall. Later in winter, the input of O_3 with higher MIF from the lower latitudes augments the high-latitude inventory $\Delta^{17}\text{O}(\text{O}_3)$ to its seasonal maxima.

Overall, the largest intra-annual variations in the tropospheric $\Delta^{17}\text{O}(\text{O}_3)$ are simulated in the BL continental air, reaching 4.5‰ in the ETNH, 3‰ in the Arctic/Antarctic and 2‰ in the ETSH, respectively. In contrast, the MBL variations do not exceed 0.5‰ in the tropics and 1.5‰ at the higher latitudes. As discussed above, the observational data do not proof the tight correspondence between the $\Delta^{17}\text{O}(\text{O}_3)$ and ambient temperatures simulated in EMAC. The cases when the latter are uncorrelated in the model are attributed to the effect of atmospheric transport/mixing in the absence of photochemical generation of ozone, *e.g.* merely in high-latitude winter. The simulated O_3 mixing and bulk isotope ratios are further compared in Figure 6.23 with the to date available observations at the surface. Shown are the statistical distributions of $[\text{O}_3]$, $\delta^{18}\text{O}(\text{O}_3)$ and $\Delta^{17}\text{O}(\text{O}_3)$ at various continental locations, which are adequately reproduced by EMAC for $[\text{O}_3]$ and $\delta^{18}\text{O}(\text{O}_3)$ but not $\Delta^{17}\text{O}(\text{O}_3)$, whose variability is underestimated by at least a factor of two. Importantly, in contrast to the MIF-only $\Delta^{17}\text{O}$ signal, the $\delta^{18}\text{O}$ of ozone is affected by the other, mass-dependent fractionations intrinsic to the photochemical turnover of O_3 . That is, the underestimated fractionations in the ozone formation reaction can be masked for $\delta^{18}\text{O}$ by the overestimated KIEs in the O_3 photolysis or in isotope exchange reactions involving atomic oxygen, but not for $\Delta^{17}\text{O}$. Actually, regarding the overestimated $\Delta^{17}\text{O}(\text{O}_3)$ averages, the opposite case is likely: If the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ in the formation of ozone are proportionally overestimated by the model, too large negative MDF KIEs alleviate the discrepancies in resulting $\delta^{18}\text{O}(\text{O}_3)$. Furthermore, a similar situation may emerge, if (hypothetically) a part of the measured tropospheric O_3 is diluted with the MDF composition. No further inferences can be made from $\delta^{18}\text{O}(\text{O}_3)$, as its rather adequately simulated values are nonetheless determined to the KIEs in the O_3 photolysis and isotope exchange of its precursors (O_2 and $\text{O}(^3\text{P})$). Being inferred indirectly, the latter is most ambiguous (see details in Sect. 3.4.2). At present, there is no sound hypothesis to put forward on what may cause the lowering of the tropospheric $\Delta^{17}\text{O}(\text{O}_3)$; it ought to be sought in a disparity between the ambient troposphere and laboratory conditions peculiarly impacting the MIF in ozone formation, or in a missing source of MDF O_3 . We remark, however, that a certain degree of qualitative agreement between the model and observations exists, as Figure 6.23 shows, in particular for the more recent observations.

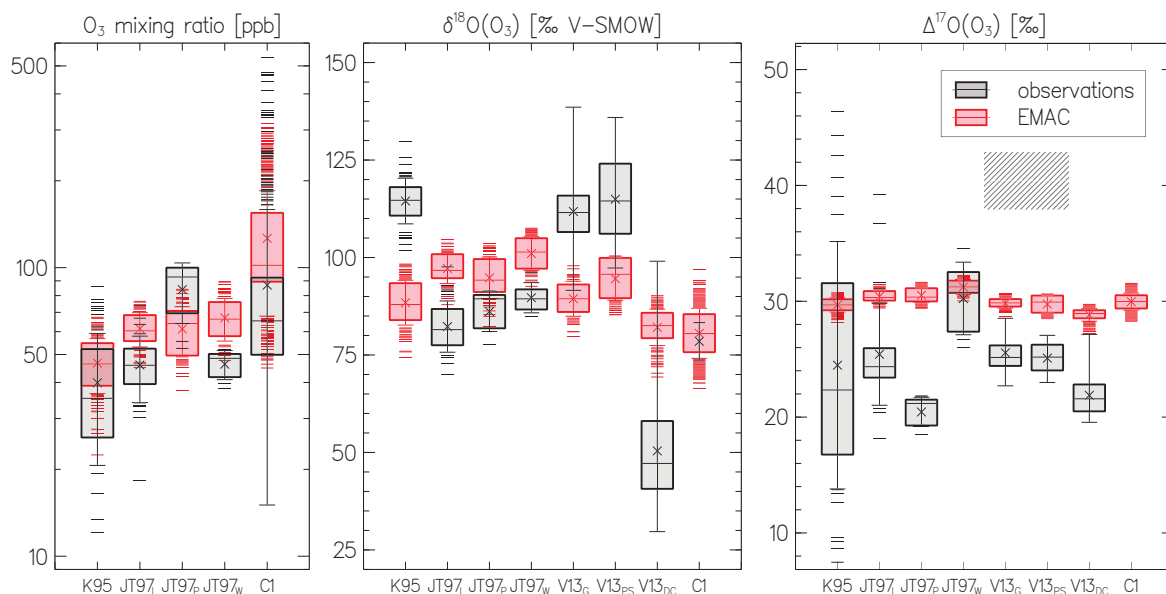


Figure 6.23 Comparison of the observed and simulated ozone mixing and bulk isotope ratios at various surface locations. Abbreviations refer to: K95 – Krankowsky *et al.*^[1995], JT97 – Johnston and Thiemens^[1997], V13 – Vicars^[2013], C1 – CARIBIC-1 data (see Sect. 4.2). Subscripts refer to the observational locations: L – La Jolla, P – Pasadena, W – White Sand, G – Grenoble, PS – R/V Polarstern (expedition No. 88), DC – Dome C. Box and whisker plots present the distribution of the compositions: Box boundaries represent the upper and lower quartiles, horizontal bars and crosses denote the median and average values, respectively. Vertical bars equate one standard deviation (for V13, minimum-maximum span), short horizontal lines denote the values outside $\pm 1\sigma$. The hatched area spans the range of $\Delta^{17}\text{O}$ in the terminal oxygen atoms of O_3 inferred by V13 (excluding DC). Except for the R/V Polarstern and C1 data, the simulated distributions are shown for the annual climatological values (60 instantaneous samples throughout the year). For C1, only the $[\text{O}_3]$ observations are available, shown $\delta^{18}\text{O}(\text{O}_3)$ value is derived indirectly from the correction of the $\delta^{18}\text{O}(\text{CO})$ data (see Appendix C for details). The unpublished observational data on $\delta^{18}\text{O}(\text{O}_3)$ and $\Delta^{17}\text{O}(\text{O}_3)$ measured at G/PS/DC are kindly provided by W. Vicars, Laboratoire de Glaciologie et de Géophysique de l'Environnement, CNRS – Université Joseph Fourier, Grenoble, France.

The likely too large $\Delta^{17}\text{O}(\text{O}_3)$ simulated in EMAC implies that the corresponding O_3 MIF signal in CO becomes overestimated. The small variations in the simulated $\Delta^{17}\text{O}(\text{O}_3)$ and linear additivity of the O_3 signal in CO allow consistently scaling the resulting $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ linearly with the average $\Delta^{17}\text{O}(\text{O}_3)$ value. Taking the most representative tropospheric $\Delta^{17}\text{O}(\text{O}_3)$ value of +25‰ (W. Vicars, pers. comm., 2013), the here inferred O_3 MIF signal in CO is to be reduced to $\sim 4/5$ of its simulated magnitude, which lowers the tropospheric estimate of $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ to +0.5‰ (see Table 6.8 above). The sensitivity studies performed with EMAC additionally provide an estimate of the contribution of ozone to the $^{18}\text{O}/^{16}\text{O}$ ratios in CO. Being more adequately simulated, ozone ^{18}O is found to augment tropospheric $\delta^{18}\text{O}(\text{CO})$ by as much as $+1.9_{2.3}^{1.7}\text{‰}$ ¹³², or comparable to about one-fifth of its observed seasonal variation. Resembling much the $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ signal, the magnitude of $\delta^{18}\text{O}(\text{O}_3 \rightarrow \text{CO})$ is threefold larger in the tropics and ETNH (about four times in the ETSH), with the largest values exceeding +6‰ in the BL. If the simulated effect is realistic, it has implications for the tropospheric mass balance of C^{18}O and compositions observed at particular locations. For instance, the average $\delta^{18}\text{O}(\text{CO})$ simulated at BHD may be affected by as much as $+(2.5\text{--}3)\text{‰}$, as opposed to the maximum of +1.5‰ diagnosed at all NH sites regarded in this study. It should be noted that alike for $\Delta^{17}\text{O}(\text{O}_3)$, intensifying reactions of CH_4 with $\text{O}(^1\text{D})$ produce an increasing with height enhancement in the stratospheric $\delta^{18}\text{O}(\text{CO})$. The estimated $\delta^{18}\text{O}(\text{O}_3 \rightarrow \text{CO})$ of $+(3.0 \pm 1.4)\text{‰}$ at ~ 100 hPa strengthens to $+(6 \pm 2.9)\text{‰}$ at ~ 50 hPa pressure altitudes, respectively.¹⁴⁵ It should be noted that this effect is small compared to the O_3 -induced artefacts reckoned in the stratospheric $\delta^{18}\text{O}(\text{CO})$ observed by CARIBIC-1 (see Appendix C), however it may affect the concomitantly derived estimate of the LMS $\delta^{18}\text{O}(\text{O}_3)$, updating it to a higher value.

6.2.8.3 Comparison with station data

We conclude the analysis of results on $\Delta^{17}\text{O}(\text{CO})$ with the examination of the compositions simulated at the selected surface locations and comparison with the available observational data. Shown below in Figure 6.24 are the time series of CO mixing ratio (left panels) and $\Delta^{17}\text{O}(\text{CO})$ (right panels) simulated in the control simulations (REF and AE), supplemented with the results obtained in the ZERO setups (Z and ZE) for $\Delta^{17}\text{O}(\text{CO})$. Both REF/AE and Z/ZE setup pairs differ only in the strength of the CO and NMHCs surface emissions (see Sect. 6.2.3.1, p. 174). The differences between the $\Delta^{17}\text{O}(\text{CO})$ simulated in these pairs equate the input of the ozone MIF to CO, $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$. One should bear in mind that the latter is reckoned for $\Delta^{17}\text{O}(\text{O}_3)$ of around +30‰, *i.e.* about 20% higher than the estimate based on the ozone $\Delta^{17}\text{O}$ signature of +25‰ would be. In addition to $\Delta^{17}\text{O}(\text{CO})$, Figure 6.24 shows the effective CO sink fractionation magnitude, $\Delta^{17}\text{O}_{\text{ECO+OH}}$ (shown as thin red lines) estimated in the Z and ZE setups (solid and dashed strokes, respectively). Embodying a pure chemical signal, $\Delta^{17}\text{O}_{\text{ECO+OH}}$ does not carry any non-zero precursor $\Delta^{17}\text{O}$ arriving to CO either from O_3 or from the surface sources. Considered MDF, the latter, as we recall above, nonetheless bear a slightly negative MIF signal ($\Delta^{17}\text{O}_{\text{src}}$, down to -0.455‰). Therefore, matching the $\Delta^{17}\text{O}_{\text{ECO+OH}}$ with the results from Z/ZK singles out the input of these MDF sources to $\Delta^{17}\text{O}(\text{CO})$. It is, as seen in Figure 6.24, always negative and may reach about -0.5‰ (*cf. ibid.* the plates (e)–(d) for the compositions at BHD/SCB), thus denoting that the dominant fraction of the oxygen constituting CO originates from the air O_2 . In contrast, $\Delta^{17}\text{O}_{\text{src}}$ at the ETNH sites (SPI/ALE) maximises only in summer owing to the largest photochemically-derived component of CO, whereas winter $\Delta^{17}\text{O}(\text{CO})$ remains nearly unaffected by the surface sources inheriting their nearly zero-MIF from the various water reservoirs (see Sect. 5.2.8, p. 138). Whenever the equal $\Delta^{17}\text{O}_{\text{ECO+OH}}$ and REF/AE $\Delta^{17}\text{O}(\text{CO})$ values are reproduced, they denote that the MIF input from ozone becomes compensated by the input from the MDF sources, *i.e.* purely the sink effective enrichment is seen in the atmospheric CO. The simulated $\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO})$ and $\Delta^{17}\text{O}_{\text{src}}$ often relate as +2:–1 (*cf.* seasonalities at BHD and SCB), however this ratio substantially decreases, provided that the simulated MIF in O_3 may be overestimated (see above).

The seasonal variations of $\Delta^{17}\text{O}(\text{CO})$ in the ETSH differ noticeably from those simulated in the NH. Thus, the annual minimum-to-maximum amplitudes at BHD and SCB on average do not exceed 1‰ and 1.5‰, respectively, owing to the stronger source-to-sink equilibrium established for CO. To compare, the NH variations may reach 2.5‰ (simulated) to above 4‰ (observed) at high latitudes. The latter in the model confirm the overestimated $\Delta^{17}\text{O}(\text{CO})$ values that correlate with underestimated $[\text{CO}]$, which is a source effect. Seen throughout December–March at ALE/SPI, the missing MDF surface component does not sufficiently attenuate the MIF signal in CO. The largest understatement of $\Delta^{17}\text{O}(\text{CO})$ in the model, on the contrary, is evidently connected with the missing sink of CO: The May–July $\Delta^{17}\text{O}(\text{CO})$ is simulated at (0.5–1.5)‰ lower than that observed. Noteworthy, about 1‰ is missing also in July–August at IZA, which, regarding the adequately reproduced $[\text{CO}]$ and $\Delta^{17}\text{O}(\text{CO})$ in March–May, suggests that the problem is of photochemical origin. Conjointly with the discrepancies seen for the simulated $\delta^{13}\text{C}(\text{CO})$ (see above, Sect. 6.2.7), it is attributed to the likely missing summertime OH in the NH. That is also confirmed by the statistics on the simulated *vs.* observed seasonal cycles. Presented in Table 6.9 below, it confirms high correlations and a tangible improvement in the reproduced variations of both, $[\text{CO}]$ and $\Delta^{17}\text{O}(\text{CO})$, when the amended surface emissions are used (AE setup). The alleviation of the biases is substantial for $[\text{CO}]$, however, these for $\Delta^{17}\text{O}(\text{CO})$ are actually below the uncertainty associated with the observational data (see Sect. 4.1, p. 67) in both setups. Whereas this is not evident to be the case for all observational sites, this reconfirms that $\Delta^{17}\text{O}(\text{CO})$ is weakly sensitive to the large increase in $[\text{CO}]$, being chiefly determined by $\Delta^{17}\text{O}_{\text{ECO+OH}}$.

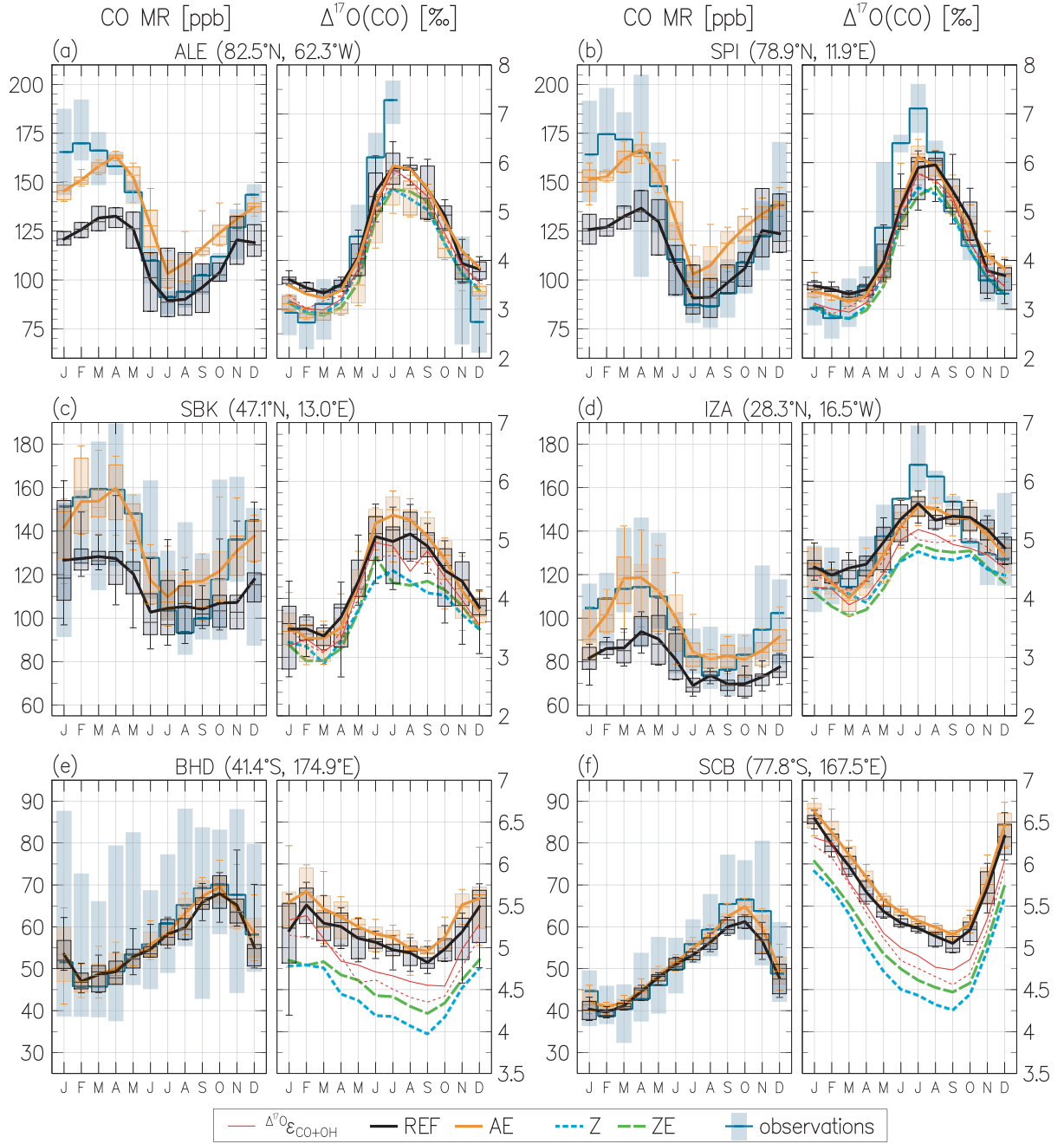


Figure 6.24 Comparison of the observed and simulated MIF signal in CO, $\Delta^{17}\text{O}(\text{CO})$. Box and whisker plots present the distribution of the compositions simulated in the control simulation (REF and AEK). Box boundaries represent the upper and lower quartiles, horizontal bars denote the median values, solid lines connect the averages, respectively. Vertical bars denote the simulated minima and maxima. The thick dotted/dashed lines present the values simulated in the Z/ZE setups, contrasting the input of ozone MIF to $\Delta^{17}\text{O}(\text{CO})$ in the simulations with the reference/amended emission setups, respectively. Analogously, the thin solid/dotted lines present the simulated sink effective $\Delta^{17}\text{O}$ enrichment in CO, $\Delta^{17}\text{O}_{\text{ECO+OH}}$, contrasting the input of the MDF sources to $\Delta^{17}\text{O}(\text{CO})$. Step-lines denote the observations, with shaded areas equating the interquartile range (IQR) of the data. Monthly distributions are shown. The compositions simulated at SBK, BHD and SCB are presented for comparison (no observational data for $\Delta^{17}\text{O}(\text{CO})$ are available).

Table 6.9 Statistics on the simulated $[\text{CO}]$ and $\Delta^{17}\text{O}(\text{CO})$ compared to the observational data

Setup	Station	CO mixing ratio			$\Delta^{17}\text{O}(\text{CO})$		
		ρ	$\sigma_{\text{obs}}/\sigma_{\text{sim}}$	bias [ppb]	ρ	$\sigma_{\text{obs}}/\sigma_{\text{sim}}$	bias [‰]
REF	ALE	0.95	0.55	-19.1	0.96	0.65	+0.03
	SPI	0.96	0.51	-15.6	0.93	0.69	-0.16
	IZA	0.89	0.69	-18.3	0.88	0.58	+0.03
AE	ALE	0.94	0.74	+3.0	0.94	0.67	+0.01
	SPI	0.95	0.68	+7.2	0.93	0.72	-0.15
	IZA	0.85	0.80	-3.6	0.89	0.74	-0.06

Notes: Shown are the correlation coefficient (ρ), the ratio of the simulated-to-observed standard deviations ($\sigma_{\text{obs}}/\sigma_{\text{sim}}$) and the annual average biases (in corresponding units) for the simulated vs. observed seasonal variations. Monthly means and standard deviations are used.

To recapitulate, the to date most consistent estimate of the atmospheric $\Delta^{17}\text{O}(\text{CO})$ distribution is inferred in this study with EMAC. Implementing a complex chemistry scheme and sufficiently detailed surface emissions setup, the latter allows to single out the (small) inputs of the mass-independently fractionated (MIF) oxygen from ozone and other atmospheric oxygen reservoirs to CO, whose MIF, in turn, is chiefly determined by the anomalous isotope fractionation in the sink reaction with OH. The model results suggest that less than 2% of the tropospheric CO inherit the oxygen atoms from ozone, which translates into additional +0.6‰ in the tropospheric $\Delta^{17}\text{O}(\text{CO})$ value. The chemical kinetics of the alkene ozonolysis and oxygen composition transfer between O_3 and CO simulated in EMAC are in good agreement with the results and analysis of Röckmann *et al.*^[1998a]. So is the estimate of the effective tropospheric sink enrichment ($\Delta^{17}\text{O}\epsilon_{\text{CO+OH}}$, inferred at +4.33‰) in comparison to $+(4.11\pm0.3)\%$ reckoned by Röckmann *et al.*^[1998b]. No insight is obtained with EMAC on the tropospheric distribution of $\Delta^{17}\text{O}(\text{O}_3)$, whose average is simulated to be +30.4‰ and is consistent with the value expected from the laboratory data. Instead, the most recent observations of ozone tropospheric MIF suggest a value of $\sim+25\%$ being the most representative, which renders the reckoned MIF signal from O_3 in CO overestimated by about 20%. The comparison of the simulated $\delta^{18}\text{O}(\text{O}_3)$ with the observational data suggests a much adequate reproduction of the former, and non-negligible implications for $\delta^{18}\text{O}$ of atmospheric CO. A significant enrichment of CO in heavy oxygen is expected in the stratosphere via the reactions of methane and $\text{O}(^1\text{D})$, provided that the latter inherits the isotope composition of O_3 . The simulated tropospheric distributions of $\Delta^{17}\text{O}(\text{CO})$ second the conclusions inferred for $\delta^{13}\text{C}(\text{CO})$, highlighting the problematic of the CO and OH in the NH, particularly the missing summertime sink and wintertime emissions (at the high latitudes). Despite the underestimated variations, the simulated $\Delta^{17}\text{O}(\text{CO})$ surface seasonal cycles are in very good agreement with the observations in the NH. For the ETS, where observations of CO MIF are not available to date, the model suggest a substantially higher average and smaller variation of $\Delta^{17}\text{O}(\text{CO})$.

7

Concluding remarks and outlook

An advanced approach to modelling of atmospheric carbon monoxide stable isotope composition is introduced in this study. Representing the atmospheric isotope chemistry and physics in unprecedented detail, it required substantial development efforts, which, however, yielded evident progress. Owing to the optimisations introduced, the numerical simulations of the comprehensive chemical mechanism are feasible now in the resource-demanding applications with the employed AC-GCM EMAC: The elaborated approach provides a simultaneous extension of a chemical mechanism of any complexity by any desired set of isotopologues, further encouraging applications of isotopes in EMAC with highly facilitated set-up and parameterisation procedures. Moreover, the developed tagging technique allowed the sophisticated budgeting of the key atmospheric species (CO, OH, HO₂ and CH₄) allotted to the various parts of the employed chemical mechanism. The target EMAC application in this study has succeeded with the concurrent simulation of up to five isotopologues of all carbon- and oxygen-bearing species and supplementary diagnostic in a comprehensive setup, with the ultimate aim of understanding and applying the stable isotope composition of atmospheric carbon monoxide.

A thorough inquiry was made on the isotope compositions of the various trace gas sources, which resulted in the *de novo* creation of the ¹³C/¹²C-inclusive trace gas emissions inventory in EMAC. Overriding some of the abstract and less credible assumptions used in the previous studies, it suggests the δ¹³C signature of the overall CO surface source of -25.3‰, which is within the range of the earlier bottom-up estimates of -(26.2–24.8)‰. Importantly, the uncertainties associated with the influx of each precursor of CO were assessed, for the first time including the concomitant isotope signatures. As for the surface CO component, its uncertainty is derived at a rather large ±68% for the emission rate and ±3‰ for the δ¹³C. That is, the current bottom-up estimates are still inaccurate to single out the discrepancies with the systematically higher surface source δ¹³C of -(23.0–22.1)‰ reckoned in the top-down (*i.e.*, inverse modelling) approaches. Noteworthy, the δ¹³C uncertainty of the overall atmospheric CO source ultimately reduces to ±1.6‰, owing to the contributions of the sources with the more certain δ¹³C signatures, primarily the *in-situ* methane oxidation (see details in Sects. 5.2.7 and 6.2.2, also Table 6.4, p. 162).

Being a stumbling stone to the unambiguous closure of the ¹³CO atmospheric budget, the latter was scrutinised in this study. Thus, the tropospheric yield of CO from CH₄ in EMAC amounts to 0.94, in line with the recent model studies suggesting values close to unity. The efficiency of the dry and wet deposition processes, in the way these are parameterised in EMAC, is found to be the minor factor determining the local photochemical yields of CO. Instead, the transport (likely convective) is rather influential, withdrawing the precursors of CO from the areas subject to efficacious deposition. For instance, in the surface layer air (where dry deposition dominates), the average yields of CO in the CH₄ and NMHCs oxidation chains are of 0.73 and 1.58, respectively, which is by 78% and 50% lower than their tropospheric averages, respectively. For the CH₄→CO chain, this means that 21% of the CO precursors in the BL are exported to the free troposphere, whereas only about 6% become deposited. As for the other *in-situ* sources, about a half of all reacted carbon from NMHC eventually produces CO, with the transport reducing the BL yields by additional 19% to 27%, depending on the source species.

The explicit simulation of the isotope effects in the deposition processes in EMAC allowed estimating one of the components of δ¹³C(CO) not qualified in previous studies, *viz.* the isotope enrichment that CO acquires through the intermediates undergoing fractionation in the removal processes. Confirmed negligible for δ¹³C(CO) (+0.15‰ on average in the troposphere), the dry deposition isotope fractionations are nonetheless tangible for formaldehyde and methanol, whose δ¹³C may acquire up to +3‰ and more than +5‰ at the surface, respectively. For CH₃OH, the effect is pronounced on the large scale, as its tropospheric δ¹³C average becomes elevated by 3‰. Noteworthy, the derived estimates for the ¹³C enrichments in the deposition processes can be straightforwardly projected for the stable oxygen isotopologues of the respective species.

Ultimately, EMAC suggests the production of CO from the CH₄ oxidation source of at least 811 Tg(CO) yr⁻¹ in the troposphere¹⁵⁰, contributing to approximately 24% and 38% of the overall CO burden in the NH and SH, respectively. High yields of CO from CH₄ lead to a more ¹³C-depleted tropospheric CO source, which results in a conspicuous underestimation of the δ¹³C(CO) on top of the adequately reproduced mixing ratios in the SH, as seen in the reference simulation (REF) of this study. Deductively this discrepancy can only be attributed to the underestimated ¹³C isotope enrichment in the tropospheric CO sink, *i.e.* likely the kinetic isotope effect (KIE) in the reaction with OH. A thorough re-analysis of the CO+OH reaction kinetics and laboratory data suggests that the magnitude of the ¹³C KIE, in addition to its pronounced pressure dependence, should be sensitive to the temperature variations. In particular, about 1‰ increase in ¹³CO enrichment per 10 K decrease in the ambient temperature is anticipated with the new *composite* CO+OH KIE parameterisation elaborated in this study. Furthermore, the effective ¹³CO+OH sink fractionation, ¹³ε_{CO+OH}, may be much different in the applied *conventional* parameterisations: The re-analysis of the previous modelling studies indicates that the tropospheric ¹³ε_{CO+OH} average varies amongst them within +(2.3–3.7)‰, owing to the dissimilar formulations of the KIE pressure dependence applied (see Sect. 6.1.4.2). That, in turn, must have perceptibly affected their results, *e.g.* the estimates of the source isotope signatures in the inverse modelling studies. To compare, the conventional and composite parameterisations in EMAC reproduce the tropospheric ¹³ε_{CO+OH} of +3.4‰ and +4.6‰, respectively, with the revisited approach being unopposed in alleviating the discrepancies in the simulated SH δ¹³C(CO).

The amendments to the trace gas emissions introduced in this study are no less important for the isotope CO composition simulated in the NH. Attributed to the anthropogenic emissions over East Asia (EDGAR inventory, ver. 3.2, see Sect. 5.2.2), an additional influx of 229 Tg(CO) yr⁻¹ (equivalent to an increase of ~16% in total surface emissions or ~14% of the overall NH CO source in REF) is required to adequately simulate CO mixing ratios in the NH mid-latitudes and the Arctic. Compared to the initial 2525 Tg(CO) yr⁻¹, the more realistic CO turnover in EMAC amounts to 2754 Tg(CO) yr⁻¹, partitioned into the principal sources as 29% (CH₄ oxidation), 23% (NMHCs oxidation), 16% (biomass burning), 14% (fossil- and biofuel use, each), and 4% (biogenic and ocean sources). The main contribution to the large uncertainty associated with this estimate (±382 Tg(CO) yr⁻¹, about ±14%) is from the biofuel use and NMHC oxidation sources, whose uncertainty factors are rather high (2–3, net of 1.7 for CO, see Sect. 5.2.7). In contrast, lower errors (typically within ±5%) are imposed on the CO budget estimates in the inverse modelling studies. The extended budgeting of the chemical interchanges simulated in EMAC was applied to infer the mutual sink and production terms of the species relevant for CO. For instance, reactions with CO account for 39% of the total OH sink of 4086 Tg(OH) yr⁻¹, competing with the 36% in the CH₄→CO chemistry shared between the reactions with CH₄ and subsequent chain intermediates as 13%:23%, respectively. Of the remaining significant sink terms, 14% is attributed to the NMHCs oxidation (including isoprene). This result, stemming from the comprehensive chemical mechanism employed in EMAC, is foremost interesting for equating the net roles of CH₄ and CO as the dominant OH reaction partners. The tropospheric lifetimes of methane and CO inferred in this study (τ_{CH₄} = 8.2 years, τ_{CO} = 50 days) are in close agreement with the estimates derived for EMAC by Taraborrelli *et al.*^[2012]. Increasing the surface emissions comprised also a collateral sensitivity study on the response of the CH₄-CO-HO₂-OH system to the perturbation of the CO abundance. Remarkably, extra CO ultimately boosts the OH turnover by an amount required to remove ~206 Tg(CO) yr⁻¹, through the production of HO₂ that follows the CO+OH reaction. This makes OH quite stable against CO, as an emission of some twenty molecules of it is required to remove one hydroxyl radical available for reaction in the troposphere.¹⁵¹ An interesting response is also seen from methane whose sink decreases by one molecule per roughly seven CO molecules emitted, which means that emitting CH₄ is about three times more effective than CO in reducing OH, when calculated per molecule. Ultimately, the importance of HO₂ for recycling OH in reactions with CO, as well as the significance of employing comprehensive chemistry schemes for studying atmospheric CO and CH₄, cannot be overstated. For example, calculated in EMAC, the tropospheric OH lifetime of τ_{OH} = 1.5 s is at least by a factor of two longer than that reckoned in the simplified CH₄-CO-OH coupled systems (see, *e.g.*, Manning^[1999], Prather^[2007]). The results obtained in the present study reiterate the essential findings of

¹⁵⁰Unless stated otherwise, the estimates presented hereinbelow are for the year 2000, reckoned with EMAC in the AEK simulation that yields the best reproduced CO and ¹³CO in this study (see Sect. 6.1.1, p. 140).

¹⁵¹With the increase in anthropogenic CO emissions, a perturbation in partly NO_x-enriched conditions is implied.

Lelieveld *et al.*^[2002], suggesting large tropospheric OH turnover. In comparison to their results, the simulated OH primary and secondary production in EMAC is some 8% greater, favouring a recycling probability of 0.53.

Recurring to the ^{13}C O, the more realistic surface emissions are found to subsequently improve its simulated distribution in the NH, particularly alleviating the discrepancies in $\delta^{13}\text{C}(\text{CO})$ averages and seasonal variations in the Arctic. A comparable effect is seen when the revisited CO+OH KIE parameterisation is applied in the model, which points at the distinct sensitivity of the variations in the high-latitude CO isotope ratios to the composition of the CO exported from the tropics. Another peculiarity is seen in the extratropical SH, where a minor (about +0.5‰) clear response to the increased emissions is seen in $\delta^{13}\text{C}(\text{CO})$, but not in the concomitant mixing ratios. The efficacious mixing of the CO inventory in the ETSH thus renders the averages of $\delta^{13}\text{C}(\text{CO})$ in the Antarctic sensitive to the changes in East Asian emission strengths. Eventually, the present study with EMAC offers an alternative closure of the tropospheric ^{13}C O budget at $\delta^{13}\text{C}(\text{CO})$ of $-29.8_{-2.0}^{+2.3}\text{‰}$ ¹³², bringing the bottom-up and inverse modelling estimates in close agreement through the amendments in the emission inventory and, more importantly, revisited CO+OH KIE parameterisation.

An effort was put in this study into reviewing the observational data on CO isotopes available to date. In particular, series of CO mixing ratio and $\delta^{13}\text{C}$ from ten observational sites were analysed and compiled into the climatological records for the year 2000 for a consistent comparison with model results. The concomitant trends analysis reveals no significant changes in the surface $\delta^{13}\text{C}(\text{CO})$ observed in the SH and small long-term tendencies (within $\pm 0.2\text{‰ yr}^{-1}$) at the NH stations covering three or more years of observations. More pronounced negative trends in $[\text{CO}]$ and $\delta^{13}\text{C}(\text{CO})$ are seen at the NH locations subject to regional emissions, in congruence with the reductions in the latter after 1990 and the corresponding repartitioning of the CO sources. An extended interpretation is given to the zonal- and temporal distributions of CO isotopes in the MBL, in particular, to the temporal correlation between the $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and mixing ratios of CO that substantially deteriorates polewards. Evident in $\delta^{13}\text{C}(\text{CO})$, yet less marked in $\delta^{18}\text{O}(\text{CO})$, it may inadvertently lead to misapplication of CO isotopes in the mixing model approach: When annual variations of tightly correlating CO and C^{18}O are treated in the Keeling-plot, the latter yields overestimated $\delta^{18}\text{O}$ signatures of the CO sources by assimilating the seasonal variations in the background reservoir $\delta^{18}\text{O}(\text{CO})$. A manifest proof of that are the uncorrelated CO and ^{13}C O variations seen at high-latitudes. A thorough analysis and processing similar to that of $\delta^{13}\text{C}/\delta^{18}\text{O}$ was also given to the surface observations of $\Delta^{17}\text{O}(\text{CO})$, including the so far unexamined low-latitude data from the Izaña station. The observations from the CARIBIC platform, also presented for the first time, feature isotope compositions of CO in the UTLS indicative for photochemically aged air. The multi-year, regular observations from CARIBIC allowed creating the unique seasonality of the Eurasian UTLS CO isotopes that captures characteristic seasonal changes in atmospheric transport (*e.g.*, triggering of the Asian monsoon conditions) in the peculiar semi-annual cycles of $[\text{CO}]$ and $\delta^{18}\text{O}(\text{CO})$. Opposing the surface station data, observations in the UTLS are more representative for the free tropospheric CO: The mutual relationship between the CARIBIC CO mixing ratio and $\delta^{13}\text{C}$, simulated in EMAC, is found particularly sensitive to both, chosen emission strengths and effective sink enrichment in CO. The CARIBIC data thus offer a strong observational evidence for the findings on ^{13}C O in the present study, in particular, for the average tropospheric $\delta^{13}\text{C}(\text{CO})$ close to -28‰ .

Last but not least, the atmospheric distribution of the anomalous, mass-independently fractionated (MIF) oxygen isotope composition in CO, $\Delta^{17}\text{O}(\text{CO})$, is consistently simulated with EMAC on a global scale for the first time. Estimated to be on average +4.7‰ in the troposphere, it is comprised of inputs from the effective sink enrichment (+4.3‰), mass-dependently fractionated (MDF) sources (−0.2‰) and the highly-MIF atmospheric O_3 (+0.6‰), respectively. The $\Delta^{17}\text{O}$ of tropospheric ozone (modulates the latter term) is simulated at +30‰, in line with that expected from the laboratory data and being used in the modelling studies on tropospheric $\Delta^{17}\text{O}$, however higher than the most likely +25‰ conferred by recent observations (see Sect. 6.2.8.2). When reckoned at this value, the ozone-derived oxygen in tropospheric CO (amounts to approximately 2% in EMAC) compensates the input of the MDF sources. In any case, the key role in determining tropospheric $\Delta^{17}\text{O}(\text{CO})$ belongs to the sink effective fractionation, $\Delta^{17}\text{O}\epsilon_{\text{sink}}$. In the BL, the latter is found to correlate tightly with the $^{13}\text{C}\epsilon_{\text{sink}}$ and $^{18}\text{O}\epsilon_{\text{sink}}$; inferred in EMAC, this correspondence importantly allows estimating the $\delta^{13}\text{C}/\delta^{18}\text{O}$ of the actual CO source at a given location, provided that $\Delta^{17}\text{O}(\text{CO})$ is observed concomitantly. That such estimate will be rather accurate is attested by the well matching simulated and observed $\Delta^{17}\text{O}(\text{CO})$, which also points at a good representation of the relevant processes in EMAC. Subsidiary sensitivity studies on the effective sink fractionations (“ZERO” setups) witness their complex and variable character, foremost due to the comparable timescales of the photochemical and transport/mixing processes altering CO, and uneven distribu-

tion of the sink KIE magnitude in the troposphere. This, for instance, limits the conventional isotope-reservoir kinetic models in predicting the averages of ϵ_{sink} (hence the overall isotope composition of CO) in a given atmospheric domain. Employing a full-fledged AC-GCM like EMAC is therefore adamant for studying CO isotopes, as exemplified by the approach to infer the sensitivity of $\Delta^{17}\text{O}(\text{CO})$ to the changes in CO, CH_4 and OH abundances (see Sect. 6.2.5.3). Thus, it is shown that equal in amount, but dissimilarly distributed in the troposphere perturbations to these species may result in utterly different responses in $\Delta^{17}\text{O}(\text{CO})$, that uniquely correlate with local and global changes in [OH], particularly at high latitudes. The MIF in CO, advantageous for the univocal correspondence between the $\Delta^{17}\text{O}(\text{CO})$ and [OH] alterations, may involve complicacies in application, owing to the low sensitivities found in the present study; further inquiries, *e.g.* probing more drastic changes to the tropospheric OH abundance, may reveal this is not the case, however.

We conclude with essential recommendations and suggestions for future research that arose in the course of the present study. These are:

- A laboratory investigation into the anticipated temperature effects in the KIEs escorting the reaction of CO and OH is necessary, at the least, for the high-pressure regimes (above 100 hPa). A further inquiry into the hitherto unexplained effect of bathing gas on the low-pressure KIEs is advisable, rather supported by an advanced theoretical study (see details in Sect. 3.4.4). Elucidating these aspects should provide new insights into the mechanism of the isotope effect escorting this most studied gas-phase reaction.
- The most certain BL CO isotope compositions simulated in EMAC are found in central and east Polynesia, particularly in February–March, when the largest photochemical component of the CO inventory is expected. An opportune measurement of the background CO isotope composition in this region is thus recommended in order to quantify the CH_4 input to CO (estimated to be 26–30 ppb contrasting the surface component below 10 ppb) and perform the most accurate verification of the $\text{CH}_4 \rightarrow \text{CO}$ isotope chemistry specifics. A highly desirable concomitant measurement of the isotope composition of formaldehyde (whose inventory is expected to bear more than 95% of CH_4 -derived carbon) should provide an in-depth information on the photochemical yield and the isotope signatures of CO derived from methane.
- Further modelling studies with EMAC are to be devoted to $\delta^{18}\text{O}(\text{CO})$, which merely requires an extra elaboration of the $^{18}\text{O}/^{16}\text{O}$ -inclusive emission setup. Simulating C^{18}O should provide additional insight into the applied emissions (*e.g.*, whether the anthropogenic or biomass-burning CO is missing over East Asia), quantify the influence of the O_3 input on the $\delta^{18}\text{O}$ -inclusive estimates of the CO turnover, and, supplemented with additional diagnostic, provide the most comprehensive estimate of the tropospheric $\delta^{18}\text{O}(\text{CO})$. Regrettably, the most recent modelling study on this subject by Park^[2010] appears inadequate, owing to the tolerated oversimplifications, in particular, neglecting the seasonal variations in the effective sink fractionation of CO. The results on $^{18}\text{O}\epsilon_{\text{sink}}$ obtained with EMAC in the present study (see Sect. 6.2.5) suggest this is an erroneous approach.
- Applying the mixing model approach (Keeling-plot) is only practicable in the cases when variations in the mixing ratio and δ -values assuredly pertain to the admixing of a source with an invariable background reservoir. As the latter for CO demonstrates pronounced seasonal mixing and isotope ratio variations, regarding the data exclusively from a given month or, in special occasions, season, in the Keeling-plot is necessary. Data from the periods when the background effective sink fractionation is expected to change rapidly (*e.g.*, May–July for the ETNH C^{18}O) should be considered with particular care. Employing the Keeling-plot approach for the annual variations in CO is likely impracticable, as seen for ^{13}CO . This remark is valid for all tracers whose background isotope compositions exhibit a distinct seasonality.
- As mentioned in Sect. 6.1.1.2 (p. 144), the hypothesis on the large variations in the observed ETSH $\delta^{13}\text{C}(\text{CH}_4)$ resulting from the additional sink of methane in reactions with chlorine radicals is not supported by the concomitant $\delta^{13}\text{C}(\text{CO})$ observations. A modelling study following that of Allan *et al.*^[2007], however including the isotopes of CO, has yet to corroborate this inference firmly.
- Some shortcomings diagnosed in EMAC require further clarification. First, markedly smooth gradients of the CO isotope ratios as a function of the concomitant mixing ratios are notable in comparison with observational data. As this artefact extends in the vertical direction, it was surmised to ensue from over-mixing occurring in the model convective transport (see Sect. 6.2.7.3 for details). The

more specific arguments for that, however, are to be brought forward, as well as a more thorough evaluation of the impact of convective transport on the efficiency of the dry deposition processes (see above, p. 219, also Sect. 6.2.2.1). Secondly, comparisons of the simulated and observed $[\text{CO}]$, $\delta^{13}\text{C}(\text{CO})$ and $\Delta^{17}\text{O}(\text{CO})$ witness a missing CO sink, hence likely underestimated OH, in the summertime NH. That the problem pertains not to the flaws of the VOCs oxidation scheme in EMAC (see Taraborrelli *et al.*^[2012]) is indicated by the discrepancies seen at high latitudes and in the UTLS (CARIBIC data), where another process favouring OH regeneration likely should exist.

- Of all atmospheric CO aspects, the least covered in the modelling studies and challenging for future research are those pertaining to the cryosphere. Shown by Haan *et al.*^[2001], photochemical production of CO occurs in snow, with anticipated implications for regional budgets. A case in point is the Arctic, where CO precursors likely accumulate in deposited snow during the winter “arctic haze” conditions, to be later on broken down to CO in spring. A rough estimate by Haan *et al.*^[2001] equates the interim influx of CO from snow into the atmosphere with that of the methane oxidation term, which is capable of affecting the seasonal dynamics of $[\text{CO}]$ at high latitudes. Another issue is the CO production in and emission from the oceans modulated by the biochemical and sea-ice dynamics. An extensive study on this complex subject is given by Tran *et al.*^[2013], who infer the sea-air fluxes of CO in the Atlantic exceeding previous estimates, and highest $[\text{CO}]$ in the ice-covered surface polar waters. Trapped CO discharges into the atmosphere with breaking ice, thus embodying another seasonal emission event in the Arctic (S. Tran, pers. comm., 2011). The importance of both, snow and ice aspects, for the atmospheric carbon monoxide at high latitudes has yet to be assessed, preferably employing an AC-GCM representing relevant processes. Rather sophisticated parameterisations of the latter are foreseen, however, the EMAC model offers highly flexible complexity to uphold their implementation.

Appendix A. Chemical mechanism of MECCA

The following tables present the chemical mechanism, that is a list of species and reactions included in the setup of the kinetic chemistry submodel MECCA employed in this study. Listed “mechanism” comprises 95 species (Table A.3, excluding isotope tagging/doubling tracers) participating in total of 183 gas-phase and 55 photolysis reactions enumerated in Tables A.1 and A.2, respectively.¹⁵² Note, the oxygen isotope exchange reactions reviewed in Sect. 3.3.3 (Table Table 3.1, p. 38) are not referenced here. The detailed mechanism may be obtained by choosing the reaction subset identified with the expression ‘(Tr || St) && G) && !Br && !I && !Hg && !Het’ in the setup routines to MECCA. Further information on MECCA can be found in Sander *et al.*^[2005] Sander *et al.*^[2011] and under <http://www.rolf-sander.net/messy/mecca>. The graphical representation of the C and O isotope composition exchange in the current mechanism is given in Appendix B (p. 239).

Table A.1 Gas Phase Reactions

Abbr.	Label ^a	Reaction / Isotope transfer ^b	Rate Coefficient ^c	Reference ^d
O chemistry				
G1000	StTrG	$O_2 + O(^1D) \rightarrow O(^3P) + O_2$	$3.3 \cdot 10^{-11} \exp(55/T)$	Sander et al. (2006)
G1001	StTrG	$O_2 + O(^3P) \rightarrow O_3$	$6 \cdot 10^{-34} \times ((T/300)^{-2.4}) \cdot C_{air}$	Sander et al. (2006)
G1002	StG	$O_3 + O(^1D) \rightarrow 2 O_2$	$1.2 \cdot 10^{-10}$	Sander et al. (2006)*
G1003	StG	$O_3 + O(^3P) \rightarrow 2 O_2$	$8 \cdot 10^{-12} \exp(-2060/T)$	Sander et al. (2006)
H+O chemistry				
G2100	StTrG	$H + O_2 \rightarrow HO_2$	$k_{3rd}(T, C_{air}, 4.4 \cdot 10^{-32}, 1.3, 4.7 \cdot 10^{-11}, 0.2, 0.6)$	Sander et al. (2006)
G2101	StG	$H + O_3 \rightarrow OH + O_2$	$1.4 \cdot 10^{-10} \exp(-470/T)$	Sander et al. (2006)
G2102	StG	$H_2 + O(^1D) \rightarrow H + OH$	$1.1 \cdot 10^{-10}$	Sander et al. (2006)
G2103	StG	$OH + O(^3P) \rightarrow H + O_2$	$2.2 \cdot 10^{-11} \exp(120/T)$	Sander et al. (2006)
G2104	StTrG	$OH + O_3 \rightarrow HO_2 + O_2$ ¹ O: $OH \rightarrow 0.5 HO_2$ ¹ O: $O_3 \rightarrow 0.5 HO_2 + O_2$	$1.7 \cdot 10^{-12} \exp(-940/T)$	Sander et al. (2006)
G2105	StTrG	$OH + H_2 \rightarrow H_2O + H$	$2.8 \cdot 10^{-12} \exp(-1800/T)$	Sander et al. (2006)
G2106	StG	$HO_2 + O(^3P) \rightarrow OH + O_2$ ¹ O: $HO_2 \rightarrow OH + 0.5 O_2$ ¹ O: $O(^3P) \rightarrow 0.5 O_2$	$3 \cdot 10^{-11} \exp(200/T)$	Sander et al. (2006)
G2107	StTrG	$HO_2 + O_3 \rightarrow OH + 2 O_2$ ¹ O: $HO_2 \rightarrow OH + 0.25 O_2$ ¹ O: $O_3 \rightarrow 0.75 O_2$	$1 \cdot 10^{-14} \exp(-490/T)$	Sander et al. (2006)
G2108a	StG	$HO_2 + H \rightarrow 2 OH$	$7.2 \cdot 10^{-11}$	Sander et al. (2006)
G2108b	StG	$HO_2 + H \rightarrow H_2 + O_2$	$6.9 \cdot 10^{-12}$	Sander et al. (2006)
G2108c	StG	$HO_2 + H \rightarrow O(^3P) + H_2O$	$1.6 \cdot 10^{-12}$	Sander et al. (2006)
G2109	StTrG	$HO_2 + OH \rightarrow H_2O + O_2$ ¹ O: $OH \rightarrow H_2O$ ¹ O: $HO_2 \rightarrow O_2$	$4.8 \cdot 10^{-11} \exp(250/T)$	Sander et al. (2006)
G2110	StTrG	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_{HO_2:HO_2}$	Christensen et al. (2002), Kircher and Sander (1984)*
G2111	StTrG	$H_2O + O(^1D) \rightarrow 2 OH$	$1.63 \cdot 10^{-10} \exp(60/T)$	Sander et al. (2006)
G2112	StTrG	$H_2O_2 + OH \rightarrow H_2O + HO_2$ ¹ O: $OH \rightarrow H_2O$ ¹ O: $H_2O_2 \rightarrow HO_2$	$1.8 \cdot 10^{-12}$	Sander et al. (2006)
N+O chemistry				
G3100	StGN	$N + O_2 \rightarrow NO + O(^3P)$	$1.5 \cdot 10^{-11} \exp(-3600/T)$	Sander et al. (2006)
G3101	StTrG	$N_2 + O(^1D) \rightarrow O(^3P) + N_2$	$2.15 \cdot 10^{-11} \exp(110/T)$	Sander et al. (2006)
G3102a	StGN	$N_2O + O(^1D) \rightarrow 2 NO$	$6.7 \cdot 10^{-11} \exp(20/T)$	Sander et al. (2006)
G3102b	StGN	$N_2O + O(^1D) \rightarrow N_2 + O_2$	$4.7 \cdot 10^{-11} \exp(20/T)$	Sander et al. (2006)
G3103	StTrGN	$NO + O_3 \rightarrow NO_2 + O_2$ ¹ O: $O_3 \rightarrow O_2 + 0.5 NO_2$ ¹ O: $NO \rightarrow 0.5 NO_2$	$3 \cdot 10^{-12} \exp(-1500/T)$	Sander et al. (2006)

¹⁵²Reactions and species set, labels, abbreviations and species names listed here are actual for MECCA version 2.5 and KPP version 2.2.1_rs3 (February 2010).

Table A.1 Gas Phase Reactions

Abbr.	Label ^a	Reaction / Isotope transfer ^b	Rate Coefficient ^c	Reference ^d
G3104	StGN	$\text{NO} + \text{N} \rightarrow \text{O}(^3\text{P}) + \text{N}_2$	$2.1 \cdot 10^{-11} \times \exp(100/T)$	Sander et al. (2006)
G3105	StGN	$\text{NO}_2 + \text{O}(^3\text{P}) \rightarrow \text{NO} + \text{O}_2$ $^1\text{O}: \text{NO}_2 \rightarrow \text{NO} + 0.5 \text{O}_2$ $^1\text{O}: \text{O}(^3\text{P}) \rightarrow 0.5 \text{O}_2$	$5.1 \cdot 10^{-12} \times \exp(210/T)$	Sander et al. (2006)
G3106	StTrGN	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ $^1\text{O}: \text{NO}_2 \rightarrow ^2/3 \text{NO}_3$ $^1\text{O}: \text{O}_3 \rightarrow ^1/3 \text{NO}_3 + \text{O}_2$	$1.2 \cdot 10^{-13} \times \exp(-2450/T)$	Sander et al. (2006)
G3107	StGN	$\text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} + \text{O}(^3\text{P})$	$5.8 \cdot 10^{-12} \times \exp(220/T)$	Sander et al. (2006)
G3108	StTrGN	$\text{NO}_3 + \text{NO} \rightarrow 2 \text{NO}_2$	$1.5 \cdot 10^{-11} \times \exp(170/T)$	Sander et al. (2006)
G3109	StTrGN	$\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$	$k_{\text{NO}_3\text{NO}_2}$	Sander et al. (2006)*
N + H chemistry				
G3110	StTrGN	$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$	$k_{\text{NO}_3\text{NO}_2}/(2.7 \cdot 10^{-27} \times \exp(11000/T))$	Sander et al. (2006)*
G3200	TrGN	$\text{NO} + \text{OH} \rightarrow \text{HONO}$	$k_{3\text{rd}}(T, C_{\text{air}}, 7.0 \cdot 10^{-31}, 2.6, 3.6 \cdot 10^{-11}, 0.1, 0.6)$	Sander et al. (2006)
G3201	StTrGN	$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ $^1\text{O}: \text{NO} \rightarrow 0.5 \text{NO}_2$ $^1\text{O}: \text{HO}_2 \rightarrow 0.5 \text{NO}_2 + \text{OH}$	$3.5 \cdot 10^{-12} \times \exp(250/T)$	Sander et al. (2006)
G3202	StTrGN	$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	$k_{3\text{rd}}(T, C_{\text{air}}, 1.8 \cdot 10^{-30}, 3.0, 2.8 \cdot 10^{-11}, 0.0, 6)$	Sander et al. (2006)
G3203	StTrGN	$\text{NO}_2 + \text{HO}_2 \rightarrow \text{HNO}_4$	$k_{\text{NO}_2\text{HO}_2}$	Sander et al. (2006)*
G3204	TrGN	$\text{NO}_3 + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} + \text{O}_2$ $^1\text{O}: \text{NO}_3 \rightarrow \text{NO}_2 + \text{OH}$ $^1\text{O}: \text{HO}_2 \rightarrow \text{O}_2$	$3.5 \cdot 10^{-12}$	Sander et al. (2006)
G3205	TrGN	$\text{HONO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$ $^1\text{O}: \text{HONO} \rightarrow \text{NO}_2$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$	$1.8 \cdot 10^{-11} \times \exp(-390/T)$	Sander et al. (2006)
G3206	StTrGN	$\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3$ $^1\text{O}: \text{HNO}_3 \rightarrow \text{NO}_3$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$	$k_{\text{HNO}_3\text{OH}}$	Sander et al. (2006)*
G3207	StTrGN	$\text{HNO}_4 \rightarrow \text{NO}_2 + \text{HO}_2$	$k_{\text{NO}_2\text{HO}_2}/(2.1 \cdot 10^{-27} \times \exp(10900/T))$	Sander et al. (2006)*
G3208	StTrGN	$\text{HNO}_4 + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$ $^1\text{O}: \text{HNO}_4 \rightarrow \text{NO}_2 + \text{O}_2$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$	$1.3 \cdot 10^{-12} \times \exp(380/T)$	Sander et al. (2006)
G3209	TrGN	$\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}$	$1.7 \cdot 10^{-12} \times \exp(-710/T)$	Kohlmann and Poppe (1999)
G3210	TrGN	$\text{NH}_2 + \text{O}_3 \rightarrow \text{NH}_2\text{O} + \text{O}_2$	$4.3 \cdot 10^{-12} \times \exp(-930/T)$	Kohlmann and Poppe (1999)
G3211	TrGN	$\text{NH}_2 + \text{HO}_2 \rightarrow \text{NH}_2\text{O} + \text{OH}$	$4.8 \cdot 10^{-07} \times \exp(-628/T) \cdot T^{-1.32}$	Kohlmann and Poppe (1999)
G3212	TrGN	$\text{NH}_2 + \text{HO}_2 \rightarrow \text{HNO} + \text{H}_2\text{O}$	$9.4 \cdot 10^{-09} \times \exp(-356/T) \cdot T^{-1.12}$	Kohlmann and Poppe (1999)
G3213	TrGN	$\text{NH}_2 + \text{NO} \rightarrow \text{HO}_2 + \text{OH} + \text{N}_2$ $^1\text{O}: \text{NO} \rightarrow \text{OH}$ $^1\text{O}: \text{O}_2 \rightarrow \text{HO}_2$	$1.92 \cdot 10^{-12} \times (T/298)^{-1.5}$	Kohlmann and Poppe (1999)
G3214	TrGN	$\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}$	$1.41 \cdot 10^{-11} \times (T/298)^{-1.5}$	Kohlmann and Poppe (1999)
G3215	TrGN	$\text{NH}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$	$1.2 \cdot 10^{-11} \times (T/298)^{-2.0}$	Kohlmann and Poppe (1999)
G3216	TrGN	$\text{NH}_2 + \text{NO}_2 \rightarrow \text{NH}_2\text{O} + \text{NO}$	$0.8 \cdot 10^{-11} \times (T/298)^{-2.0}$	Kohlmann and Poppe (1999)
G3217	TrGN	$\text{NH}_2\text{O} + \text{O}_3 \rightarrow \text{NH}_2 + \text{O}_2$ $^1\text{O}: \text{NH}_2\text{O} \rightarrow \text{O}_2$ $^1\text{O}: \text{O}_3 \rightarrow \text{O}_2$	$1.2 \cdot 10^{-14}$	Kohlmann and Poppe (1999)
G3218	TrGN	$\text{NH}_2\text{O} \rightarrow \text{NHOH}$	$1.3 \cdot 10^3$	Kohlmann and Poppe (1999)
G3219	TrGN	$\text{HNO} + \text{OH} \rightarrow \text{NO} + \text{H}_2\text{O}$ $^1\text{O}: \text{HNO} \rightarrow \text{NO}$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$	$8.0 \cdot 10^{-11} \times \exp(-500/T)$	Kohlmann and Poppe (1999)
G3220	TrGN	$\text{HNO} + \text{NHOH} \rightarrow \text{NH}_2\text{OH} + \text{NO}$ $^1\text{O}: \text{NO} \rightarrow \text{OH}$ $^1\text{O}: \text{NO} \rightarrow \text{OH}$	$1.66 \cdot 10^{-12} \times \exp(-1500/T)$	Kohlmann and Poppe (1999)
G3221	TrGN	$\text{HNO} + \text{NO}_2 \rightarrow \text{HONO} + \text{NO}$ $^1\text{O}: \text{HNO} \rightarrow \text{NO}$ $^1\text{O}: \text{NO}_2 \rightarrow \text{HONO}$	$1.0 \cdot 10^{-12} \times \exp(-1000/T)$	Kohlmann and Poppe (1999)
G3222	TrGN	$\text{NHOH} + \text{OH} \rightarrow \text{HNO} + \text{H}_2\text{O}$ $^1\text{O}: \text{NHOH} \rightarrow \text{HNO}$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$	$1.66 \cdot 10^{-12}$	Kohlmann and Poppe (1999)
G3223	TrGN	$\text{NH}_2\text{OH} + \text{OH} \rightarrow \text{NHOH} + \text{H}_2\text{O}$ $^1\text{O}: \text{NH}_2\text{OH} \rightarrow \text{NHOH}$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$	$4.13 \cdot 10^{-11} \times \exp(-2138/T)$	Kohlmann and Poppe (1999)

Table A.1 Gas Phase Reactions

Abbr.	Label ^a	Reaction / Isotope transfer ^b	Rate Coefficient ^c	Reference ^d
G3224	TrGN	$\text{HNO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{NO}$ $^1\text{O}: \text{HNO} \rightarrow \text{NO}$ $^1\text{O}: \text{O}_2 \rightarrow \text{HO}_2$	$3.65 \cdot 10^{-14} \times \exp(-4600/T)$	Kohlmann and Poppe (1999)
C₁ chemistry				
G4100	StG	$\text{CH}_4 + \text{O}(^1\text{D}) \rightarrow 0.75 \text{CH}_3\text{O}_2 + 0.75 \text{OH} + 0.25 \text{HCHO} + 0.4 \text{H} + 0.05 \text{H}_2$ $^1\text{O}: \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$ $^1\text{O}: \text{O}(^1\text{D}) \rightarrow \text{OH} + \text{HCHO}$	$1.5 \cdot 10^{-10}$	Sander et al. (2006)
G4101	StTrG	$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$ $^1\text{O}: \text{O}_2 \rightarrow \text{CH}_3\text{O}_2$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$	$1.85 \cdot 10^{-20} \times \exp(2.82 \cdot \log(T) - 987/T)$	Atkinson (2003)*
G4102	TrG	$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{HCHO} + \text{HO}_2$	$2.9 \cdot 10^{-12} \times \exp(-345/T)$	Sander et al. (2006)
G4103	StTrG	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{OOH} + \text{O}_2$	$4.1 \cdot 10^{-13} \times \exp(750/T)$	Sander et al. (2006)*
G4104	StTrGN	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{HCHO} + \text{NO}_2 + \text{HO}_2$ $^1\text{O}: \text{CH}_3\text{O}_2 \rightarrow 0.5 \text{NO}_2 + \text{HCHO}$ $^1\text{O}: \text{NO} \rightarrow 0.5 \text{NO}_2$ $^1\text{O}: \text{O}_2 \rightarrow \text{HO}_2$	$2.8 \cdot 10^{-12} \times \exp(300/T)$	Sander et al. (2006)
G4105	TrGN	$\text{CH}_3\text{O}_2 + \text{NO}_3 \rightarrow \text{HCHO} + \text{HO}_2 + \text{NO}_2$ $^1\text{O}: \text{CH}_3\text{O}_2 \rightarrow 0.5 \text{NO}_2 + \text{HCHO}$ $^1\text{O}: \text{NO}_3 \rightarrow 0.5 \text{NO}_2 + \text{HO}_2$	$1.3 \cdot 10^{-12}$	Atkinson et al. (1999)
G4106a	StTrG	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 2 \text{HCHO} + 2 \text{HO}_2$	$9.5 \cdot 10^{-14} \times \exp(390/T) / (1 + 1/26.2 \times \exp(1130/T))$	Sander et al. (2006)
G4106b	StTrG	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{OH} + \text{O}_2$	$9.5 \cdot 10^{-14} \times \exp(390/T) / (1 + 26.2 \times \exp(-1130/T))$	Sander et al. (2006)
G4107	StTrG	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow 0.7 \text{CH}_3\text{O}_2 + 0.3 \text{HCHO} + 0.3 \text{OH} + \text{H}_2\text{O}$ $^1\text{O}: \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O}_2 + \text{HCHO} + \text{OH}$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$	$k_{\text{CH}_3\text{OOH}+\text{OH}}$	Sander et al. (2006)*
G4108	StTrG	$\text{HCHO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O} + \text{HO}_2$ $^1\text{O}: \text{HCHO} \rightarrow \text{CO}$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$ $^1\text{O}: \text{O}_2 \rightarrow \text{HO}_2$	$9.52 \cdot 10^{-18} \times \exp(2.03 \cdot \log(T) + 636/T)$	Sivakumaran et al. (2003)
G4109	TrGN	$\text{HCHO} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{CO} + \text{HO}_2$	$3.4 \cdot 10^{-13} \times \exp(-1900/T)$	Sander et al. (2006)*
G4110	StTrG	$\text{CO} + \text{OH} \rightarrow \text{H} + \text{CO}_2$	$1.57 \cdot 10^{-13} + C_{\text{air}} \cdot 3.54 \cdot 10^{-33}$	McCabe et al. (2001)
G4111	TrG	$\text{HCOOH} + \text{OH} \rightarrow \text{HO}_2$	$4.0 \cdot 10^{-13}$	Sander et al. (2006)
C₂ chemistry				
G4200	TrGC	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{EtO}_2 + \text{H}_2\text{O}$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$ $^1\text{O}: \text{O}_2 \rightarrow \text{EtO}_2$	$1.49 \cdot 10^{-17} \times T^2 \times \exp(-499/T)$	Atkinson (2003)
G4201	TrGC	$\text{C}_2\text{H}_6 + \text{O}_3 \rightarrow \text{HCHO} + 0.22 \text{HO}_2 + 0.12 \text{OH} + 0.23 \text{CO} + 0.54 \text{HCOOH} + 0.1 \text{H}_2$ $^1\text{O}: \text{O}_3 \rightarrow \text{HCHO} + \text{OH} + \text{CO} + 0.5 \text{HCOOH} + \text{CO}_2 + 0.5 \text{H}_2\text{O}_2$ $^1\text{O}: \text{O}_2 \rightarrow \text{HO}_2$ $^1\text{O}: \text{H}_2\text{O} \rightarrow 0.5 \text{HCOOH} + 0.5 \text{H}_2\text{O}_2$	$1.2 \cdot 10^{-14} \times \exp(-2630/T)$	Sander et al. (2006)*
G4202	TrGC	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \frac{2}{3} \text{C}_3\text{H}_6\text{O}_2$ $^1\text{O}: \text{O}_2 \rightarrow \text{C}_3\text{H}_6\text{O}_2$	$k_{3rd}(T, C_{\text{air}}, 1.0 \cdot 10^{-28}, 4.5, 8.8 \cdot 10^{-12}, 0.85, 0.6)$	Sander et al. (2006)
G4203	TrGC	$\text{EtO}_2 + \text{HO}_2 \rightarrow \text{EtOOH}$ $^1\text{O}: \text{EtO}_2 \rightarrow \text{EtOOH}$ $^1\text{O}: \text{HO}_2 \rightarrow \text{O}_2$	$7.5 \cdot 10^{-13} \times \exp(700/T)$	Sander et al. (2006)
G4204	TrGNC	$\text{EtO}_2 + \text{NO} \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 + \text{NO}_2$ $^1\text{O}: \text{EtO}_2 \rightarrow 0.5 \text{NO}_2 + \text{CH}_3\text{CHO}$ $^1\text{O}: \text{NO} \rightarrow 0.5 \text{NO}_2$ $^1\text{O}: \text{O}_2 \rightarrow \text{HO}_2$	$2.6 \cdot 10^{-12} \times \exp(365/T)$	Sander et al. (2006)
G4205	TrGNC	$\text{EtO}_2 + \text{NO}_3 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 + \text{NO}_2$ $^1\text{O}: \text{EtO}_2 \rightarrow \text{CH}_3\text{CHO} + 0.5 \text{O}_2$ $^1\text{O}: \text{NO}_3 \rightarrow \text{NO}_2 + 0.5 \text{O}_2$ $^1\text{O}: \text{O}_2 \rightarrow \text{HO}_2$	$2.3 \cdot 10^{-12}$	Atkinson et al. (1999)
G4206	TrGC	$\text{EtO}_2 + \text{CH}_3\text{O}_2 \rightarrow 0.75 \text{HCHO} + \text{HO}_2 + 0.75 \text{CH}_3\text{CHO} + 0.25 \text{CH}_3\text{OH}$ $^1\text{O}: \text{EtO}_2 \rightarrow \text{CH}_3\text{CHO} + 0.5 \text{O}_2$ $^1\text{O}: \text{CH}_3\text{O}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{OH} + 0.5 \text{O}_2$ $^1\text{O}: \text{O}_2 \rightarrow \text{HO}_2$ $^1\text{C}: \text{EtO}_2 \rightarrow \text{CH}_3\text{CHO}$ $^1\text{C}: \text{CH}_3\text{O}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{OH}$	$1.6 \cdot 10^{-13} \times \exp(195/T)$	see notes
G4207	TrGC	$\text{EtOOH} + \text{OH} \rightarrow 0.3 \text{EtO}_2 + 0.7 \text{CH}_3\text{CHO} + 0.7 \text{OH}$ $^1\text{O}: \text{EtOOH} \rightarrow \text{EtO}_2 + \text{CH}_3\text{CHO} + \text{OH}$ $^1\text{O}: \text{OH} \rightarrow \text{H}_2\text{O}$	$k_{\text{CH}_3\text{OOH}+\text{OH}}$	see notes

Table A.1 Gas Phase Reactions

Abbr.	Label ^a	Reaction / Isotope transfer ^b	Rate Coefficient ^c	Reference ^d
G4208	TrGC	CH ₃ CHO + OH → PA + H ₂ O ¹ O: OH → H ₂ O ¹ O: CH ₃ CHO → ¹ / ₃ PA ¹ O: O ₂ → ² / ₃ PA	4.4·10 ⁻¹² ·exp(365/T)	Atkinson et al. (2006)
G4209	TrGNC	CH ₃ CHO + NO ₃ → PA + HNO ₃ ¹ O: NO ₃ → HNO ₃ ¹ O: CH ₃ CHO → ¹ / ₃ PA ¹ O: O ₂ → ² / ₃ PA	1.4·10 ⁻¹² ·exp(-1900/T)	Sander et al. (2006)
G4210	TrGC	CH ₃ COOH + OH → CH ₃ O ₂ + CO ₂ + H ₂ O ¹ O: CH ₃ COOH → CO ₂ ¹ O: OH → H ₂ O ¹ O: O ₂ → CH ₃ O ₂	4.2·10 ⁻¹⁴ ·exp(855/T)	Atkinson et al. (2006)
G4211a	TrGC	PA + HO ₂ → PAA ¹ O: PA → PAA ¹ O: HO ₂ → O ₂	4.3·10 ⁻¹³ ·exp(1040/T)/(1+1/37·exp(660/T))	Tyndall et al. (2001)
G4211b	TrGC	PA + HO ₂ → CH ₃ COOH + O ₃ ¹ O: HO ₂ → ² / ₃ O ₃ ¹ O: PA → ¹ / ₃ O ₃ + CH ₃ COOH	4.3·10 ⁻¹³ ·exp(1040/T)/(1+37·exp(-660/T))	Tyndall et al. (2001)
G4212	TrGNC	PA + NO → CH ₃ O ₂ + NO ₂ ¹ O: PA → 0.5 NO ₂ + CO ₂ ¹ O: NO → 0.5 NO ₂ ¹ O: O ₂ → CH ₃ O ₂	8.1·10 ⁻¹² ·exp(270/T)	Tyndall et al. (2001)
G4213	TrGNC	PA + NO ₂ → PAN	kPAN _{O₂}	Sander et al. (2006)
G4214	TrGNC	PA + NO ₃ → CH ₃ O ₂ + NO ₂ ¹ O: PA → CO ₂ + 0.5 O ₂ ¹ O: NO ₃ → NO ₂ + 0.5 O ₂ ¹ O: O ₂ → CH ₃ O ₂	4·10 ⁻¹²	Canosa-Mas et al. (1996)
G4215a	TrGC	PA + CH ₃ O ₂ → HCHO + HO ₂ + CH ₃ O ₂ + CO ₂ ¹ O: PA → CO ₂ ¹ O: CH ₃ O ₂ → HCHO ¹ O: O ₂ → CH ₃ O ₂ + HO ₂ ¹ C: PA → CH ₃ O ₂ + CO ₂ ¹ C: CH ₃ O ₂ → HCHO	0.9·2·10 ⁻¹² ·exp(500/T)	Sander et al. (2006)
G4215b	TrGC	PA + CH ₃ O ₂ → CH ₃ COOH + HCHO ¹ O: PA → CH ₃ COOH ¹ O: CH ₃ O ₂ → HCHO ¹ C: PA → CH ₃ COOH ¹ C: CH ₃ O ₂ → HCHO	0.1·2·10 ⁻¹² ·exp(500/T)	Sander et al. (2006)
G4216	TrGC	PA + EtO ₂ → 0.82 CH ₃ O ₂ + CH ₃ CHO + 0.82 HO ₂ + 0.18 CH ₃ COOH ¹ O: PA → CH ₃ COOH + CH ₃ O ₂ + 0.5 CO ₂ ¹ O: EtO ₂ → CH ₃ CHO + 0.5 CO ₂ ¹ O: O ₂ → HO ₂ ¹ C: PA → CH ₃ COOH + CH ₃ O ₂ + CO ₂ ¹ C: EtO ₂ → CH ₃ CHO	4.9·10 ⁻¹² ·exp(211/T)	Atkinson et al. (1999), Kirchner and Stockwell (1996)*
G4217	TrGC	PA + PA → 2 CH ₃ O ₂ + 2 CO ₂ + O ₂	2.5·10 ⁻¹² ·exp(500/T)	Tyndall et al. (2001)
G4218	TrGC	PAA + OH → PA ¹ O: PAA → PA ¹ O: OH → H ₂ O	kCH ₃ OOH _{OH}	see notes
G4219	TrGNC	NACA + OH → NO ₂ + HCHO + CO ¹ O: NACA → NO ₂ + HCHO + CO ¹ O: OH → H ₂ O	5.6·10 ⁻¹² ·exp(270/T)	see notes
G4220	TrGNC	PAN + OH → HCHO + NO ₂ ¹ O: PAN → HCHO + NO ₂ + CO ¹ O: OH → H ₂ O	2·10 ⁻¹⁴	see notes
G4221	TrGNC	PAN → PA + NO ₂	kPAN _M	Sander et al. (2006)*
C₃ chemistry				
G4300	TrGC	C ₃ H ₈ + OH → 0.82 PrO ₂ + 0.18 EtO ₂ + H ₂ O ¹ O: OH → H ₂ O ¹ O: O ₂ → PrO ₂ + EtO ₂	1.65·10 ⁻¹⁷ ·T ² ·exp(-87/T)	Atkinson (2003)

Table A.1 Gas Phase Reactions

Abbr.	Label ^a	Reaction / Isotope transfer ^b	Rate Coefficient ^c	Reference ^d
G4301	TrGC	$C_3H_6 + O_3 \rightarrow 0.57 HCHO + 0.47 CH_3CHO + \frac{1}{3} OH + 0.26 HO_2 +$ $0.07 CH_3O_2 + 0.06 EtO_2 + 0.23 PA + 0.04 CH_3COCHO + 0.06 CH_4 +$ $0.31 CO + 0.22 HCOOH + 0.03 CH_3OH$ $^1O: O_3 \rightarrow HCHO + CH_3CHO + OH + 0.5 EtO_2 + \frac{1}{3} PA + 0.5 CH_3COCHO +$ $CO + 0.5 HCOOH$ $^1O: O_2 \rightarrow HO_2 + 0.5 EtO_2 + \frac{2}{3} PA + 0.5 CH_3COCHO + CH_3O_2 + CH_3OH$ $^1O: H_2O \rightarrow 0.5 HCOOH$	$6.5 \cdot 10^{-15} \exp(-1900/T)$	Sander et al. (2006)*
G4302	TrGC	$C_3H_6 + OH \rightarrow C_3H_6O_2$ $^1O: O_2 \rightarrow C_3H_6O_2$	$k_{3rd}(T, C_{air}, 8 \cdot 10^{-27}, 3.5 \cdot 3 \cdot 10^{-11}, 0, 0.5)$	Atkinson et al. (1999)
G4303	TrGNC	$C_3H_6 + NO_3 \rightarrow ONIT$	$4.6 \cdot 10^{-13} \exp(-1155/T)$	Atkinson et al. (1999)
G4304	TrGC	$PrO_2 + HO_2 \rightarrow PrOOH$ $^1O: PrO_2 \rightarrow PrOOH$ $^1O: HO_2 \rightarrow O_2$	$k_{PrO_2HO_2}$	Atkinson (1997)*
G4305	TrGNC	$PrO_2 + NO \rightarrow 0.96 CH_3COCH_3 + 0.96 HO_2 + 0.96 NO_2 + 0.04 PrONO_2$ $^1O: PrO_2 \rightarrow 0.5 NO_2 + PrONO_2 + CH_3COCH_3$ $^1O: NO \rightarrow 0.5 NO_2$ $^1O: O_2 \rightarrow HO_2$	k_{PrO_2NO}	Atkinson et al. (1999)*
G4306	TrGC	$PrO_2 + CH_3O_2 \rightarrow CH_3COCH_3 + 0.8 HCHO + 0.8 HO_2 + 0.2 CH_3OH$ $^1O: PrO_2 \rightarrow CH_3COCH_3$ $^1O: CH_3O_2 \rightarrow HCHO + CH_3OH$ $^1O: O_2 \rightarrow HO_2$ $^1C: PrO_2 \rightarrow CH_3COCH_3$ $^1C: CH_3O_2 \rightarrow HCHO + CH_3OH$	$k_{PrO_2CH_3O_2}$	Kirchner and Stockwell (1996)
G4307	TrGC	$PrOOH + OH \rightarrow 0.3 PrO_2 + 0.7 CH_3COCH_3 + 0.7 OH$ $^1O: PrOOH \rightarrow PrO_2 + CH_3COCH_3 + OH$ $^1O: OH \rightarrow H_2O$	$k_{CH_3OOH OH}$	see notes
G4308	TrGC	$C_3H_6O_2 + HO_2 \rightarrow C_3H_6OOH$ $^1O: C_3H_6O_2 \rightarrow C_3H_6OOH$ $^1O: HO_2 \rightarrow O_2$	$6.5 \cdot 10^{-13} \exp(650/T)$	Müller and Brasseur (1995)
G4309	TrGNC	$C_3H_6O_2 + NO \rightarrow 0.98 CH_3CHO + 0.98 HCHO + 0.98 HO_2 + 0.98 NO_2 +$ $0.02 ONIT$ $^1O: C_3H_6O_2 \rightarrow 0.5 NO_2 + CH_3CHO + HCHO + ONIT$ $^1O: NO \rightarrow 0.5 NO_2$ $^1O: O_2 \rightarrow HO_2$	$4.2 \cdot 10^{-12} \exp(180/T)$	Müller and Brasseur (1995)*
G4310	TrGC	$C_3H_6OOH + OH \rightarrow 0.5 C_3H_6O_2 + 0.5 ACETOL + 0.5 OH + H_2O$ $^1O: C_3H_6OOH \rightarrow C_3H_6O_2 + ACETOL + OH$ $^1O: OH \rightarrow H_2O$	$3.8 \cdot 10^{-12} \exp(200/T)$	Müller and Brasseur (1995)
G4311	TrGC	$CH_3COCH_3 + OH \rightarrow ACETO_2 + H_2O$ $^1O: CH_3COCH_3 \rightarrow \frac{1}{3} ACETO_2$ $^1O: O_2 \rightarrow \frac{2}{3} ACETO_2$ $^1O: OH \rightarrow H_2O$	$1.33 \cdot 10^{-13} + 3.82 \cdot 10^{-11} \exp(-2000/T)$	Sander et al. (2006)
G4312	TrGC	$ACETO_2 + HO_2 \rightarrow ACETP$ $^1O: ACETO_2 \rightarrow ACETP$ $^1O: HO_2 \rightarrow O_2$	$8.6 \cdot 10^{-13} \exp(700/T)$	Tyndall et al. (2001)
G4313	TrGNC	$ACETO_2 + NO \rightarrow NO_2 + PA + HCHO$ $^1O: ACETO_2 \rightarrow 0.5 NO_2 + HCHO + \frac{1}{3} PA$ $^1O: NO \rightarrow 0.5 NO_2$ $^1O: O_2 \rightarrow \frac{2}{3} PA$	$2.9 \cdot 10^{-12} \exp(300/T)$	Sander et al. (2006)
G4314	TrGC	$ACETO_2 + CH_3O_2 \rightarrow 0.5 CH_3COCHO + 0.5 CH_3OH + 0.3 PA + 0.8 HCHO +$ $0.3 HO_2 + 0.2 ACETOL$ $^1O: ACETO_2 \rightarrow CH_3COCHO + \frac{1}{3} PA + 0.3 HCHO + ACETOL$ $^1O: CH_3O_2 \rightarrow CH_3OH + 0.5 HCHO$ $^1O: O_2 \rightarrow \frac{2}{3} PA + HO_2$ $^1C: ACETO_2 \rightarrow CH_3COCHO + PA + HCHO + ACETOL$ $^1C: CH_3O_2 \rightarrow CH_3OH$	$7.5 \cdot 10^{-13} \exp(500/T)$	Tyndall et al. (2001)
G4315	TrGC	$ACETP + OH \rightarrow 0.3 ACETO_2 + 0.7 CH_3COCHO + 0.7 OH$ $^1O: ACETP \rightarrow ACETO_2 + CH_3COCHO + OH$ $^1O: OH \rightarrow H_2O$	$k_{CH_3OOH OH}$	see notes
G4316	TrGC	$ACETOL + OH \rightarrow CH_3COCHO + HO_2$ $^1O: ACETOL \rightarrow CH_3COCHO$ $^1O: O_2 \rightarrow HO_2$ $^1O: OH \rightarrow H_2O$	$2.15 \cdot 10^{-12} \exp(305/T)$	Dillon et al. (2006)

Table A.1 Gas Phase Reactions

Abbr.	Label ^a	Reaction / Isotope transfer ^b	Rate Coefficient ^c	Reference ^d
G4317	TrGC	CH ₃ COCHO + OH → PA + CO ¹ O: CH ₃ COCHO → ¹ / ₃ PA + CO ¹ O: O ₂ → ² / ₃ PA ¹ O: OH → H ₂ O	8.4·10 ⁻¹³ ·exp(830/T)	Tyndall et al. (1995)
G4318	TrGNC	MPAN + OH → ACETOL + NO ₂ ¹ O: MPAN → ACETOL + NO ₂ ¹ O: OH → H ₂ O	3.2·10 ⁻¹¹	Orlando et al. (2002)
G4319	TrGNC	MPAN → MVKO ₂ + NO ₂	kPANM	see notes
G4320	TrGNC	PrONO ₂ + OH → CH ₃ COCH ₃ + NO ₂ ¹ O: PrONO ₂ → CH ₃ COCH ₃ + NO ₂ ¹ O: OH → H ₂ O	6.2·10 ⁻¹³ ·exp(-230/T)	Atkinson et al. (1999)
C₄ chemistry				
G4400	TrGC	C ₄ H ₁₀ + OH → C ₄ H ₉ O ₂ + H ₂ O ¹ O: O ₂ → C ₄ H ₉ O ₂ ¹ O: OH → H ₂ O	1.81·10 ⁻¹⁷ ·T ² ·exp(114/T)	Atkinson (2003)
G4401	TrGC	C ₄ H ₉ O ₂ + CH ₃ O ₂ → 0.88 MEK + 0.68 HCHO + 1.23 HO ₂ + 0.12 CH ₃ CHO + 0.12 EtO ₂ + 0.18 CH ₃ OH ¹ O: C ₄ H ₉ O ₂ → MEK + CH ₃ CHO + EtO ₂ ¹ O: CH ₃ O ₂ → HCHO + CH ₃ OH ¹ O: O ₂ → HO ₂ ¹ C: C ₄ H ₉ O ₂ → MEK + CH ₃ CHO + EtO ₂ ¹ C: CH ₃ O ₂ → HCHO + CH ₃ OH	kPrO ₂ CH ₃ O ₂	see notes
G4402	TrGC	C ₄ H ₉ O ₂ + HO ₂ → C ₄ H ₉ OOH ¹ O: C ₄ H ₉ O ₂ → C ₄ H ₉ OOH ¹ O: HO ₂ → O ₂	kPrO ₂ HO ₂	see note
G4403	TrGNC	C ₄ H ₉ O ₂ + NO → 0.84 NO ₂ + 0.56 MEK + 0.56 HO ₂ + 0.28 EtO ₂ + 0.84 CH ₃ CHO + 0.16 ONIT ¹ O: C ₄ H ₉ O ₂ → 0.5 NO ₂ + MEK + CH ₃ CHO + ² / ₃ ONIT ¹ O: NO → 0.5 NO ₂ + ¹ / ₃ ONIT ¹ O: O ₂ → HO ₂ + EtO ₂	kPrO ₂ NO	see notes
G4404	TrGC	C ₄ H ₉ OOH + OH → 0.15 C ₄ H ₉ O ₂ + 0.85 MEK + 0.85 OH + 0.85 H ₂ O ¹ O: C ₄ H ₉ OOH → C ₄ H ₉ O ₂ + MEK + OH ¹ O: OH → H ₂ O	kCH ₃ OOH OH	see notes
G4405	TrGC	MVK + O ₃ → 0.45 HCOOH + 0.9 CH ₃ COCHO + 0.1 PA + 0.19 OH + 0.22 CO + 0.32 HO ₂ ¹ O: MVK → 0.5 CH ₃ COCHO + ¹ / ₃ PA ¹ O: O ₃ → 0.5 CH ₃ COCHO + 0.5 HCOOH + OH + CO ¹ O: O ₂ → HO ₂ + ² / ₃ PA ¹ O: H ₂ O → 0.5 HCOOH	0.5·(1.36·10 ⁻¹⁵ ·exp(-2112/T) + 7.51·10 ⁻¹⁶ ·exp(-1521/T))	Pöschl et al. (2000)
G4406	TrGC	MVK + OH → MVKO ₂ ¹ O: MVK → 0.25 MVKO ₂ ¹ O: OH → 0.25 MVKO ₂ ¹ O: O ₂ → 0.5 MVKO ₂	0.5·(4.1·10 ⁻¹² ·exp(452/T) + 1.9·10 ⁻¹¹ ·exp(175/T))	Pöschl et al. (2000)
G4407	TrGC	MVKO ₂ + HO ₂ → MVKOOH ¹ O: MVKO ₂ → MVKOOH ¹ O: HO ₂ → O ₂	1.82·10 ⁻¹³ ·exp(1300/T)	Pöschl et al. (2000)
G4408	TrGNC	MVKO ₂ + NO → NO ₂ + 0.25 PA + 0.25 ACETOL + 0.75 HCHO + 0.25 CO + 0.75 HO ₂ + 0.5 CH ₃ COCHO ¹ O: MVKO ₂ → 0.5 NO ₂ + ¹ / ₃ PA + ACETOL + HCHO + CO + CH ₃ COCHO ¹ O: NO → 0.5 NO ₂ ¹ O: O ₂ → HO ₂ + ² / ₃ PA	2.54·10 ⁻¹² ·exp(360/T)	Pöschl et al. (2000)
G4409	TrGNC	MVKO ₂ + NO ₂ → MPAN ¹ O: MVKO ₂ → 0.8 MPAN ¹ O: NO ₂ → 0.2 MPAN	0.25·k _{3rd} (T, C _{air} , 9.7·10 ⁻²⁹ , 5.6, 9.3·10 ⁻¹² , 1.5, 0.6)	Pöschl et al. (2000)*
G4410	TrGC	MVKO ₂ + CH ₃ O ₂ → 0.5 CH ₃ COCHO + 0.375 ACETOL + 0.125 PA + 1.125 HCHO + 0.875 HO ₂ + 0.125 CO + 0.25 CH ₃ OH ¹ O: MVKO ₂ → CH ₃ COCHO + ACETOL + ¹ / ₃ PA + 0.778 HCHO + CO ¹ O: CH ₃ O ₂ → 0.222 HCHO + CH ₃ OH ¹ O: O ₂ → ² / ₃ PA + HO ₂ ¹ C: MVKO ₂ → CH ₃ COCHO + ACETOL + PA + 0.778 HCHO + CO ¹ C: CH ₃ O ₂ → 0.222 HCHO + CH ₃ OH	2·10 ⁻¹²	von Kuhlmann (2001)
G4411	TrGC	MVKO ₂ + MVKO ₂ → ACETOL + CH ₃ COCHO + 0.5 CO + 0.5 HCHO + HO ₂	2·10 ⁻¹²	Pöschl et al. (2000)

Table A.1 Gas Phase Reactions

Abbr.	Label ^a	Reaction / Isotope transfer ^b	Rate Coefficient ^c	Reference ^d
G4412	TrGC	MVKOOH + OH → MVK ₂ ¹ O: MVKOOH → MVK ₂ ¹ O: OH → H ₂ O	3·10 ⁻¹¹	Pöschl et al. (2000)
G4413	TrGC	MEK + OH → MEK ₂ ¹ O: MEK → ¹ / ₃ MEK ₂ ¹ O: OH → H ₂ O ¹ O: O ₂ → ² / ₃ MEK ₂	1.3·10 ⁻¹² ·exp(-25/T)	Atkinson et al. (1999)
G4414	TrGC	MEK ₂ + HO ₂ → MEKOOH ¹ O: MEK ₂ → MEKOOH ¹ O: HO ₂ → O ₂	kPrO ₂ HO ₂	see notes
G4415	TrGNC	MEK ₂ + NO → 0.985 CH ₃ CHO + 0.985 PA + 0.985 NO ₂ + 0.015 ONIT ¹ O: MEK ₂ → 0.5 NO ₂ + CH ₃ CHO + ¹ / ₃ PA + 0.75 ONIT ¹ O: NO → 0.5 NO ₂ + 0.25 ONIT ¹ O: O ₂ → ² / ₃ PA	kPrO ₂ NO	see notes
G4416	TrGC	MEKOOH + OH → 0.8 MeCOCO + 0.8 OH + 0.2 MEK ₂ ¹ O: MEKOOH → MeCOCO + MEK ₂ + OH ¹ O: OH → H ₂ O	kCH ₃ OOH ₂ OH	see notes
G4417	TrGNC	ONIT + OH → MEK + NO ₂ + H ₂ O ¹ O: ONIT → MEK + NO ₂ ¹ O: OH → H ₂ O	1.7·10 ⁻¹²	Atkinson et al. (1999)*
C₅ chemistry				
G4500	TrGC	ISOP + O ₃ → 0.28 HCOOH + 0.65 MVK + 0.1 MVK ₂ + 0.1 PA + 0.14 CO + 0.58 HCHO + 0.09 H ₂ O ₂ + 0.08 CH ₃ O ₂ + 0.25 OH + 0.25 HO ₂ ¹ O: O ₃ → 0.5 HCOOH + MVK + ¹ / ₃ MVK ₂ + ¹ / ₃ PA + CO + 0.081 HCHO + 0.5 H ₂ O ₂ + OH ¹ O: O ₂ → ² / ₃ MVK ₂ + ² / ₃ PA + 0.919 HCHO + CH ₃ O ₂ + HO ₂ ¹ O: H ₂ O → 0.5 HCOOH + 0.5 H ₂ O ₂	7.86·10 ⁻¹⁵ ·exp(-1913/T)	Pöschl et al. (2000)
G4501	TrGC	ISOP + OH → ISO ₂ ¹ O: O ₂ → ISO ₂	2.54·10 ⁻¹¹ ·exp(410/T)	Pöschl et al. (2000)
G4502	TrGNC	ISOP + NO ₃ → ISON ¹ O: O ₂ → 0.4 ISON ¹ O: NO ₃ → 0.6 ISON	3.03·10 ⁻¹² ·exp(-446/T)	Pöschl et al. (2000)
G4503	TrGC	ISO ₂ + HO ₂ → ISOOH ¹ O: ISO ₂ → ISOOH ¹ O: HO ₂ → O ₂	2.22·10 ⁻¹³ ·exp(1300/T)	Boyd et al. (2003)*
G4504a	TrGNC	ISO ₂ + NO → 0.956 NO ₂ + 0.956 MVK + 0.956 HCHO + 0.956 HO ₂ + 0.044 ISON	2.54·10 ⁻¹² ·exp(360/T)	Pöschl et al. (2000)*
G4505	TrGC	ISO ₂ + CH ₃ O ₂ → 0.5 MVK + 1.25 HCHO + HO ₂ + 0.25 CH ₃ COCHO + 0.25 ACETOL + 0.25 CH ₃ OH ¹ O: ISO ₂ → MVK + 0.8 HCHO + CH ₃ COCHO + ACETOL ¹ O: CH ₃ O ₂ → 0.2 HCHO + CH ₃ OH ¹ O: O ₂ → HO ₂	2·10 ⁻¹²	von Kuhlmann (2001)
G4506	TrGC	ISO ₂ + ISO ₂ → 2 MVK + HCHO + HO ₂ ¹ O: ISO ₂ → MVK + HCHO ¹ O: O ₂ → HO ₂	2·10 ⁻¹²	Pöschl et al. (2000)
G4507	TrGC	ISOOH + OH → MVK + OH ¹ O: ISOOH → OH + MVK ¹ O: O ₂ → H ₂ O	1·10 ⁻¹⁰	Pöschl et al. (2000)
G4508	TrGNC	ISON + OH → ACETOL + NACA ¹ O: ISON → ACETOL + NACA ¹ O: OH → H ₂ O	1.3·10 ⁻¹¹	Pöschl et al. (2000)
Cl chemistry				
G6100	StTrGCl	Cl + O ₃ → ClO + O ₂	2.8·10 ⁻¹¹ ·exp(-250/T)	Atkinson et al. (2007)
G6101	StGCl	ClO + O(³ P) → Cl + O ₂	2.5·10 ⁻¹¹ ·exp(110/T)	Atkinson et al. (2007)
G6102a	StTrGCl	ClO + ClO → Cl ₂ + O ₂	1.0·10 ⁻¹² ·exp(-1590/T)	Atkinson et al. (2007)
G6102b	StTrGCl	ClO + ClO → 2 Cl + O ₂	3.0·10 ⁻¹¹ ·exp(-2450/T)	Atkinson et al. (2007)
G6102c	StTrGCl	ClO + ClO → Cl + OCIO	3.5·10 ⁻¹³ ·exp(-1370/T)	Atkinson et al. (2007)
G6102d	StTrGCl	ClO + ClO → Cl ₂ O ₂	kClOCIO	Atkinson et al. (2007)
G6103	StTrGCl	Cl ₂ O ₂ → ClO + ClO	kClOCIO/(9.3·10 ⁻²⁸ ·exp(8835/T))	Atkinson et al. (2007), Sander et al. (2006)*
G6200	StGCl	Cl + H ₂ → HCl + H	3.9·10 ⁻¹¹ ·exp(-2310/T)	Atkinson et al. (2007)
G6201a	StGCl	Cl + HO ₂ → HCl + O ₂	4.4·10 ⁻¹¹ - 7.5·10 ⁻¹¹ ·exp(-620/T)	Atkinson et al. (2007)

Table A.1 Gas Phase Reactions

Abbr.	Label ^a	Reaction / Isotope transfer ^b	Rate Coefficient ^c	Reference ^d
G6201b	StGCl	Cl + HO ₂ → ClO + OH	$7.5 \cdot 10^{-11} \times \exp(-620/T)$	Atkinson et al. (2007)
G6202	StTrGCl	Cl + H ₂ O ₂ → HCl + HO ₂	$1.1 \cdot 10^{-11} \times \exp(-980/T)$	Atkinson et al. (2007)
G6203	StGCl	ClO + OH → 0.94 Cl + 0.94 HO ₂ + 0.06 HCl + 0.06 O ₂	$7.3 \cdot 10^{-12} \times \exp(300/T)$	Atkinson et al. (2007)
G6204	StTrGCl	ClO + HO ₂ → HOCl	$2.2 \cdot 10^{-12} \times \exp(340/T)$	Atkinson et al. (2007)
G6205	StTrGCl	HCl + OH → Cl + H ₂ O	$1.7 \cdot 10^{-12} \times \exp(-230/T)$	Atkinson et al. (2007)
G6206	StGCl	HOCl + OH → ClO + H ₂ O	$3.0 \cdot 10^{-12} \times \exp(-500/T)$	Sander et al. (2006)
G6300	StTrGNCl	ClO + NO → NO ₂ + Cl	$6.2 \cdot 10^{-12} \times \exp(295/T)$	Atkinson et al. (2007)
G6301	StTrGNCl	ClO + NO ₂ → ClNO ₂	$k_{3rdiupac}(T, C_{air}, 1.6 \cdot 10^{-31}, 3.4, 7 \cdot 10^{-11}, 0, 0.4)$	Atkinson et al. (2007)
G6302	TrGCl	ClNO ₂ → ClO + NO ₂	$6.918 \cdot 10^{-7} \times \exp(-10909/T) \cdot C_{air}$	Anderson and Fahey (1990)
G6303	StGNCl	ClNO ₂ + O(³ P) → ClO + NO ₃	$4.5 \cdot 10^{-12} \times \exp(-900/T)$	Atkinson et al. (2007)
G6304	StTrGNCl	ClNO ₂ + Cl → Cl ₂ + NO ₃	$6.2 \cdot 10^{-12} \times \exp(145/T)$	Atkinson et al. (2007)
G6400	StTrGCl	Cl + CH ₄ → HCl + CH ₃ O ₂ ¹ O: O ₂ → CH ₃ O ₂	$6.6 \cdot 10^{-12} \times \exp(-1240/T)$	Atkinson et al. (2006)
G6401	StTrGCl	Cl + HCHO → HCl + CO + HO ₂ ¹ O: HCHO → CO ¹ O: O ₂ → HO ₂	$8.1 \cdot 10^{-11} \times \exp(-34/T)$	Atkinson et al. (2006)
G6402	StTrGCl	Cl + CH ₃ OOH → HCHO + HCl + OH	$5.9 \cdot 10^{-11}$	Atkinson et al. (2006)*
G6403	StTrGCl	ClO + CH ₃ O ₂ → HO ₂ + Cl + HCHO	$3.3 \cdot 10^{-12} \times \exp(-115/T)$	Sander et al. (2006)
G6404	StGCl	CCl ₄ + O(¹ D) → ClO + 3 Cl	$3.3 \cdot 10^{-10}$	Sander et al. (2006)
G6405	StGCl	CH ₃ Cl + O(¹ D) → OH + Cl	$1.65 \cdot 10^{-10}$	see notes
G6406	StGCl	CH ₃ Cl + OH → H ₂ O + Cl	$2.4 \cdot 10^{-12} \times \exp(-1250/T)$	Sander et al. (2006)
G6407	StGCCl	CH ₃ CCl ₃ + O(¹ D) → OH + 3 Cl	$3 \cdot 10^{-10}$	see notes
G6408	StTrGCCl	CH ₃ CCl ₃ + OH → H ₂ O + 3 Cl	$1.64 \cdot 10^{-12} \times \exp(-1520/T)$	Sander et al. (2006)
G6409	TrGCCl	Cl + C ₂ H ₄ → ² /3 C ₂ H ₄ O ₂ + HCl ¹ O: O ₂ → C ₂ H ₄ O ₂	$k_{3rdiupac}(T, C_{air}, 1.85 \cdot 10^{-29}, 3.3, 6.0 \cdot 10^{-10}, 0, 0.4)$	Atkinson et al. (2006)
G6410	TrGCCl	Cl + CH ₃ CHO → HCl + PA	$7.9 \cdot 10^{-11}$	Atkinson et al. (2006)*
G6500	StGFCl	CF ₂ Cl ₂ + O(¹ D) → ClO + Cl	$1.4 \cdot 10^{-10}$	Sander et al. (2006)
G6501	StGFCl	CFCl ₃ + O(¹ D) → ClO + 2 Cl	$2.3 \cdot 10^{-10}$	Sander et al. (2006)
S chemistry				
G9200	StTrGS	SO ₂ + OH → H ₂ SO ₄ + HO ₂ ¹ O: SO ₂ → 0.5 H ₂ SO ₄ ¹ O: OH → 0.25 H ₂ SO ₄ ¹ O: H ₂ O → 0.25 H ₂ SO ₄ ¹ O: O ₂ → HO ₂	$k_{3rd}(T, C_{air}, 3.3 \cdot 10^{-31}, 4.3, 1.6 \cdot 10^{-12}, 0, 0.6)$	Sander et al. (2006)
G9400a	TrGS	DMS + OH → CH ₃ SO ₂ + HCHO ¹ O: O ₂ → CH ₃ SO ₂ + HCHO	$1.13 \cdot 10^{-11} \times \exp(-253/T)$	Atkinson et al. (2004)*
G9400b	TrGS	DMS + OH → DMSO + HO ₂ ¹ O: OH → DMSO ¹ O: O ₂ → HO ₂	k_{DMSOH}	Atkinson et al. (2004)*
G9401	TrGNS	DMS + NO ₃ → CH ₃ SO ₂ + HNO ₃ + HCHO ¹ O: NO ₃ → HNO ₃ ¹ O: O ₂ → CH ₃ SO ₂ + HCHO	$1.9 \cdot 10^{-13} \times \exp(520/T)$	Atkinson et al. (2004)
G9402	TrGS	DMSO + OH → 0.6 SO ₂ + HCHO + 0.6 CH ₃ O ₂ + 0.4 HO ₂ + 0.4 CH ₃ SO ₃ H ¹ O: OH → 0.5 SO ₂ + ¹ /3 CH ₃ SO ₃ H ¹ O: DMSO → 0.5 SO ₂ + ¹ /3 CH ₃ SO ₃ H ¹ O: O ₂ → CH ₃ O ₂ + HCHO + HO ₂ + ¹ /3 CH ₃ SO ₃ H	$1 \cdot 10^{-10}$	Hynes and Wine (1996)
G9403	TrGS	CH ₃ SO ₂ → SO ₂ + CH ₃ O ₂ ¹ O: CH ₃ SO ₂ → SO ₂ ¹ O: O ₂ → CH ₃ O ₂	$1.9 \cdot 10^{13} \times \exp(-8661/T)$	Barone et al. (1995)
G9404	TrGS	CH ₃ SO ₂ + O ₃ → CH ₃ SO ₃ ¹ O: CH ₃ SO ₂ → ² /3 CH ₃ SO ₃ ¹ O: O ₃ → ¹ /3 CH ₃ SO ₃	$3 \cdot 10^{-13}$	Barone et al. (1995)
G9405	TrGS	CH ₃ SO ₃ + HO ₂ → CH ₃ SO ₃ H ¹ O: CH ₃ SO ₃ → CH ₃ SO ₃ H	$5 \cdot 10^{-11}$	Barone et al. (1995)
G9600	TrGScl	DMS + Cl → CH ₃ SO ₂ + HCl + HCHO ¹ O: O ₂ → CH ₃ SO ₂ + HCHO	$3.3 \cdot 10^{-10}$	Atkinson et al. (2004)

Notes:

^{a)} Labels denote the groups reactions belong to, such as: gas-phase (G), photolysis (J), troposphere/stratosphere relevant (Tr/St), NMHC and VOC C₂–C₅ chemistry (C) and nitrogen/sulphur/chlorine chemistry (N/S/Cl), respectively.

^{b)} The isotope transfer (denoted for oxygen- and carbon-bearing species with ¹O and ¹C, respectively) is given in case it differs from or does not straightforwardly follow the reaction stoichiometry. In some cases the stoichiometric coefficients may not preserve atomic content on the LHS and RHS, therefore they should be considered as defining the shares of educts in product's compositions.

Notes:

- c) Rate coefficients for three-body reactions are defined via the functions $k_{3rd}(T, C_{air}, k_0^{300}, n, k_{inf}^{300}, m, f_c)$ and $k_{3rdiupac}(T, C_{air}, k_0^{300}, n, k_{inf}^{300}, m, f_c)$, where T denotes temperature, C_{air} is the concentration of air molecules (per cm^3). Note, $k_{3rdiupac}$ is used by Atkinson et al. (2005) for three-body reactions. Using the auxiliary variables $k_0(T)$, $k_{inf}(T)$, and k_{ratio} , k_{3rd} and $k_{3rdiupac}$ are defined as:

$$k_0(T) = k_0^{300} \times \left(\frac{300K}{T} \right)^n, \quad k_{inf}(T) = k_{inf}^{300} \times \left(\frac{300K}{T} \right)^m, \quad k_{ratio} = \frac{k_0(T) \cdot C_{air}}{k_{inf}(T)}, \quad N = 0.75 - 1.27 \times \log(f_c)$$

$$k_{3rd} = \frac{k_0(T) \cdot C_{air}}{1 + k_{ratio}} \times f_c^{\left(\frac{1}{1 + (\log_{10}(k_{ratio}))^2} \right)}, \quad k_{3rdiupac} = \frac{k_0(T) \cdot C_{air}}{1 + k_{ratio}} \times f_c^{\left(\frac{1}{1 + (\log_{10}(k_{ratio})/N)^2} \right)}$$

- d) References are given separately below (p. 237). Additional notes on the reactions marked with asterisks (*):

- G1002 The path leading to $2\text{O}(^1\text{P}) + \text{O}_2$ results in a null cycle regarding odd oxygen and is neglected in original MECCA reactions list. The correct composition exchange is accounted for in the isotope exchange reactions (see reaction IEX05, Sect. 3.3.3, p. 37).
- G2110 The rate coefficient is: $\text{kHO}_2\text{HO}_2 = (1.5 \cdot 10^{-12} \times \exp(19/T) + 1.7 \cdot 10^{-33} \times \exp(1000/T) \cdot C_{air}) \cdot (1 + 1.4 \cdot 10^{-21} \times \exp(2200/T) \cdot \{\text{H}_2\text{O}\})$. The value for the first (pressure-independent) part is from Christensen et al. (2002), the water term from Kirchner and Sander (1984).
- G3109 The rate coefficient is: $\text{kNO}_2\text{NO}_2 = k_{3rd}(T, C_{air}, 2 \cdot 10^{-30}, 4.4, 1.4 \cdot 10^{-12}, 0.7, 0.6)$.
- G3110 The rate coefficient is defined as backward reaction divided by equilibrium constant.
- G3203 The rate coefficient is: $\text{kNO}_2\text{HO}_2 = k_{3rd}(T, C_{air}, 1.8 \cdot 10^{-31}, 3.2, 4.7 \cdot 10^{-12}, 1.4, 0.6)$.
- G3206 The rate coefficient is: $\text{kHNO}_3\text{OH} = 2.4 \cdot 10^{-14} \times \exp(460/T) + 1/(1/(6.5 \cdot 10^{-38} \times \exp(1335/T) \cdot C_{air}) + 1/(2.7 \cdot 10^{-17} \times \exp(2199/T)))$.
- G3207 The rate coefficient is defined as backward reaction divided by equilibrium constant.
- G4103 Sander et al. (2006) recommend a zero product yield for HCHO .
- G4107 The rate coefficient is: $\text{kCH}_3\text{OOH} + \text{OH} = 3.8 \cdot 10^{-12} \times \exp(200/T)$.
- G4109 The same temperature dependence assumed as for $\text{CH}_3\text{CHO} + \text{NO}_3$.
- G4201 The product distribution is from von Kuhlmann (2001) (see also Neeb et al. (1998)).
- G4206 The rate coefficient was calculated by von Kuhlmann (pers. comm. 2004, R. Sander) using self reactions of CH_3OO and $\text{C}_2\text{H}_5\text{OO}$ from Sander et al. (2003) and geometric mean as suggested by Madronich and Calvert (1990) and Kirchner and Stockwell (1996). The product distribution (branching = 0.5/0.25/0.25) is calculated by von Kuhlmann (pers. comm. 2004, R. Sander) based on Villenave and Lesclaux (1996) and Tyndall et al. (2001).
- G4207 Same value as for G4107: $\text{CH}_3\text{OOH} + \text{OH}$ assumed.
- G4213 The rate coefficient is: $\text{kPANO}_2 = k_{3rd}(T, C_{air}, 8.5 \cdot 10^{-29}, 6.5, 1.1 \cdot 10^{-11}, 1, 0.6)$.
- G4216 The value $1.0 \cdot 10^{-11}$ is from Atkinson et al. (1999), the temperature dependence from Kirchner and Stockwell (1996).
- G4218 Same value as for G4107: $\text{CH}_3\text{OOH} + \text{OH}$ assumed.
- G4219 According to Pöschl et al. (2000), the same value as for $\text{CH}_3\text{CHO} + \text{OH}$ can be assumed.
- G4220 This is 50% of the upper limit given by Sander et al. (2003), as suggested by von Kuhlmann (2001).
- G4221 The rate coefficient is: $\text{kPANM} = \text{kPANO}_2/9 \cdot 10^{-29} \times \exp(-14000/T)$, i.e. the rate coefficient is defined as backward reaction divided by equilibrium constant.
- G4301 The product distribution is for terminal olefin carbons from Zaveri and Peters (1999).
- G4304 The rate coefficient is: $\text{kPrO}_2\text{HO}_2 = 1.9 \cdot 10^{-13} \times \exp(1300/T)$. Value for generic $\text{RO}_2 + \text{HO}_2$ reaction from Atkinson (1997) is used.
- G4305 The rate coefficient is: $\text{kPrO}_2\text{NO} = 2.7 \cdot 10^{-12} \times \exp(360/T)$.
- G4306 The rate coefficient is: $\text{kPrO}_2\text{CH}_3\text{O}_2 = 9.46 \cdot 10^{-14} \times \exp(431/T)$. The product distribution is from von Kuhlmann (2001).
- G4307 Same value as for G4107: $\text{CH}_3\text{OOH} + \text{OH}$ assumed.
- G4309 The products are from von Kuhlmann (2001).
- G4315 Same value as for G4107: $\text{CH}_3\text{OOH} + \text{OH}$ assumed.
- G4319 Same value as for PAN assumed.
- G4401 Same value as for propyl group assumed ($\text{kPrO}_2\text{CH}_3\text{O}_2$).
- G4402 Same value as for propyl group assumed (kPrO_2HO_2).
- G4403 Same value as for propyl group assumed (kPrO_2NO).
- G4404 Same value as for G4107: $\text{CH}_3\text{OOH} + \text{OH}$ assumed.
- G4409 The factor 0.25 was recommended by U. Pöschl (pers. comm. 2004, R. Sander).
- G4414 Same value as for propyl group assumed (kPrO_2HO_2).
- G4415 Same value as for propyl group assumed (kPrO_2NO).
- G4416 Same value as for G4107: $\text{CH}_3\text{OOH} + \text{OH}$ assumed.
- G4417 Value for $\text{C}_4\text{H}_9\text{ONO}_2$ used here.
- G4503 Same temperature dependence assumed as for other $\text{RO}_2 + \text{HO}_2$ reactions.
- G4504 Yield of 12% RONO_2 assumed as suggested in Table 2 of Sprengnether et al. (2002).
- G6102 The rate coefficient is: $\text{kClOClO} = k_{3rdiupac}(T, C_{air}, 2 \cdot 10^{-32}, 4, 10^{-11}, 0, 0.45)$.
- G6103 The rate coefficient is defined as backward reaction divided by equilibrium constant.
- G6204 At low temperatures, there may be a minor reaction channel leading to $\text{O}_3 + \text{HCl}$ that it is neglected here.
- G6402 The initial products are probably HCl and CH_2OOH (Atkinson et al., 2006). It is assumed that CH_2OOH dissociates into HCHO and OH .
- G6405 Average of reactions with CH_3Br and CH_3F from Sander et al. (2006) (B. Steil, pers. comm., R. Sander).
- G6407 Rough extrapolation from reactions with CH_3CF_3 , CH_3CClF_2 , and $\text{CH}_3\text{CCl}_2\text{F}$ from Sander et al. (2006).
- G9400 Addition path. The rate coefficient is: $\text{kDMSOH} = 1.0 \cdot 10^{-39} \times \exp(5820/T) \cdot \{\text{O}_2\} / (1 + 5.0 \cdot 10^{-30} \times \exp(6280/T) \cdot \{\text{O}_2\})$.
- G9400a Abstraction path. The assumed reaction sequence (omitting H_2O and O_2 as products) and is: $\text{DMS} + \text{OH} \rightarrow \text{CH}_3\text{SCH}_2$, $\text{CH}_3\text{SCH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{SCH}_2\text{OO}$, $\text{CH}_3\text{SCH}_2\text{OO} + \text{NO} \rightarrow \text{CH}_3\text{SCH}_2\text{O} + \text{NO}_2$, $\text{CH}_3\text{SCH}_2\text{O} \rightarrow \text{CH}_3\text{S} + \text{HCHO}$, $\text{CH}_3\text{S} + \text{O}_3 \rightarrow \text{CH}_3\text{SO}$, $\text{CH}_3\text{SO} + \text{O}_3 \rightarrow \text{CH}_3\text{SO}_2$, $\text{DMS} + \text{OH} + \text{NO} + 2\text{O}_3 \rightarrow \text{CH}_3\text{SO}_2 + \text{HCHO} + \text{NO}_2$. Neglecting the effect on O_3 and NO_x , the remaining reaction is: $\text{DMS} + \text{OH} + \text{O}_3 \rightarrow \text{CH}_3\text{SO}_2 + \text{HCHO}$.

Table A.2 Photolysis Reactions

Abbr.	Labels ^{a)}	Reaction / Isotope transfer ^{b)}	Rate Coefficient ^{c)}	Reference ^{d)}
O, H+O chemistry				
J1000	StTrGJ	$O_2 + hv \rightarrow O(^3P) + O(^3P)$	$jx(ipO_2)$	see notes
J1001a	StTrGJ	$O_3 + hv \rightarrow O(^1D)$	$jx(ipO(^1D))$	see notes
J1001b	StTrGJ	$O_3 + hv \rightarrow O(^3P)$	$jx(ipO(^3P))$	see notes
J2100	StGJ	$H_2O + hv \rightarrow H + OH$	$jx(ipH_2O)$	see notes
J2101	StTrGJ	$H_2O_2 + hv \rightarrow 2 OH$	$jx(ipH_2O_2)$	see notes
N+O, N+H chemistry				
J3100	StGNJ	$N_2O + hv \rightarrow O(^1D)$	$jx(ipN_2O)$	see notes
J3101	StTrGNJ	$NO_2 + hv \rightarrow NO + O(^3P)$	$jx(ipNO_2)$	see notes
J3102	StGNJ	$NO + hv \rightarrow N + O(^3P)$	$jx(ipNO)$	see notes
J3103a	StTrGNJ	$NO_3 + hv \rightarrow NO_2 + O(^3P)$	$jx(ipNO_2O)$	see notes
J3103b	StTrGNJ	$NO_3 + hv \rightarrow NO$	$jx(ipNOO_2)$	see notes
J3104a	StTrGNJ	$N_2O_5 + hv \rightarrow NO_2 + NO_3$	$jx(ipN_2O_5)$	see notes
J3104b	StGNJ	$N_2O_5 + hv \rightarrow NO + O(^3P) + NO_3$	$jx(ipNO_3NOO)$	see notes
J3200	TrGJ	$HONO + hv \rightarrow NO + OH$	$jx(ipHONO)$	see notes
J3201	StTrGNJ	$HNO_3 + hv \rightarrow NO_2 + OH$	$jx(ipHNO_3)$	see notes
J3202	StTrGNJ	$HNO_4 + hv \rightarrow \frac{2}{3} NO_2 + \frac{2}{3} HO_2 + \frac{1}{3} NO_3 + \frac{1}{3} OH$	$jx(ipHNO_4)$	see notes
C₁–C₅ chemistry				
J4100	StTrGJ	$CH_3OOH + hv \rightarrow HCHO + OH + HO_2$ $^1O: CH_3OOH \rightarrow OH + HCHO$ $^1O: O_2 \rightarrow HO_2$	$jx(ipCH_3OOH)$	see notes
J4101a	StTrGJ	$HCHO + hv \rightarrow H_2 + CO$	$jx(ipCOH_2)$	see notes
J4101b	StTrGJ	$HCHO + hv \rightarrow H + CO + HO_2$ $^1O: HCHO \rightarrow CO$ $^1O: O_2 \rightarrow HO_2$	$jx(ipCHOH)$	see notes
J4102	StGJ	$CO_2 + hv \rightarrow CO + O(^3P)$	$jx(ipCO_2)$	see notes
J4103	StGJ	$CH_4 + hv \rightarrow CO + 0.31 H + 0.69 H_2 + 1.155 H_2O$ $^1O: O_2 \rightarrow CO + H_2O$	$jx(ipCH_4)$	see notes
J4200	TrGCJ	$EtOOH + hv \rightarrow CH_3CHO + HO_2 + OH$ $^1O: EtOOH \rightarrow CH_3CHO + OH$ $^1O: O_2 \rightarrow HO_2$	$jx(ipCH_3OOH)$	see notes
J4201	TrGCJ	$CH_3CHO + hv \rightarrow CH_3O_2 + HO_2 + CO$ $^1O: CH_3CHO \rightarrow CO$ $^1O: O_2 \rightarrow CH_3O_2 + HO_2$	$jx(ipCH_3CHO)$	see notes
J4202	TrGCJ	$PAA + hv \rightarrow CH_3O_2 + OH$ $^1O: PAA \rightarrow OH$ $^1O: O_2 \rightarrow CH_3O_2$	$jx(ipPAA)$	see notes
J4203	TrGNJ	$NACA + hv \rightarrow NO_2 + HCHO + CO$	$0.19 \cdot jx(ipCHOH)$	see notes
J4204	TrGNJ	$PAN + hv \rightarrow 0.6 PA + 0.6 NO_2 + 0.4 CH_3O_2 + 0.4 NO_3 + 0.4 CO_2$ $^1O: PAN \rightarrow PA + NO_2 + NO_3 + CO_2$ $^1O: O_2 \rightarrow CH_3O_2$	$jx(ipPAN)$	see notes
J4300	TrGCJ	$PrOOH + hv \rightarrow CH_3COCH_3 + HO_2 + OH$ $^1O: PrOOH \rightarrow CH_3COCH_3 + OH$ $^1O: O_2 \rightarrow HO_2$	$jx(ipCH_3OOH)$	see notes
J4301	TrGCJ	$CH_3COCH_3 + hv \rightarrow PA + CH_3O_2$ $^1O: CH_3COCH_3 \rightarrow \frac{1}{3} PA$ $^1O: O_2 \rightarrow \frac{2}{3} PA + CH_3O_2$	$jx(ipCH_3COCH_3)$	see notes
J4302	TrGCJ	$ACETOL + hv \rightarrow PA + HCHO + HO_2$ $^1O: ACETOL \rightarrow \frac{1}{3} PA + HCHO$ $^1O: O_2 \rightarrow \frac{2}{3} PA + HO_2$	$0.074 \cdot jx(ipCHOH)$	see notes
J4303	TrGCJ	$CH_3COCHO + hv \rightarrow PA + CO + HO_2$ $^1O: CH_3COCHO \rightarrow \frac{1}{3} PA + CO$ $^1O: O_2 \rightarrow \frac{2}{3} PA + HO_2$	$jx(ipCH_3COCHO)$	see notes
J4304	TrGCJ	$ACETP + hv \rightarrow PA + HO_2 + OH$ $^1O: ACETP \rightarrow \frac{1}{3} PA + OH$ $^1O: O_2 \rightarrow \frac{2}{3} PA + HO_2$	$jx(ipCH_3OOH)$	see notes
J4305	TrGNJ	$MPAN + hv \rightarrow ACETOL + NO_2$	$jx(ipPAN)$	see notes
J4306	TrGNJ	$PrONO_2 + hv \rightarrow CH_3COCH_3 + NO_2 + HO_2$ $^1O: PrONO_2 \rightarrow CH_3COCH_3 + NO_2$ $^1O: O_2 \rightarrow HO_2$	$3.7 \cdot jx(ipPAN)$	see notes

Table A.2 Photolysis Reactions

Abbr.	Labels ^{a)}	Reaction / Isotope transfer ^{b)}	Rate Coefficient ^{c)}	Reference ^{d)}
J4400	TrGCJ	$C_4H_9OOH + hv \rightarrow OH + \frac{2}{3} MEK + \frac{2}{3} HO_2 + \frac{1}{3} EtO_2 + \frac{1}{3} CH_3CHO$ 'O: $C_4H_9OOH \rightarrow OH + MEK + CH_3CHO$ 'O: $O_2 \rightarrow HO_2 + EtO_2$	$jx(ipCH_3OOH)$	see notes
J4401	TrGCJ	$MVK + hv \rightarrow PA + HCHO + CO + HO_2$ 'O: $MVK \rightarrow \frac{1}{3} PA + CO$ 'O: $O_2 \rightarrow \frac{2}{3} PA + HCHO + HO_2$	$0.019 \cdot jx(ipCHO_2) + 0.015 \cdot jx(ipCH_3COCHO)$	see notes
J4402	TrGCJ	$MVKOOH + hv \rightarrow OH + 0.5 CH_3COCHO + 0.25 ACETOL + 0.75 HCHO + 0.75 HO_2 + 0.25 PA + 0.25 CO$ 'O: $MVKOOH \rightarrow OH + CH_3COCHO + ACETOL + 0.5 HCHO + \frac{1}{3} PA + CO$ 'O: $O_2 \rightarrow HO_2 + 0.5 HCHO + \frac{2}{3} PA$	$jx(ipCH_3OOH)$	see notes
J4403	TrGCJ	$MEK + hv \rightarrow PA + EtO_2$ 'O: $MEK \rightarrow \frac{1}{3} PA$ 'O: $O_2 \rightarrow \frac{2}{3} PA + EtO_2$	$0.42 \cdot jx(ipCHOH)$	see notes
J4404	TrGCJ	$MEKOOH + hv \rightarrow PA + CH_3CHO + OH$ 'O: $MEKOOH \rightarrow \frac{1}{3} PA + CH_3CHO + OH$ 'O: $O_2 \rightarrow \frac{2}{3} PA$	$jx(ipCH_3OOH)$	see notes
J4405	TrGCJ	$MeCOCO + hv \rightarrow 2 PA$ 'O: $MeCOCO \rightarrow \frac{1}{3} PA$ 'O: $O_2 \rightarrow \frac{2}{3} PA$	$2.15 \cdot jx(ipCH_3COCHO)$	see notes
J4406	TrGNCJ	$ONIT + hv \rightarrow NO_2 + \frac{2}{3} MEK + \frac{2}{3} HO_2 + \frac{1}{3} EtO_2 + \frac{1}{3} CH_3CHO$ 'O: $ONIT \rightarrow NO_2 + MEK + CH_3CHO$ 'O: $O_2 \rightarrow HO_2 + EtO_2$	$3.7 \cdot jx(ipPAN)$	see notes
J4500	TrGCJ	$ISOOH + hv \rightarrow MVK + HCHO + HO_2 + OH$ 'O: $ISOOH \rightarrow MVK + HCHO + OH$ 'O: $O_2 \rightarrow HO_2$	$jx(ipCH_3OOH)$	see notes
J4501	TrGNCJ	$ISON + hv \rightarrow MVK + HCHO + NO_2 + HO_2$ 'O: $ISON \rightarrow MVK + HCHO + NO_2$ 'O: $O_2 \rightarrow HO_2$	$3.7 \cdot jx(ipPAN)$	see notes
Cl chemistry				
J6000	StTrGCLJ	$Cl_2 + hv \rightarrow Cl + Cl$	$jx(ipCl_2)$	see notes
J6100	StTrGCLJ	$Cl_2O_2 + hv \rightarrow 2 Cl$	$1.4 \cdot jx(ipCl_2O_2)$	see notes*
J6101	StTrGCLJ	$OCIO + hv \rightarrow ClO + O(^3P)$	$jx(ipOCIO)$	see notes
J6200	StGCLJ	$HCl + hv \rightarrow Cl + H$	$jx(ipHCl)$	see notes
J6201	StTrGCLJ	$HOCl + hv \rightarrow OH + Cl$	$jx(ipHOCl)$	see notes
J6300	TrGNCJ	$ClNO_2 + hv \rightarrow Cl + NO_2$	$jx(ipClNO_2)$	see notes
J6301a	StTrGNCJ	$ClNO_3 + hv \rightarrow Cl + NO_3$	$jx(ipClNO_3)$	see notes
J6301b	StTrGNCJ	$ClNO_3 + hv \rightarrow ClO + NO_2$	$jx(ipClONO_2)$	see notes
J6400	StGCLJ	$CH_3Cl + hv \rightarrow Cl + CH_3O_2$ 'O: $O_2 \rightarrow CH_3O_2$	$jx(ipCH_3Cl)$	see notes
J6401	StGCLJ	$CCl_4 + hv \rightarrow 4 Cl$	$jx(ipCCl_4)$	see notes
J6402	StGCCJ	$CH_3CCl_3 + hv \rightarrow 3 Cl$	$jx(ipCH_3CCl_3)$	see notes
J6500	StGFCLJ	$CFCl_3 + hv \rightarrow 3 Cl$	$jx(ipCFCl_3)$	see notes
J6501	StGFCLJ	$CF_2Cl_2 + hv \rightarrow 2 Cl$	$jx(ipCF_2Cl_2)$	see notes
J9002	StGSJ	$SF_6 + hv \rightarrow PROD$	$jx(ipSF_6)$	see notes

Notes:

- ^{a)} Labels denote the groups reactions belong to, such as: gas-phase (G), photolysis (J), troposphere/stratosphere relevant (Tr/St), NMHC and VOC C₂–C₅ chemistry (C) and nitrogen/sulphur/chlorine chemistry (N/S/Cl), respectively.
- ^{b)} The isotope transfer (denoted for oxygen-bearing species with 'O:') is given in case it differs from or does not straightforwardly follow the reaction stoichiometry. In some cases the stoichiometric coefficients may not preserve atomic content on the LHS and RHS, therefore they should be considered as defining the shares of educts in product's compositions.
- ^{c)} Photodissociation rate coefficients (or J-values, denoted as $jx(ipHCl)$, for example) are calculated with an external module and then supplied to the MECCA chemistry.
- ^{d)} References are given separately below (p. 237). Additional notes on the reactions marked with asterisks (*):

J6100 Stimpfle et al. (2004) claim that the combination of absorption cross sections from Burkholder et al. (1990) and the Cl₂O₂ formation rate coefficient by Sander et al. (2003) can approximately reproduce the observed Cl₂O₂/ClO ratios and ozone depletion. They give an almost zenith-angle independent ratio of 1.4 for Burkholder et al. (1990) to Sander et al. (2003) J-values. The IUPAC recommendation for the Cl₂O₂ formation rate is about 5 to 15% less than the value by Sander et al. (2003) but more than 20% larger than the value by Sander et al. (2000). The J-values by Burkholder et al. (1990) are within the uncertainty range of the IUPAC recommendation.

Table A.3 List of chemical species

Abbr.	Species	Elemental composition	Abbr.	Species	Elemental composition
Oxygen			Carbon₁		
O(¹ D)	singlet D oxygen atom	O	CH ₄	methane	C + 4H
O(³ P)	triplet P oxygen atom	O	CH ₃ OH	methanol	C + 4H + O
O ₂	oxygen	2O	CH ₃ O ₂	methyl peroxy radical	C + 3H + 2O
O ₃	ozone	3O	CH ₃ OOH	methyl peroxide	C + 4H + 2O
Hydrogen			HCHO	methanal (formaldehyde)	C + 2H + O
H	hydrogen atom	H	CO	carbon monoxide	C + O
H ₂	hydrogen	2H	HCOOH	formic acid	C + 2H + 2O
OH	hydroxyl radical	O + H	CO ₂	carbon dioxide	C + 2O
HO ₂	hydroperoxy radical	H + 2O	Carbon₂		
H ₂ O	water	2H + O	C ₂ H ₆	ethane	2C + 6H
H ₂ O ₂	hydrogen peroxide	2H + 2O	C ₂ H ₄	ethene	2C + 4H
Nitrogen			C ₂ H ₂	ethyne	2C + 2H
N	nitrogen atom	N	EtO ₂	ethylperoxy radical	2C + 5H + 2O
N ₂	nitrogen	2N	EtOOH	ethyl hydroperoxide	2C + 6H + 2O
NH ₃	ammonia	N + 3H	CH ₃ CHO	acetaldehyde	2C + 4H + O
N ₂ O	nitrous oxide	2N + O	CH ₃ COOH	acetic acid	2C + 4H + 2O
NO	nitric oxide	N + O	PA	peroxy acetyl radical	2C + 3H + 3O
NO ₂	nitrogen dioxide	N + 2O	PAA	peroxy acetic acid	2C + 4H + 3O
NO ₃	nitrogen trioxide	N + 3O	NACA	nitro-oxy acetaldehyde	2C + 3H + 4O + N
N ₂ O ₅	dinitrogen pentoxide	2N + 5O	PAN	peroxyacetylnitrate	2C + 3H + 5O + N
HONO	nitrous acid	H + N + 2O	Carbon₃		
HNO ₃	nitric acid	H + N + 3O	C ₃ H ₈	propane	3C + 8H
HNO ₄	peroxynitric acid	H + N + 4O	C ₃ H ₆	propene	3C + 6H
NH ₂	aminogen radical	2H + N	PrO ₂	propane peroxyradical, secondary only	3C + 7H + 2O
HNO	nitroxyl	H + N + O	PrOOH	hydroperoxide from PrO ₂	3C + 8H + 2O
NHOH, NH ₂ O	nitroxyl radical (isomers)	2H + N + O	C ₃ H ₆ O ₂	hydroxyperoxyradical from propene+OH	3C + 7H + 3O
NH ₂ OH	hydroxylamine	3H + N + O	C ₃ H ₆ OOH	C ₃ H ₆ OHOH = hydroxyhydroperoxides from C ₃ H ₆	3C + 8H + 3O
Chlorine			CH ₃ COCH ₃	acetone	3C + 6H + O
Cl	chlorine atom	Cl	ACETO ₂	peroxyradical from acetone	3C + 5H + 3O
Cl ₂	chlorine	2Cl	ACETP	hydroperoxide from ACETO ₂	3C + 6H + 3O
ClO	chlorine oxide	Cl + O	ACETOL	HO-CH ₂ -CO-CH ₃ = hydroxy acetone	3C + 6H + 2O
HCl	hydrochloric acid	H + Cl	CH ₃ COCHO	methylglyoxal	3C + 4H + 2O
HOCl	hypochlorous acid	H + O + Cl	PrONO ₂	i-propyl nitrate	N + 3C + 3O + ... ^{a)}
Cl ₂ O ₂	dichlorine dioxide	2Cl + 2O	Carbon₄		
ClOClO	chlorine dioxide	Cl + 2O	C ₄ H ₁₀	n-butane, representative of higher alkanes	4C + 10H
ClNO ₂	nitrohydrochloric acid	Cl + 2O + N	C ₄ H ₉ O ₂	peroxyradical from butane+OH	4C + 9H + 2O
ClNO ₃	chlorine nitrate	Cl + N + 3O	C ₄ H ₉ OOH	hydroperoxides from C ₄ H ₁₀	4C + 10H + 2O
CCl ₄	tetrachloro methane	C + 4Cl	MVK	CH ₃ -CO-CH=CH ₂ = methyl vinyl ketone (+methacrolein)	4C + 6H + O
CH ₃ Cl	chloromethane	C + 3H + Cl	MVKO ₂	MVK/MACR peroxy radicals	4C + 7H + 4O
CH ₃ CCl ₃	1,1,1-trichloroethane = methyl chloroform = MCF	2C + 3H + 3Cl	MVKOOH	MVK hydroperoxides	4C + 8H + 4O
CF ₂ Cl ₂	dichlorodifluoromethane = F12	C + 2F + 2Cl	MEK	methyl ethyl ketone (+all higher ketones)	4C + 8H + O
CFCl ₃	trichlorofluoromethane = F11	C + F + 3Cl	MEKO ₂	peroxyradical from MEK; multiply oxygenated peroxy radicals	4C + 7H + 3O
Sulphur			MEKOOH	hydroperoxides from MEK	4C + 8H + 3O
SO	sulfur monoxide	S + O	MeCOCO	CH ₃ -CO-CO-CH ₃ , (+multiply oxygenated C>3 compounds)	4C + 6H + 2O
SO ₂	sulfur dioxide	S + 2O	ONIT	organic nitrates from higher alkyl nitrates, +C ₃ H ₆ +NO ₃	N + 4C + 3O + ... ^{a)}
H ₂ SO ₄	sulfuric acid	2H + S + 4O	MPAN	peroxymethacryloyl nitrate; peroxymethacrylic nitric anhydride	4C + 5H + 5O + N
CH ₃ SO ₃ H	methane sulfonic acid (MSA)	C + 4H + S + 3O	Carbon₅		
DMS	dimethyl sulfide	2C + 6H + S	ISOP	isoprene	5C + 8H
DMSO	dimethyl sulfoxide: CH ₃ SOCH ₃	2C + 6H + S + O	ISO ₂	isoprene (hydroxy) peroxy radicals	5C + 9H + 3O
CH ₃ SO ₂	methylsulfonyl radical	C + 3H + S + 2O	ISOOH	isoprene (hydro)peroxides	5C + 10H + 3O
CH ₃ SO ₃	methylsulphonic acid radical	C + 3H + S + 3O	ISON	organic nitrates from ISO ₂ and ISOP+NO ₃	N + 5C + 3O + ... ^{a)}
SF ₆	sulfur hexafluoride	S + 6F			

Notes:

^{a)} Only nitrogen composition is accounted for in the original MECCA species setup.¹⁵² Carbon and oxygen composition is added during the isotope extension of the mechanism. For the lumped species, the average number of oxygen atoms constituting them is assumed.

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Appendix B. Species interchanges charts

Charts B.1 and B.2 (pp. 241, 242) in the following are produced by the parsing tools of MECCA-TAG as the additional diagnostic information on the studied chemical mechanism. They depict the carbon and the oxygen isotope composition interchanges resulting from the set of reactions included in the MECCA mechanism employed in this study (listed in Appendix A, p. 225) and additional information on the composition transfer supplied to MECCA-TAG during the isotopic tagging (see Sect. 3.3 for the details).

Each chart consists of balloons (representing species compartments) and arrows connecting them (representing the direction of exchange between a pair of species). Each arrow is captioned with the sign including the educt and product species and a set of reactions providing this pair exchange. For example, one may find a caption ‘ $\text{NO}_2 > \text{O}_2$: G3105 G3106’, which means “in this mechanism, NO_2 reacts (giving its composition) to O_2 in reactions G3105, G3106”. The latter abbreviations are used to find a particular reaction in the MECCA mechanism (listed in Tables A.1 and A.2, pp. 225–234).

The chemical mechanism employed is rather comprehensive, the numbers of species and reactions they act in reach hundreds. Thus, unfortunately, these detailed graphs are only suitable to be printed on the paper of formats A3 and larger. The reader possessing a PDF copy of this manuscript, nevertheless, can use the zoom and the context search tools (available in PDF files viewers usually under “View” and “Edit → Search” menu) to find the exchange information for a given pair of species, using the sample provided above.

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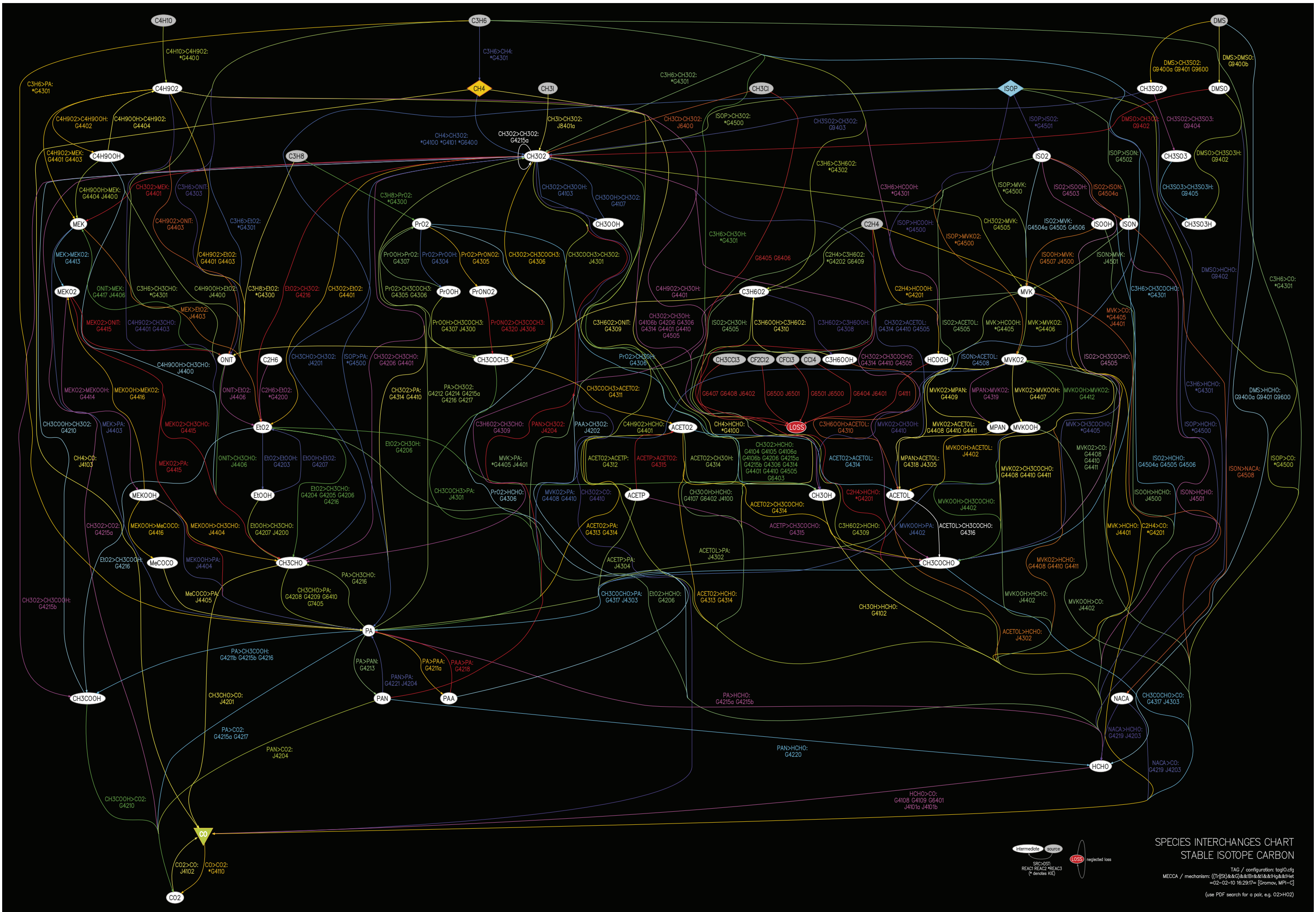


Chart B.1 Carbon interchanges between the species in the chemical mechanism of MECCA employed in this study.

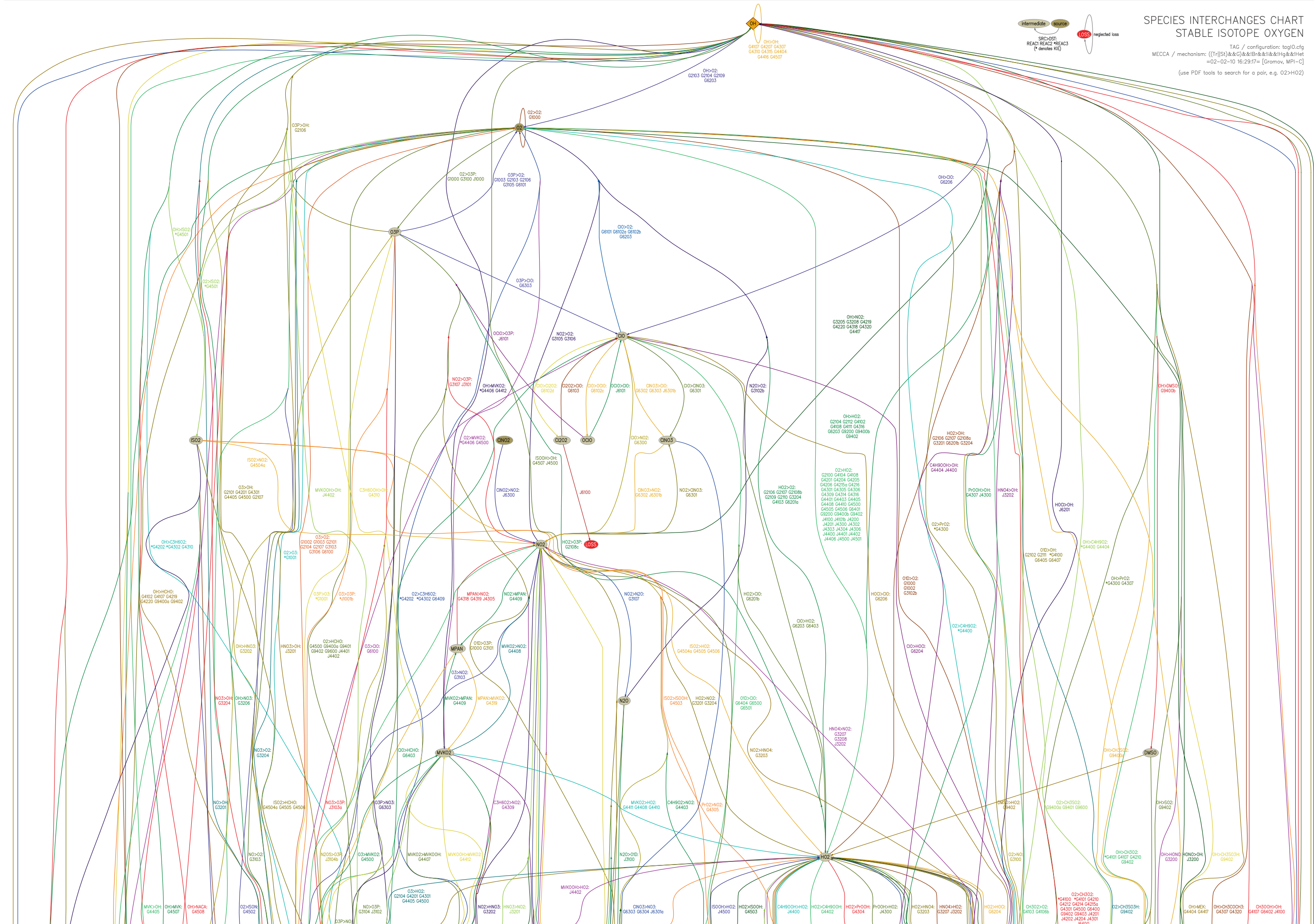


Chart B.2 Oxygen interchanges between the species in the chemical mechanism of MECCA employed in this study.

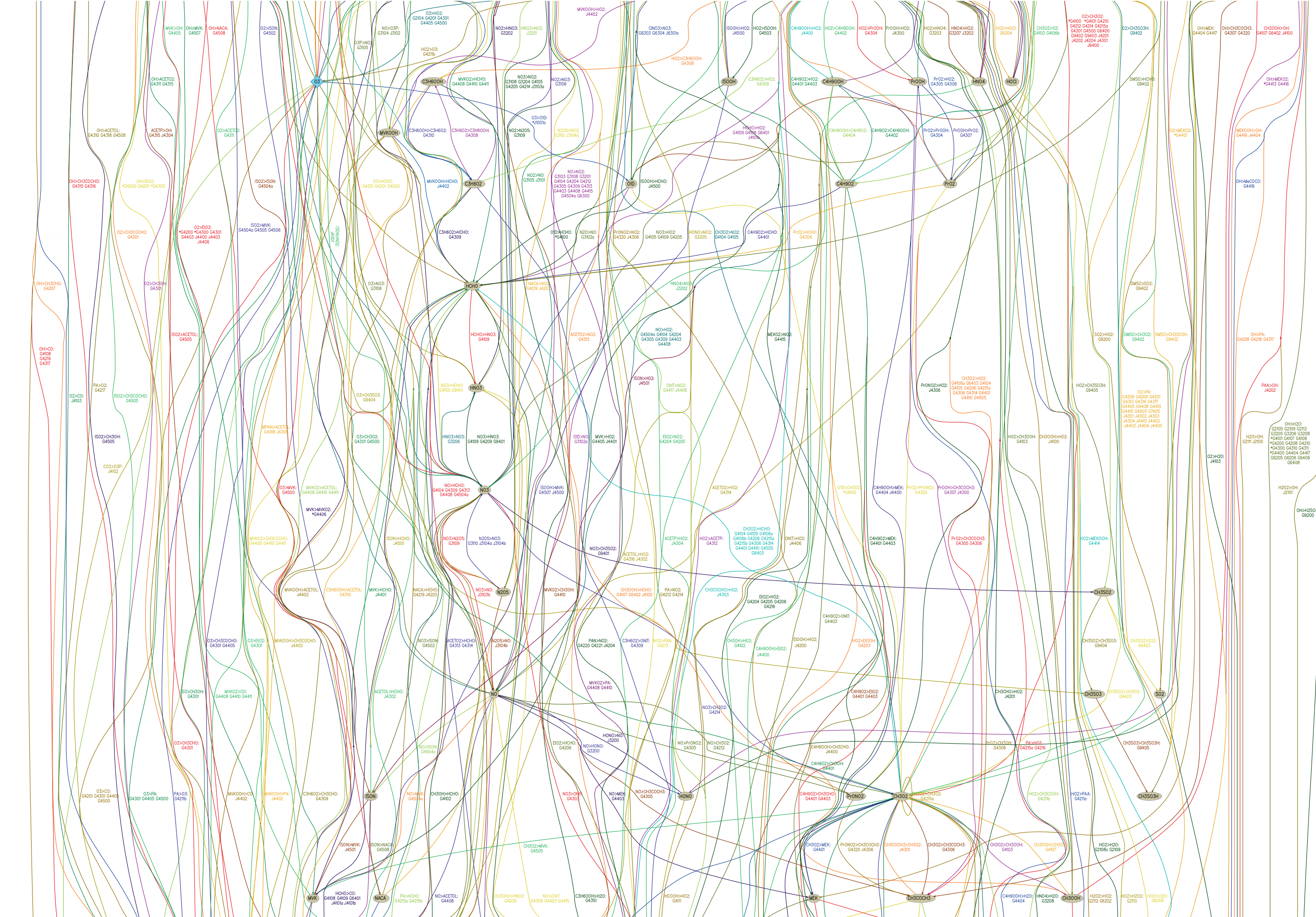


Chart B.2 Oxygen interchanges between the species in the chemical mechanism of MECCA employed in this study (continued).



Chart B.2 Oxygen interchanges between the species in the chemical mechanism of MECCA employed in this study (*last page*).

Appendix C. Correction of the CARIBIC-1 CO data

In this supplement, the analysis and correction procedure for the C1 WAS contaminated CO samples is described. The contamination is evident in Figure C.1 (panel (c)) in the large $\delta^{18}\text{O}(\text{CO})$ departures from the observed typical relationship, reaching beyond +18‰ as the mixing ratio decreases. The concomitant shifts in $\delta^{13}\text{C}(\text{CO})$ are less discernible due to the $\delta^{13}\text{C}$ signature of the artefact CO source being close to that of the typical tropospheric/UTLS sources (*ibid.*, panel (d), also see below). It is beyond doubt, however, that the oxygen composition originates from ozone, whose large enrichment in heavy oxygen (above +70‰ in $\delta^{18}\text{O}$) is exclusive in the atmosphere to induce such large deviations. In Figure C.1 (panel (c)), it is also notable that not only the samples with low [CO] are affected, *i.e.* elevations of (3–10)‰ above the typical $\delta^{18}\text{O}(\text{CO})$ maxima are present in samples with mixing ratios up to 100 ppb. These, however, result from the dilution of the least affected tropospheric samples with high [CO], by the substantially contaminated, CO-poor (*i.e.*, below 50 ppb) stratospheric air, sampled throughout ~20 minutes into the same WAS canister. Essentially, such artificial, sampling-induced mixing renders an unambiguous determination of the artefact source' isotope signature impossible, because neither the proportion nor the isotope composition of the admixed air parcels is actually known. The discrepancies between the WAS and on-line measured (using a GC-reducing gas analyser, see Zahn *et al.*^[2000]) CO mixing ratios in C1, a possible indication that the contamination pertains specifically to the WAS samples, generally lie within ± 4.5 ppb and happen to be random with respect to any operational parameter or measured characteristic in C1.¹⁵³ In addition, the discrepancy between WAS and on-line [CO] does not correlate with the anomaly in $\delta^{18}\text{O}(\text{CO})$; the latter, however, manifests a clear but complex function of the $[\text{O}_3]$ average. It is thus plausible that the C1 on-line and WAS data evince similar CO abundances.

A salient difference, however, is marked for the O_3 -CO distributions obtained along the same routes in the two different phases of the CARIBIC project (shown in Figure C.1, panel (a)). In CARIBIC Phase Two (hereafter referred to as "C2") ongoing since December 2004, the more advanced instrumentation and improved inlet system compared to C1 are employed (Brenninkmeijer *et al.*^[2007]). In particular, the on-line CO analysis in C2 is done by the vacuum ultraviolet (VUV) fluorescence instrument with lower measurement uncertainty and higher temporal resolution (± 3 ppb over 30 s in C1 *vs.* ± 2 ppb in ~2 s in C2, Zahn *et al.*^[2000], Scharffe *et al.*^[2012]). The detection frequency for $[\text{O}_3]$ has increased as well, from one in 16 s in C1 to 5 s⁻¹ samples in C2 (Zahn *et al.*^[2000], Brenninkmeijer *et al.*^[2007]). The distributions shown in Figure C.1 (panel (a)) are in effect the statistics on CO mixing ratios gathered for the samples with respective O_3 abundances clustered in 20 ppb bins, *i.e.* the average and spread (IQR, see note⁴⁸ on p. 76) of [CO] as a function of $[\text{O}_3]$ analysed on-line. Shown are the entire datasets (for C2, until December 2012), hence large [CO] IQRs in the bins with $[\text{O}_3]$ below 400 ppb primarily reflect large seasonal changes in the tropospheric CO abundance detected at the corresponding ozone levels. With O_3 amplifying, [CO] increasingly becomes stratospheric, and its variability drops to mere ± 1.5 ppb and below, as O_3 surpasses 500 ppb. Notwithstanding the comparable C1 and C2 [CO] spreads, from 400 ppb of O_3 on, the C1 CO mixing ratios start to level off, with no samples below 35 ppb detected, whereas C2 levels show a continuous decline. By the 580 ppb O_3 bin, the levels in C1 reach some extra 15 ppb in [CO] of $40.1^{+0.3}_{-1.1}$ ppb compared to the C2 average of $25.6^{+0.5}_{-0.6}$ ppb. Overall, the conspicuously high C1 [CO] is marked in 221 samples, of which 169 and 60 emerge as statistically significant mild and extreme outliers¹⁵⁴, respectively, with respect to the C2 statistics ($N \sim 250 \cdot 10^2$).

There are three factors that may lead to the (artefact) distributions such as seen for C1 [CO] at the large ozone abundances, namely:

(1) Strong (linear) natural mixing, such as enhanced stratosphere-troposphere exchange (STE), when the [CO] outside the statistically expected range ensues from the integration of the compositions with much

¹⁵³ Overall, the WAS and on-line measured CO mixing ratios correlate extremely well ($R^2 = 0.96$, slope 0.98, $N = 413$). The quoted mixing ratio discrepancy remained after several calibrations between the two systems had been performed. It is likely to result from the differences in the detection methods and from a drift of the calibration standards used (see details in Brenninkmeijer *et al.*^[2001]). The integrity of the WAS CO is further affirmed by the unsystematic distribution of the contaminated compositions with respect to the sampling canisters (an example of the opposite case for $\delta^{18}\text{O}(\text{CO}_2)$ in C1 is discussed by Assonov *et al.*^[2009]).

¹⁵⁴ The conventions here follow Natrella^[2003], *i.e.* ± 1.5 and ± 3 IQR ranges define the inner and outer fences of the C2 [CO] distribution in every ozone bin, respectively. The numbers quoted are the sums for the C1 bins with average $[\text{O}_3]$ of 420–620 ppb.

dissimilar ratios of the tracers' abundances, *viz.* $\rho_{\text{O}_3:\text{CO}} = [\text{O}_3]/[\text{CO}]$. For example, mixing of two air parcels in a 15%:85% proportion (by moles of air) with typical $\rho_{\text{O}_3:\text{CO}}$ of 700/24 (stratospheric) and 60/125 (tropospheric), respectively, yields an integrated composition with $\rho_{\text{O}_3:\text{CO}}$ of $\sim 600/40$ which indeed corresponds to the C1 data (this case is exemplified by the mixing curve in Figure C.1). Nonetheless, occurrences of rather high (compared to the typical 24–26 ppb) stratospheric CO mixing ratios (in our case, ~ 40 ppb at the concomitant $[\text{O}_3]$ of 500–600 ppb) are exceptional¹⁵⁵ and, for instance, were never observed by C2, whereas the C1 outliers were registered in some 12 flights during 1997–2001. No relation between these outliers and the 1997/1998 large-scale $[\text{CO}]$ perturbation event (see above, *e.g.* p. 69) was established, otherwise elevated CO mixing ratios should manifest themselves at lower $[\text{O}_3]$ as well. Besides, other tracers detected by CARIBIC give good evidence that there was no such strongly STE-mixed air captured by C1. That is, the binned distributions (similar to that for $[\text{CO}]$, presented in Figure C.2) for the water vapour and de-trended N_2O as a function of ozone are greatly similar in C1 and C2. Whereas the small relative variation in atmospheric $[\text{N}_2\text{O}]$ solely confirms matching $[\text{O}_3]$ in CARIBIC, the stratospheric $[\text{H}_2\text{O}]$ distributions witness no $\rho_{\text{O}_3:\text{H}_2\text{O}}$ characteristic for the strong mixing conditions required for the corresponding $\rho_{\text{O}_3:\text{CO}}$ from C1, suggesting the latter being unnaturally low.

(2) Mixing effects can also originate artificially, emanating from sampling peculiarities or data processing. Since the sampling in CARIBIC is not stationary, a mere 30 s long pumping of an air probe implies integration of the compositions encountered along some 7–8 km, owing to the high aircraft speed. This distance, for example, may fit a transect between tropospheric and stratospheric filaments of much different compositions. The effect of such 'translational mixing' can be simulated by averaging the sampling data with higher temporal frequency over longer time intervals. In this respect, the substantially more frequent (by a factor of ~ 15 , see above) CO data in C2 were artificially averaged over a set of increasing intervals to reckon whether longer sampling in C1 could be the culprit for skewing its CO– O_3 distribution. As a result, the original C2 ~ 2 s data and their 30 s averages (equivalent to the C1 CO sample injection time) differ negligibly, as do the respective $\rho_{\text{O}_3:\text{CO}}$ values; the actual CO– O_3 statistic at $[\text{O}_3]$ of 400 ppb and above remains robust for integrals of up to 300 s. Based on this result, the estimate of a characteristic UTLS 'mixing resolution', *i.e.* the scale at which the spatial gradients caused by the STE exceed the natural $[\text{CO}]$ variation, has a lower threshold of ~ 80 km or slightly greater. Furthermore, a very strong artificial mixing equivalent to an averaging interval of at least 20 minutes (comparable to C1 WAS sampling time) is required to yield the stratospheric outliers with $\rho_{\text{O}_3:\text{CO}}$ characteristic for the C1 data. It is therefore unlikely that any natural or artificial mixing processes are involved in the stratospheric $[\text{CO}]$ discrepancies seen in C1.

¹⁵⁵ An example of such is given by Pan *et al.*^[2004], who describe the observation of uncommonly high LMS CO abundances caused by a deep stratospheric intrusion event on top of enhanced STE at NH high latitudes in spring.

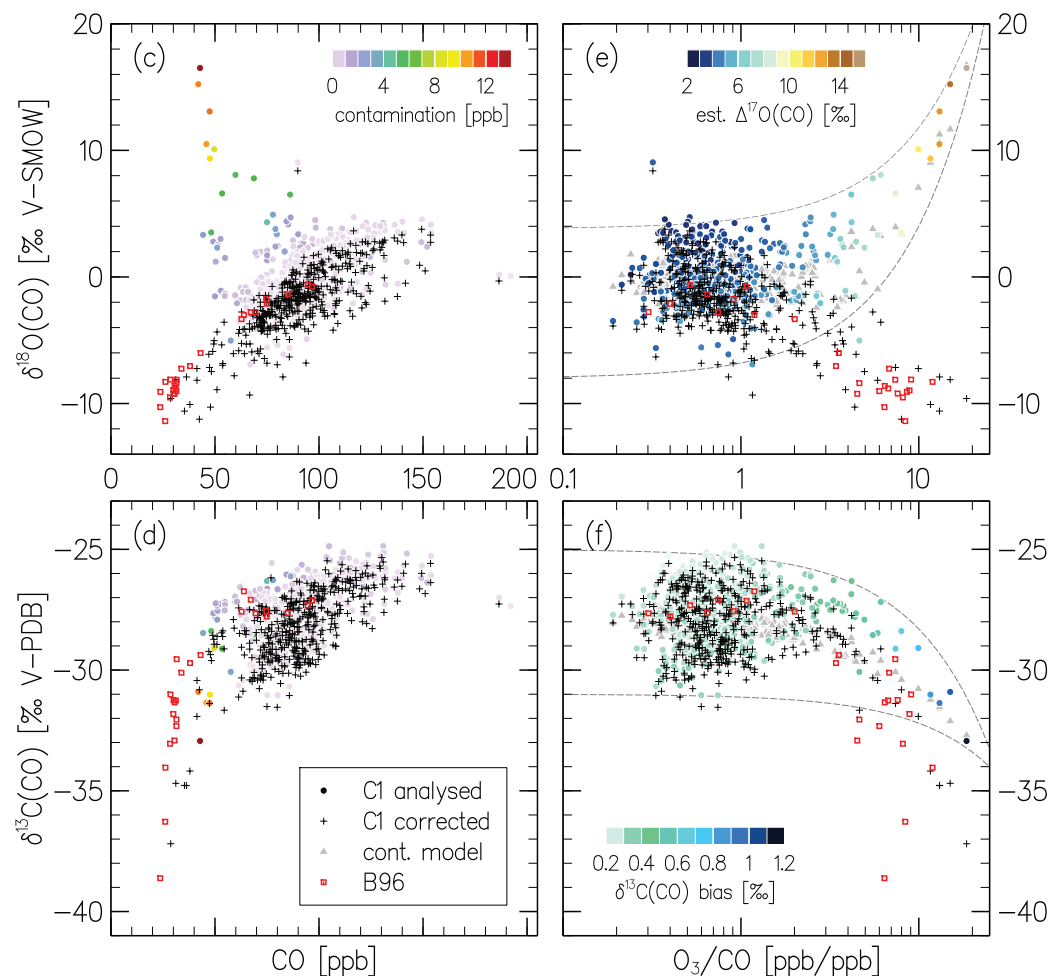
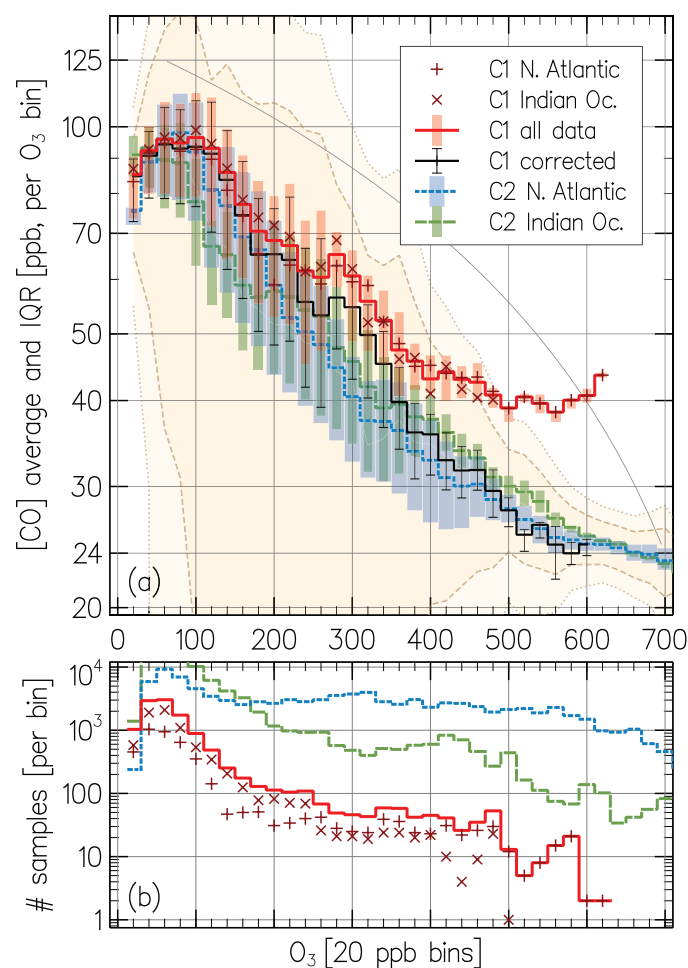


Figure C.1 Left: Comparison of the CO and ozone mixing ratios along the Atlantic and Indian Ocean routes analysed in CARIBIC during phases One (C1) and Two (C2) using the on-line instrumentation. Panel (a): Averages of [CO] from the samples with respective [O₃] falling in ± 10 ppb bins; the vertical bars denote the IQR of the [CO] distributions. The dashes and dotted lines show the inner and outer statistical fences for the aggregate of C2 data, respectively, demarking the ranges of mild and extreme outliers. The solid line exemplifies the mixing curve for parcels with very different $p_{O_2:CO}$ values. Panel (b): Number of samples selected in the corresponding O₃ bins. Right: Distributions of the analysed and corrected $\delta^{13}C(CO)$ and $\delta^{18}O(CO)$ from C1 WAS data as function of CO mixing ratio and in [O₃]/[CO] coordinates. Note the identical colour coding in panels (c) and (d). The grey triangles denote the results of the contamination model for $^{18}O\delta_{i,s,c} = (+4, -10, +78.5)\text{‰}$ and $^{13}C\delta_{i,s,c} = (-26.5, -31, -32.8)\text{‰}$, respectively (see text). The dashed lines envelope the approximate variation in the contamination model results for the range of $^{18}O\delta_i$ within -4‰ to $+8\text{‰}$, and of $^{13}C\delta_i$ within -31‰ to -24‰ , respectively. The colour code in panel (f) denotes the bias in the analysed $\delta^{13}C(CO)$ due to the overabundant C¹⁷O, *i.e.* unexpectedly high $\Delta^{17}O(CO)$ values. Red symbols (B96) refer to the observations of CO isotopes in the UTLS by Brenninkmeijer *et al.*^[1996].

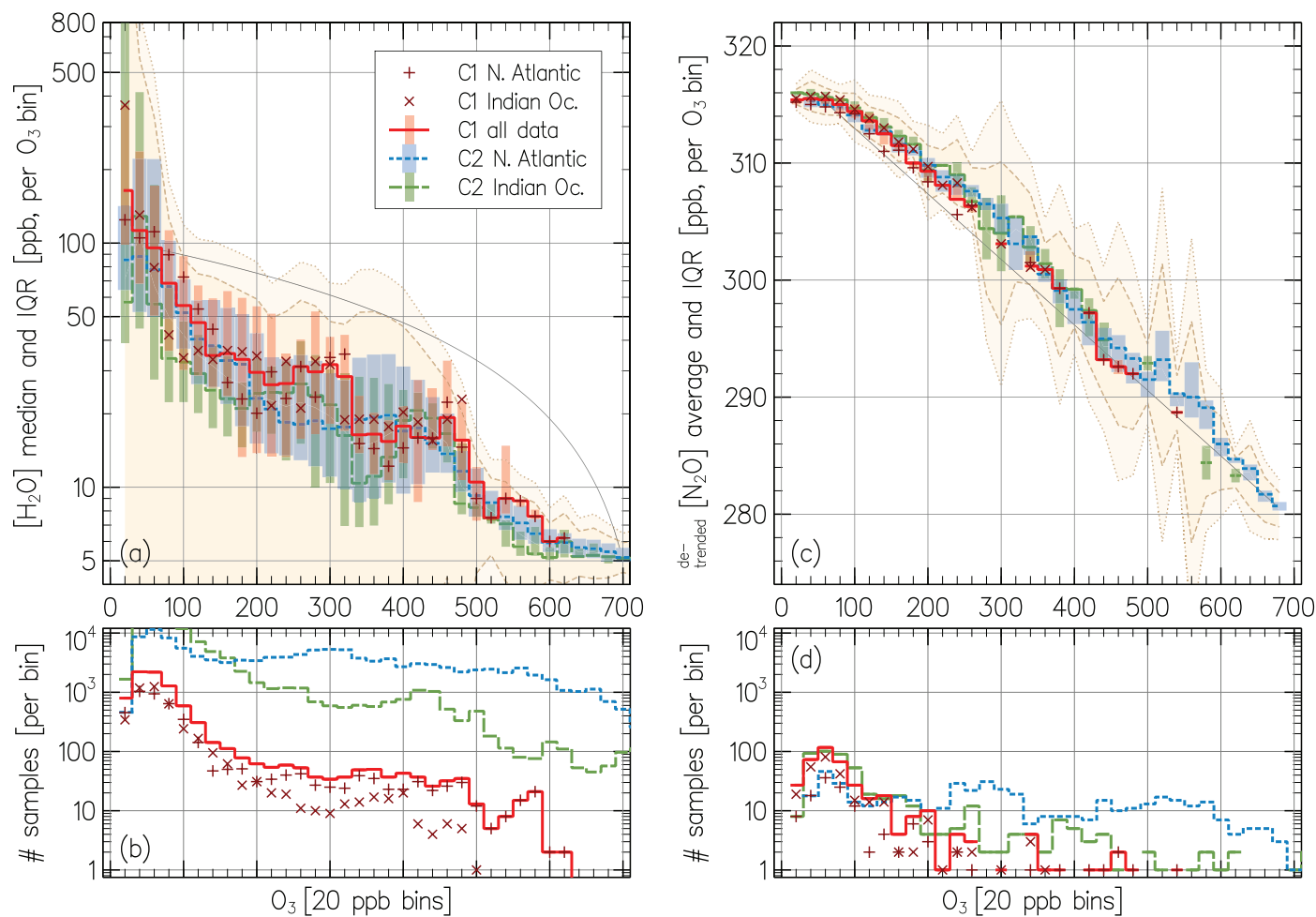


Figure C.2 (complements Figure C.1) Distributions of the water vapour and (de-trended) N_2O mixing ratios as a function of concomitant ozone abundance analysed in CARIBIC during phases One (C1) and Two (C2) along the Atlantic and Indian Ocean routes. Left: Panel (a): Median of $[\text{H}_2\text{O}]$ from the samples with corresponding $[\text{O}_3]$ falling in ± 10 ppb bins; the vertical bars denote the IQR of the $[\text{H}_2\text{O}]$ distributions. The dashes and dotted lines show the inner and outer statistical fences for the aggregate of C2 data, respectively, demarking the ranges of mild and extreme outliers. The solid line exemplifies the mixing curve for parcels with very different $\rho_{\text{O}_2:\text{H}_2\text{O}}$ values (tropospheric 60/95 and stratospheric 700/5, respectively, corresponding the $[\text{CO}]$ mixing line shown in Figure C.1). Panel (b): Number of samples selected in the corresponding O_3 bins. Right: Panels (c) and (d): Analogous distributions for N_2O . Note, the N_2O data comes from the WAS analyses in both C1 and C2, thus it is subject to sampling-mixing effects (see text). In contrast to the H_2O - O_3 distributions, ruling out potential strong STE is impeded by the low variation in atmospheric $[\text{N}_2\text{O}]$. The N_2O - O_3 distributions, however, complementary attest that the C1 and C2 $[\text{O}_3]$ profiles agree well.

(3) It is sensible to surmise that the sample contamination in C1 has occurred likely prior the probed air has reached the analytical instrumentation in the container, since elevated stratospheric CO mixing ratios are confirmed by both, WAS and on-line data. Two more indications, *viz.* growing [CO] discrepancy with increasing O₃ abundance, and the strong concomitant signal in $\delta^{18}\text{O}(\text{CO})$, suggest that the ozone-mediated photochemical production of CO took place. It is possible to infer the ozone-exclusive functional dependence of the contamination strength C_c , discriminating the C1 outliers from respective C2 data in the following kinetic framework:

$$\begin{aligned} \text{O}_3 &\xrightarrow{\text{O}_3 k_r} \left(\left(\dots + \text{X} \xrightarrow{{}^X k_r} \right)_K \right)_{(\kappa-1)} \rightarrow \lambda_{\text{O}_3} \text{CO} \\ C_c &= \int_{\tau_c} \prod_{\kappa} \text{O}_3 k_r [\text{O}_3] \prod_K {}^X k_r [\text{X}] dt \propto \lambda_{\text{O}_3} k_r [\text{O}_3]^\kappa \tau_c \end{aligned} \quad (6.4)$$

where k_r denotes the overall pseudo-first-order rate coefficient of the reaction chain leading to the artefact CO production with the respective yield λ_{O_3} . The individual rate coefficients ${}^X k_r$ and $\text{O}_3 k_r$ pertain to the unknown compound(s) X and ozone reacting with the integral stoichiometry factors K and κ , respectively. The relation defined by Eq. (6.4) provides the best approximation for C_c as a function of [O₃] at $\kappa = 2.06 \pm 0.38$, strongly suggesting two chain steps involving O₃ or its derivatives. At $\kappa = 2$, the ratio $C_c/[\text{O}_3]^2$ (essentially proportional to the reaction rate k_r and time τ_c) is found to be $(4.59 \pm 0.11) \cdot 10^{-5} \text{ ppb}^{-1}$ (adj. $R^2 = 0.83$, red. $\chi^2 = 1.02$). The low uncertainty (within $\pm 3\%$) of this estimate signifies a mere dependence of the contamination source on the ozone abundance, as well as much comparable reaction times τ_c . That is, the probed air was likely uniformly exposed to the contamination conditions in the sampling line, rather than during the more variable (typically within 1–2 days) periods of storage in the WAS canisters. The estimated artefact source strength C_c spans approximately 7–18 ppb throughout the respective [O₃] range of 400–620 ppb, and, when subtracted, yields the corrected C1 CO–O₃ distribution conformable to those of C2 (shown as black line in Figure C.1, panel (a)). It is possible to constrain the overall yield λ_{O_3} of CO molecules in the artefact source chain to be between unity and one-half, comparing the magnitude of C_c to the discrepancy between the [O₃] measured in C1 and C2 (± 20 ppb, taken equal to the [O₃] bin size through the well-matching N₂O–O₃ and H₂O–O₃ distributions shown in Figure C.2). Lower λ_{O_3} values, otherwise, should have resulted in a noticeable (*i.e.*, greater than 20 ppb) decrease in the C1 WAS O₃ abundances with respect to the C2 levels.

Having estimated the contamination strength from the on-line CARIBIC data, one can apply it for correcting the respective C1 WAS data, specifically the CO isotope ratios. As it was mentioned above, the WAS compositions are also subject to strong sample-mixing effects that yield apparent $\delta^{18}\text{O}(\text{CO})$ outliers marked even for relatively high [CO] up to 100 ppb (see Figure C.1, panel (c)). It is thus necessary to distinguish the proportions of the least modified (tropospheric) and significantly contaminated (stratospheric) components, in order to exclusively correct the composition of the latter in the resultant WAS sample mix. On the other hand, the correction approach should be dexterous to determine the contamination source isotope signatures as well. In practice, it is adequate to use an unsophisticated isotope mass-balance model formulated as

$$\begin{cases} {}^i \delta_a C_a = (C_a - C_c) {}^i \delta_t + C_s ({}^i \delta_s - {}^i \delta_t) + \varphi_s C_c {}^i \delta_c \\ \varphi_s = C_s / (C_a - C_c) \end{cases} \quad (6.5)$$

where indices a , c , t and s distinguish the abundances C and isotope compositions ${}^i \delta$ (i refers to ^{13}C or ^{18}O) pertaining to the analysed sample, estimated contamination, typical tropospheric and stratospheric air, respectively. The first two RHS members in Eq. (6.5) determine the “true”, non-contaminated composition in question of the abundance $(C_a - C_c)$ including the stratospheric component C_s . The last member describes the contamination component C_c (reckoned at the average O₃ abundance for a given C_s) weighted by the stratospheric air quotient φ_s . So the closer the “true” abundance $(C_a - C_c)$ to stratospheric (C_s), the closer φ_s is to unity. Ultimately, the contamination model (CM) defined in Eq. (6.5) allows inferring the sensitivity of the analysed isotope compositions ${}^i \delta_a$ to the contamination source in the range of sampled [CO], that is C_a .

For instance, for a typical stratospheric component C_s of 30 ppb or less (and the remaining isotope signatures ${}^i \delta$ in their typical range), the CM gauges the sensitivity of ${}^i \delta_a$ to the contamination significant only when the sample’s respective $\rho_{\text{O}_3:\text{CO}}$ value (the [O₃]/[CO] ratio) exceeds ~ 3 . That is generally the case for all samples with ozone abundances of 200 ppb and higher. Such relationship is indeed observed for the analysed

CO isotope ratios, as seen in Figure C.1 (panels (e), (f)) presenting the WAS data as a function of $\rho_{\text{O}_3:\text{CO}}$. Both $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$ monotonically converge as $\rho_{\text{O}_3:\text{CO}}$ grows, because deeper stratospheric compositions happen *less often* to mix with the tropospheric ones. Importantly, $\rho_{\text{O}_3:\text{CO}}$ embodies a measure of both, mixing and contamination processes, as opposed to φ , which mostly correlates with the mixing intensity but does not highlight the contamination character. In other words, the scatter in $^i\delta_a$ observed at a particular $\rho_{\text{O}_3:\text{CO}}$ value originates from the variations in φ , and $(^i\delta_s - ^i\delta_t)$, that is the dissimilarity between the tropospheric and stratospheric CO isotope signatures. The marked $\rho_{\text{O}_3:\text{CO}}$ -dependent relationship, in turn, is sensible in the contamination framework, because greater $[\text{O}_3]$ prompts more artefact CO produced, and lower overall $[\text{CO}]$ implies greater sensitivity to the contamination. Calculations with the CM confirm, however, that the variations in $^i\delta_a$ caused by the mixing effects (mostly by the variations in $^{18}\text{O}\delta_t$ and φ_t) are substantial even at high $\rho_{\text{O}_3:\text{CO}}$ values. For example, a typical $\sim 8\text{‰}$ variation in the tropospheric $\delta^{18}\text{O}(\text{CO})$ scales down to still noticeable scatter of $\sim 4\text{‰}$ in $^{18}\text{O}\delta_a$ at $\rho_{\text{O}_3:\text{CO}}$ of 10 and above.

On the other hand, fitting the observed data in the CM framework indicates that the slopes of $^i\delta_a(\rho_{\text{O}_3:\text{CO}})$ are chiefly determined by the contamination source signature ($^i\delta_c$), whereas the other parameters (*i.e.*, $^i\delta_s$, $^i\delta_t$ and φ_t) merely adjust the average (slope intercept) and variation of $^i\delta_a$. It is hence feasible to obtain an independent estimate of the contamination source isotope signature in a regression analysis by fitting the actual C_a , $^i\delta_a$, C_c and $[\text{O}_3]$ available from the on-line/WAS data. Practically, one finds the range of $^i\delta_c$ values at which the CM yields the range of slopes through the observed $\delta^{13}\text{C}(\text{CO})$ and $\delta^{18}\text{O}(\text{CO})$, as exemplified by the dashed lines in Figure C.1 (panels (e) and (f)). A typical fit calculated using some invariable $^i\delta_{t,s,c}$, estimated φ_t , C_c and actual C_a from the WAS data is presented besides (grey symbols). In this particular case, the variation of the expected $\delta^{18}\text{O}(\text{CO})$ and $\delta^{13}\text{C}(\text{CO})$ is underestimated being driven merely by the changes in φ_t . In reality, the difference between the stratospheric and tropospheric compositions ($^i\delta_s - ^i\delta_t$) is variable as well and enhances the spread caused by φ_t , *i.e.* by mixing only. To yield the observed $^{18}\text{O}\delta_a$ variation in the CM, a typical $(^{18}\text{O}\delta_t - ^{18}\text{O}\delta_s)$ value of $(20 \pm 5)\text{‰}$ is required, which is in good agreement with the estimates of average tropospheric and stratospheric $\delta^{18}\text{O}(\text{CO})$ of $+9.5_{-3.8}^{+10.3}\text{‰}$ and $-8.9_{-2.3}^{+1.8}\text{‰}$, respectively (Brenninkmeijer *et al.*^[1996], see also Sects. 4.2 and 3.5.1, refs. to Table 3.7, p. 56).

Ultimately, the CM analysis returns the artefact CO isotope signatures in a relatively narrow range. The regression yields $^{18}\text{O}\delta_c = (+78.5 \pm 4.8)\text{‰}$ and $^{13}\text{C}\delta_c = (-32.8 \pm 3.2)\text{‰}$, respectively, with the uncertainties denoting the $\pm 2\sigma$ of the $^i\delta_c$ values best-fitting the $^i\delta_a(\rho_{\text{O}_3:\text{CO}})$ slopes through the observational data. The inferred $^{18}\text{O}\delta_c$ signature unambiguously pertains to ozone and is somewhat lower compared to the measured mid-latitude LMS $\delta^{18}\text{O}(\text{O}_3)$ average of $(+95.8 \pm 6.4)\text{‰}$ (see Krankowsky *et al.*^[2007] and references therein), albeit in a good agreement with the tropospheric estimates of $(+91.0 \pm 5.9)\text{‰}$ (Krankowsky *et al.*^[1995]) and $(+86.0 \pm 11.2)\text{‰}$ (Johnston and Thiemens^[1997]). Noteworthy, lowering of $^{18}\text{O}\delta_c$ may result from the moderate fractionation due to the KIEs likely escorting the artefact CO production. Although not quantifiable here, they cannot be ruled out, recalling that the yield λ_{O_3} of CO in the $\text{O}_3 \rightarrow \text{CO}$ chain may be lower than unity (see above, p. 249). Concerning the $^{13}\text{C}\delta_c$ signature, its value is typical for the $\delta^{13}\text{C}$ of a wide range of organic compounds, *e.g.* tropospheric VOCs (see, *e.g.*, Sect. 5.2.5). The ^{13}C KIEs are not known too, but may play a more substantial (than the ^{18}O KIEs) role in determining the $^{13}\text{C}\delta_c$ value, owing to the readily available C for the artefact CO production (the source strength C_c primarily depending on $[\text{O}_3]$ corroborates that). Besides, the conditions that upheld the reaction of ozone (or its derivatives) followed by the production of CO are vague. A few hypotheses ought to be scrutinised here. First, a rapid $\text{O}_3 \rightarrow \text{CO}$ reaction rate is expected, owing to short (*i.e.*, fraction of a second) exposure time of the probed air to the contamination. Accounting for the typical C1 sampling conditions¹⁵⁶, the overall reaction rate coefficient (k_t in Eq. (6.4)) must be of the order of $7.4 \cdot 10^{-15}/\tau_t$ [$\text{molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$], where τ_t is the exposure time. Taking the simplest case of one unknown compound X at a tiny abundance of 0.1 ppt reacting over $\tau_t = 1/100 \text{ s}$ with ozone, the respective $2\text{O}_3 + \text{X} \rightarrow \text{CO}$ reaction rate coefficient $k_{\text{O}_3+\text{X}}$ must be of $\sim 1.1 \cdot 10^{-18}$ [$\text{molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$]. This number proportionally decreases with growing τ_t and $[\text{X}]$, if we take less strict exposure conditions. Reckoned above estimate renders very likely the surmise that some organic compound could have been ozonolysed to produce CO, as $k_{\text{O}_3+\text{X}}$ is well within the order of the rate coefficients for ozonolysis of (cyclo-, poly-) alkenes as well as C_{4+} oxygenates (see Oyama^[2000] and references therein). In the case of alkenes, the evidence of direct transfer of oxygen isotope composition to the product CO from ozone was estab-

¹⁵⁶These are: sampled air pressure (200 hPa) and temperature (216K typical for UTLS to $\sim 340\text{K}$ for the heated inlet), air intake rate ($\sim 12.85 \cdot 10^{-3} \text{ moles s}^{-1}$, corresponding 350L STP of air sampled in 1200 s), inlet/tubing volume (11.5 to 1150 cm^3 , unknown, gauged to yield exposure times of 0.01 to 1 s, respectively).

lished in the laboratory (Röckmann *et al.*^[1998a]). Second, a more complex surface physics and heterogeneous chemistry on the heated inlet or supplying tubing may be involved. Such can be the tracers' surface adsorption, (catalytic) decomposition of ozone and its reaction with VOCs or with surface carbon that also may lead to the production of CO (see Oyama^[2000] for a review). It is probable that sub- to ppt amounts of organics have remained on the walls of the sampling line exposed to highly polluted tropospheric air, to be later broken down by the ample stratospheric ozone. Unfortunately, the scope for a further inquiry into the implications of admissible although implex surface effects in the C1 CO contamination problem is currently limited.

Finally, the CM may be straightforwardly employed for the correction of the analysed compositions. The samples adjusted for the artefact CO are presented alongside in Figure C.1 (panels (c) to (f), grey “pluses”). Fortunately, the C1 data may be contrasted with the available comprehensive UTLS isotope CO observations by Brenninkmeijer *et al.*^[1996] (referred to hereafter as “B96”, denoted with red symbols in Figure C.1). Obtained in several aircraft flights between New Zealand and Antarctic in October 1993, these data represent the ETSH compositions exquisitely covering the range of atmospheric conditions from typical tropospheric to essentially LMS. Regarding the adjusted C1 CO mixing ratios, the CM correction redistributes the bulk of most contaminated samples (clustered within 40–60 ppb) below 50 ppb, with the minima reaching 30 ppb conformable with characteristic LMS abundances. Substantial (larger than 1 ppb) adjustments to [CO] pertain to the samples with abundances of up to 100 ppb, but only those with respective $\rho_{\text{O}_3:\text{CO}}$ above ~ 2 . Overall, these amount to 60, or $\sim 15\%$ of the total 410 WAS samples apt for correction. In comparison to the B96 data, C1 CO reflects generally a larger span of the NH upper tropospheric CO up to 150 ppb, as well as higher stratospheric minima (28.7 *vs.* 23.7 ppb, respectively), howbeit these could result from the mixing effects in the WAS or from the constraint on the flight altitude in C1 that reduces the likelihood of encountering deeper stratospheric air.

Judging by the much compact corrected distribution of $\delta^{18}\text{O}(\text{CO})$, the CM is well suited for estimating the contamination magnitude, yielding the slope of adjusted $\delta^{18}\text{O}(\text{CO})$ *vs.* [CO] in C1 analogous to that of B96. A few perceptibly low $\delta^{18}\text{O}(\text{CO})$ at [CO] between 60 and 100 ppb may result from the overestimated ϕ , values, yet the concomitant $\delta^{13}\text{C}(\text{CO})$ values do not confirm that. Alternatively, these samples may represent an aged tropospheric air largely modified by the effective sink fractionation that elevates $\delta^{13}\text{C}(\text{CO})$ but lowers $\delta^{18}\text{O}(\text{CO})$, respectively. The well-matching correspondence between the C1 and B96 data is more discernible in the plots with $\rho_{\text{O}_3:\text{CO}}$ being the abscissa, where the transition between the exclusively tropospheric ($\rho_{\text{O}_3:\text{CO}} < 1$) and stratospheric ($\rho_{\text{O}_3:\text{CO}} > 7$) $\delta^{18}\text{O}(\text{CO})$ is marked. The growing scatter in C1 $\delta^{18}\text{O}(\text{CO})$ towards lower $\rho_{\text{O}_3:\text{CO}}$ values resembles a typical mixing pattern, with the tropospheric endmembers seasonally varying within $\pm 4\%$. In the B96 data, conformably, merely the shift towards the October tropospheric average of $+2\%$ is seen. Importantly, the corrected C1 CO corroborates the finding of B96 that the stratospheric endmembers' $\delta^{18}\text{O}(\text{CO})$ is likely to be found around -9% . Moreover, this evidence comes through the much more regular observations in the NH, that is, the relevant samples (with $\rho_{\text{O}_3:\text{CO}} > 2$) were observed by C1 all year round except for in February, March and September. In contrast to $\delta^{18}\text{O}(\text{CO})$, LMS $\delta^{13}\text{C}(\text{CO})$ presents a more involved case, with the relative ^{13}C abundance in CO progressively decreasing with higher $\rho_{\text{O}_3:\text{CO}}$. The reason for this is the substantial dissimilarity between the relevant photochemical CO sources in their $\delta^{13}\text{C}$ signatures, as opposed to those for $\delta^{18}\text{O}$. In the LMS, CO is exclusively produced from CH_4 reacting with OH, $\text{O}(^1\text{D})$ and atomic Cl, and the relative importance of the latter two increases as we go deeper into the stratosphere. The $\delta^{18}\text{O}$ of CO from the $\text{CH}_4 + \text{O}(^1\text{D}) + \text{Cl}$ reactions is much similar to that in reaction with OH dominating in the troposphere. That is perhaps due to the same source O_2 (and concomitant KIEs) entering the intermediate methyl radical (CH_3) produced in the initial CH_4 oxidation step.¹⁵⁷ This very first step, however, is escorted with very different ^{13}C KIEs in reactions with $\text{O}(^1\text{D})$ and Cl, both leading to CO with $\delta^{13}\text{C}$ signatures lower than that of the $\text{CH}_4 + \text{OH}$ source (see Sects. 3.4.1.1 and 5.2.6, also 6.2.7.3). In particular, the methane reaction with Cl yields CO with $\delta^{13}\text{C}$ of around -110% , extremely light even in comparison with $\sim -60\%$ from the $\text{O}(^1\text{D})$ -mediated oxidation. Further, B96 elucidate that the fraction of their stratospheric data pertains to the ozone hole conditions characterised with a large free Cl radical availability. Essentially these samples contribute to the large scatter in

¹⁵⁷ See details in Sects. 3.3.2.3 and 3.4.2. A clear indication (although qualitative only) that the $\delta^{18}\text{O}$ signature of CO stemming from $\text{CH}_4 + \text{Cl}$ is lower than that from $\text{CH}_4 + \text{O}(^1\text{D})$ is present in B96, developed in the mutual variations in LMS $\delta^{18}\text{O}(\text{CO})$ and $\delta^{13}\text{C}(\text{CO})$, respectively. Noteworthy, reactions of CH_4 with $\text{O}(^1\text{D})$ yield CH_3 only in $\sim 75\%$ of the cases, whereas the remaining pathways proceed with direct production of $\text{CH}_3\text{O}/\text{CH}_2\text{OH}$ ($\sim 20\%$) and HCHO ($\sim 5\%$), respectively (Sander *et al.*^[2006]). These could account for the CO with much higher $\delta^{18}\text{O}$ arriving from O_2 or $\text{O}(^1\text{D})$. The latter is likely to inherit its isotope composition from the highly enriched ozone (see also Sect. 6.2.8, p. 210). The $\delta^{18}\text{O}(\text{CO})$ from the $\text{O}(^1\text{D})$ pathway is thus to be within -1% to $+13\%$, as opposed to -9% in reactions of CH_4 with Cl.

$\delta^{13}\text{C}(\text{CO})$ seen in Figure C.2 (panel (f)) at the $\rho_{\text{O}_3:\text{CO}}$ above ~ 3 . The intensified CH_4+Cl source lightens CO, whereas the $\rho_{\text{O}_3:\text{CO}}$ ratio decreases at the expense of the concomitantly low $[\text{O}_3]$ and elevated $[\text{CO}]$. This way the points become shifted lower-left from the otherwise expected monotonically converging distribution seen in the corrected C1 $\delta^{13}\text{C}(\text{CO})$ data. An interesting observation is the least variable $\delta^{13}\text{C}(\text{CO})$ at the $\rho_{\text{O}_3:\text{CO}}$ values between 2 and 3 that locate the region where the effective CO ^{13}C sink cancels out due to the inversion of the $^{13}\text{CO}+\text{OH}$ KIE with decreasing pressure (see Sect. 3.4.4 for details).

Last but not least, the C1 $\delta^{13}\text{C}(\text{CO})$ data went through the ancillary correction owing to the specifics of the laboratory determination of the CO isotopologues' abundances. Atmospheric O_3 carries an anomalous (or mass-independently fractionated, MIF) composition with a substantially higher relative enrichment in ^{17}O (equivalent to $\Delta^{17}\text{O}$ of $\sim +30\text{‰}$) compared to the majority of terrestrial oxygen reservoirs that are mass-dependently fractionated (*i.e.*, with $\Delta^{17}\text{O}$ of $\sim 0\text{‰}$) (see details in Sects. 3.2, 3.4.3 and 5.2.8). CO is a MIF tracer as well, possessing, however, a modest signal of $\Delta^{17}\text{O}(\text{CO}) = (4 \pm 2)\text{‰}$ (see, *e.g.*, Sect. 4.1.3). Therefore, large contamination of CO by O_3 induces proportionally large changes to $\Delta^{17}\text{O}(\text{CO})$ that exceed its natural atmospheric variation. On the other hand, MIF has implications in the analytical determination of $\delta^{13}\text{C}(\text{CO})$, because the presence of C^{17}O species interferes with the mass-spectrometric measurement of the abundances of ^{13}CO possessing the same molecular mass. If it is not possible to infer the exact $\text{C}^{17}\text{O}/\text{C}^{18}\text{O}$ ratio in the analysed sample, analytical techniques usually involve assumptions (*e.g.*, mass-dependently fractionated compositions or a certain non-zero $\Delta^{17}\text{O}$ value) with respect to the C^{17}O abundances (Assonov and Brenninkmeijer^[2001]). In effect for the C1 CO data, the artefact CO produced from O_3 had contributed with unexpectedly high C^{17}O abundances that led to the overestimated analysed $\delta^{13}\text{C}(\text{CO})$. Reckoning (with the CM) the contamination magnitude and assuming the typical ozone MIF composition being $^{17}\Delta$, it is possible to estimate the respective bias $^{13}\text{C}\delta_b$ as

$$\begin{cases} ^{13}\text{C}\delta_b = 7.2568 \cdot 10^{-2} \left(^{17}\Delta_n (\text{C}_a - \varphi_c \text{C}_c) + ^{17}\Delta_c \varphi_c \text{C}_c \right) (\text{C}_a)^{-1} \\ ^{17}\Delta_n = 1.6 + \left(0.213 (\text{C}_a - \text{C}_c)^{-1} \right) \end{cases}, \quad (6.6)$$

where $^{17}\Delta_n$ denotes the natural, *i.e.* expected “true” variation in $\Delta^{17}\text{O}(\text{CO})$, expressed as a function of the reciprocal “true” $[\text{CO}]$. The remaining parameters in Eq. (6.6) pertain to the contamination model (Eqs. (6.4)–(6.5)). Having no better proxy, the fit for $^{17}\Delta_n$ is derived from the $\Delta^{17}\text{O}(\text{CO})$ simulated at the C1 domain with EMAC in this study (“AE” simulation, see Sect. 6.2.1, p. 164), and provides typical values within $+(3\text{--}5)\text{‰}$ for tropospheric CO, asymptotically reaching around $+6\text{‰}$ for the LMS CO. For the ozone MIF signature $^{17}\Delta_c$, the value of $+30\text{‰}$ is adopted (see Sects. 3.4.3, 3.5.1 and 6.2.8.2 for references). The coefficient that proportionates $^{13}\text{C}\delta_b$ with $^{17}\Delta_c$ and $^{17}\Delta_n$ essentially defines the bias that the analysed $\delta^{13}\text{C}(\text{CO})$ receives due to unaccounted MIF (*e.g.*, if the MIF sample is assumed to be mass-dependently fractionated). In case of mass-spectrometric detection of CO isotopes, it is about extra $+0.73\text{‰}$ in the analysed $\delta^{13}\text{C}(\text{CO})$ per every $+10\text{‰}$ of $\Delta^{17}\text{O}(\text{CO})$ exceeding the assumed value (Assonov and Brenninkmeijer^[2001]). The estimated overall (contaminated) $\Delta^{17}\text{O}(\text{CO})$ signature and magnitude of $^{13}\text{C}\delta_b$ are presented in the colour-code of the points in Panels (e) and (f) of Figure C.1, respectively. Thus, the most contaminated compositions at $\rho_{\text{O}_3:\text{CO}}$ above ~ 6 are reckoned to carry $\Delta^{17}\text{O}(\text{CO})$ exceeding the upper limit of $+7\text{‰}$ of the natural variation in CO, ranging up to $+14\text{‰}$ when the fraction of the artefact CO in the sample reaches $\sim 1/2$. Accordingly, the largest $\delta^{13}\text{C}(\text{CO})$ biases reach $+1.2\text{‰}$, however for the majority of the LMS compositions the correction amounts to $+(0.4\text{--}0.6)\text{‰}$, and below that for the tropospheric ones. To note, $^{13}\text{C}\delta_b$ contributes to some $1/4$ of the overall correction to the WAS $\delta^{13}\text{C}(\text{CO})$ inferred here.

Recapitulating, the above given analysis corroborates that: (1) The O_3 -mediated contamination of CO is confirmed in C1, as seen in both, the on-line and WAS $[\text{CO}]$ and $\delta^{18}\text{O}(\text{CO})$ data. The fraction of the substantially affected samples amounts to $\sim 15\%$ of the total number of WAS data. The notably elevated stratospheric CO abundances marked in C1 are gauged statistically significant outliers with respect to the large C2 CO observations statistic. The comparison of the simultaneously measured (in both C1 and C2) water vapour and N_2O abundances rules out any potential mixing effects that may have contributed to the uncommonly high CO in C1, *e.g.* a strong natural STE or artificial sampling-mixing effects. (2) Of the remaining hypotheses, the rapid ozone-mediated photochemical production of CO appears plausible. The differences in $[\text{CO}]$ between the C1 and C2 data were analysed in the kinetic contamination model. The latter suggests that a photochemical chain converting likely two O_3 molecules and readily available unknown carbonaceous compound(s) into one artefact CO may explain the contamination. The estimates of the contamination reaction rate confirm that even

reacted in very short time, tiny amounts of organics (*e.g.* sub-ppt levels of alkenes) are capable of producing CO amounts comparable to the contamination observed. The source of organics is not ascertained, as well as the potential involvement of the heterogeneous chemistry on the surfaces of the inlet/tubing of the C1 sampling system. (3) In conjunction with an isotope mass-balance model, the CM provides independent estimates of the isotope signatures of the contamination source. Oxygen isotopes confirm the highly enriched composition of the artefact CO of $(+78.5 \pm 4.8)\text{‰}$ characteristic for O_3 . The concomitant $\delta^{13}\text{C}$ signature of $(-32.8 \pm 3.2)\text{‰}$ is typical for a wide range of organics. In addition, analytical biases in the measured C1 $\delta^{13}\text{C}(\text{CO})$ due to uncommonly large C^{17}O from O_3 were estimated. This all ultimately allowed performing necessary corrections to the C1 WAS CO mixing and isotope ratio data.

Appendix D. EMAC results supplementary plots

Current supplement presents the detailed distributions of the selected species/characteristics simulated with EMAC model in this study. Aggregated in two-paged Plates below, averages over various domains, dimensions and time frames are shown. Table D.1 lists these, complemented with Figure D.1 describing the legend used for the plots with two-dimensional distributions (first page of each Plate). In the latter, the abbreviations identifying the simulation (see Table 6.5, p. 165), integral averages and the means, minima and maxima in a particular domain (plot) are quoted. The second page of each Plate presents the one-dimensional distributions of the respective characteristics (*e.g.*, zonal averages). Note that the error bars denote the variations in different characteristics and/or dimensions (these, *e.g.*, may be seasonal variations in monthly zonal averages or latitudinal span of the values in particular domain).

Table D.1 Domains, zonal partitioning and averages presented in the supplementary plots

<i>Abbr.</i>	<i>Analysed domain</i>	<i>Description</i>		
SRF	Surface	Lowest model layer		
BL	Boundary Layer	Layers under planetary boundary layer (PBL) height		
MBL	Marine BL	BL masked over the continents and areas distinctly subject to pollution		
FT	Free Troposphere	Layers above the BL and below the tropopause		
TP	Tropopause	Values at the tropopause height		
S	Stratosphere	Layers above the tropopause height		
ATM	Entire model domain			
<i>Zonal partitioning</i>			<i>Area</i>	
GLOBAL	Globe		(90°N–90°S)	
NH/SH	Northern/Southern Hemisphere			
TROP	Tropics		(23.4°N–23.4°S)	
ETNH/ETSH	Extratropical NH/SH		outside Tropics	
<i>Averages</i>			<i>Averaging over (curve)</i>	<i>Variation (error bars)</i>
ZA	Zonal Average		lon./alt.	seasonal
TS	Time Series		lon./lat./alt.	latitudinal
VP	Vertical Profile of the zonal average		lon./lat.	seasonal

Note: The planetary boundary layer and tropopause heights are diagnosed in EMAC.

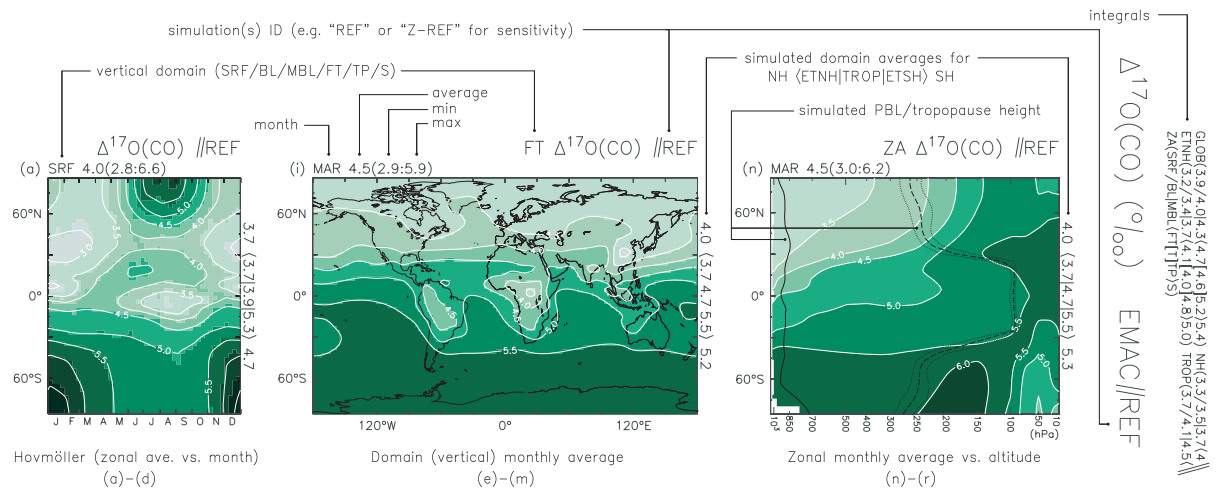
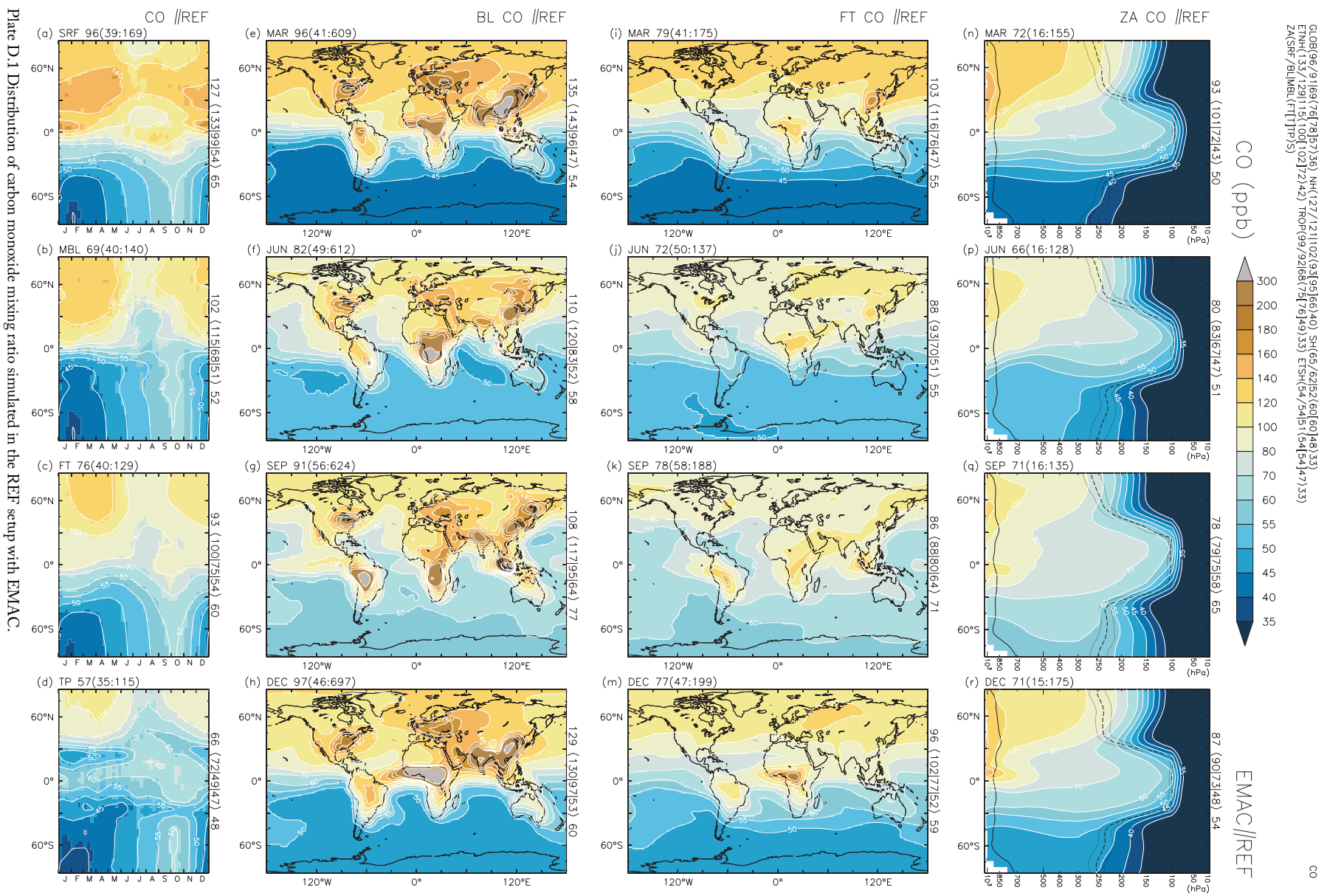
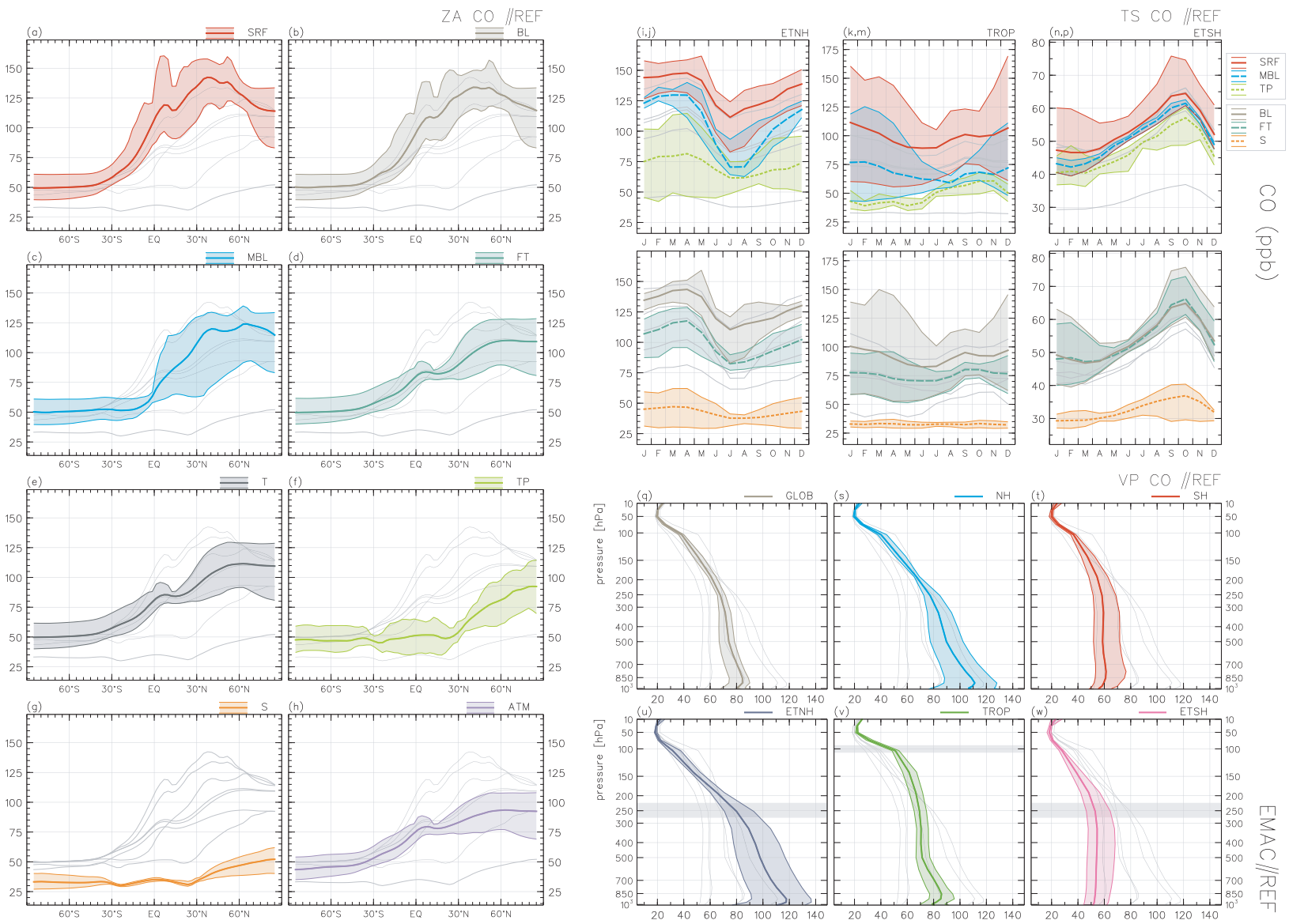
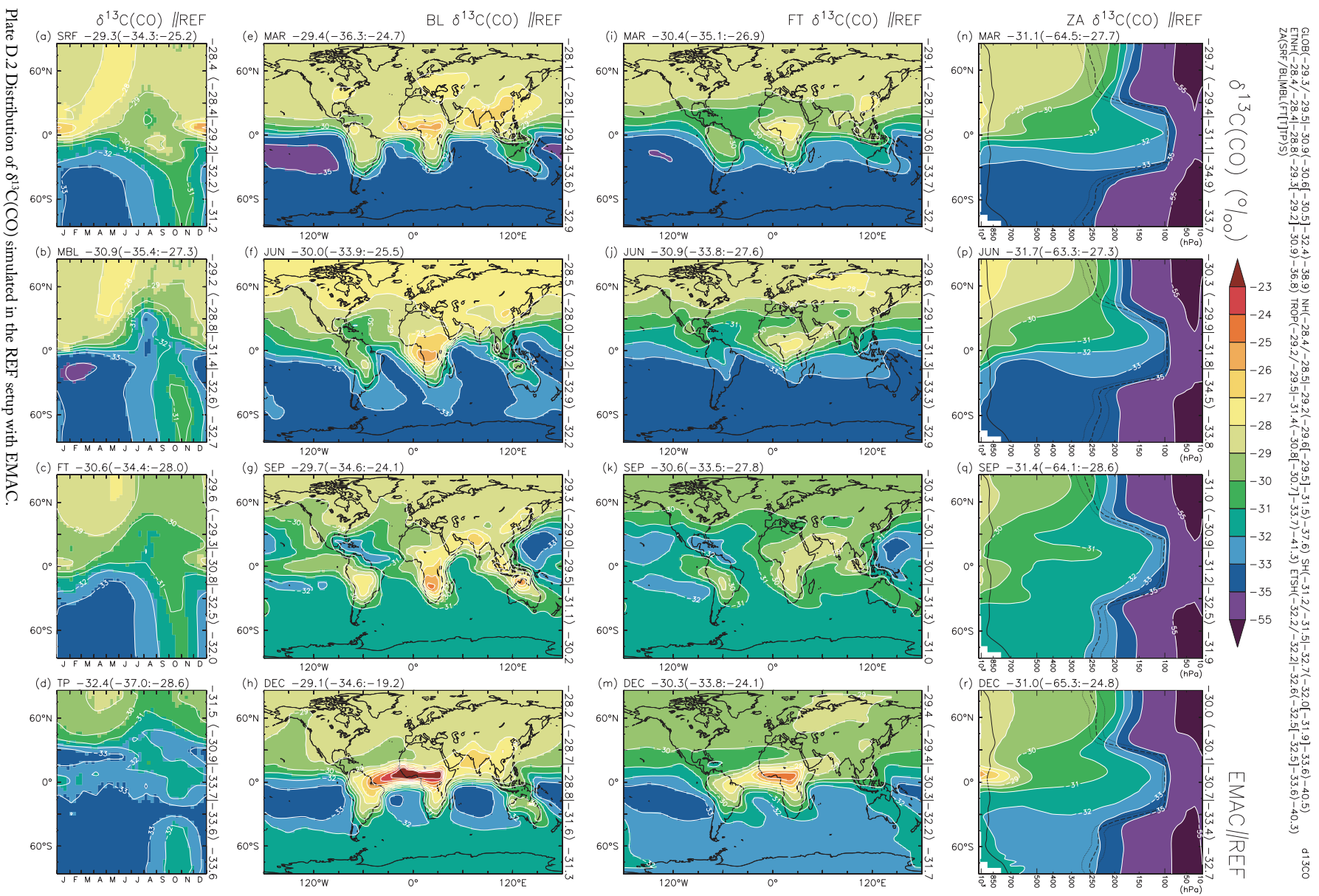
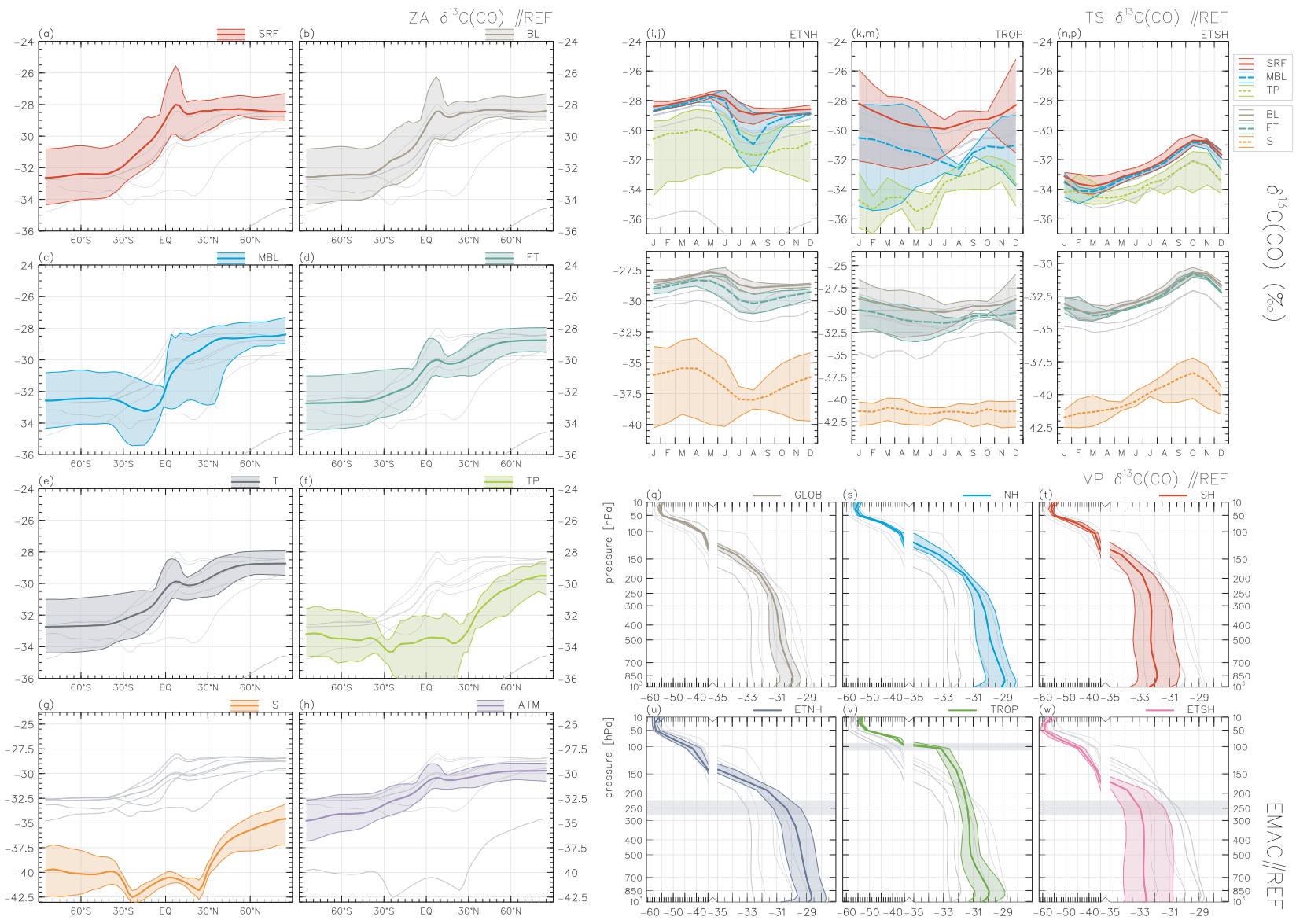


Figure D.1 Legend to the Plates presenting the 3D simulation results with EMAC. In the zonal average (ZA) plots, the dotted lines denote the latitudinal variation of the tropopause height.





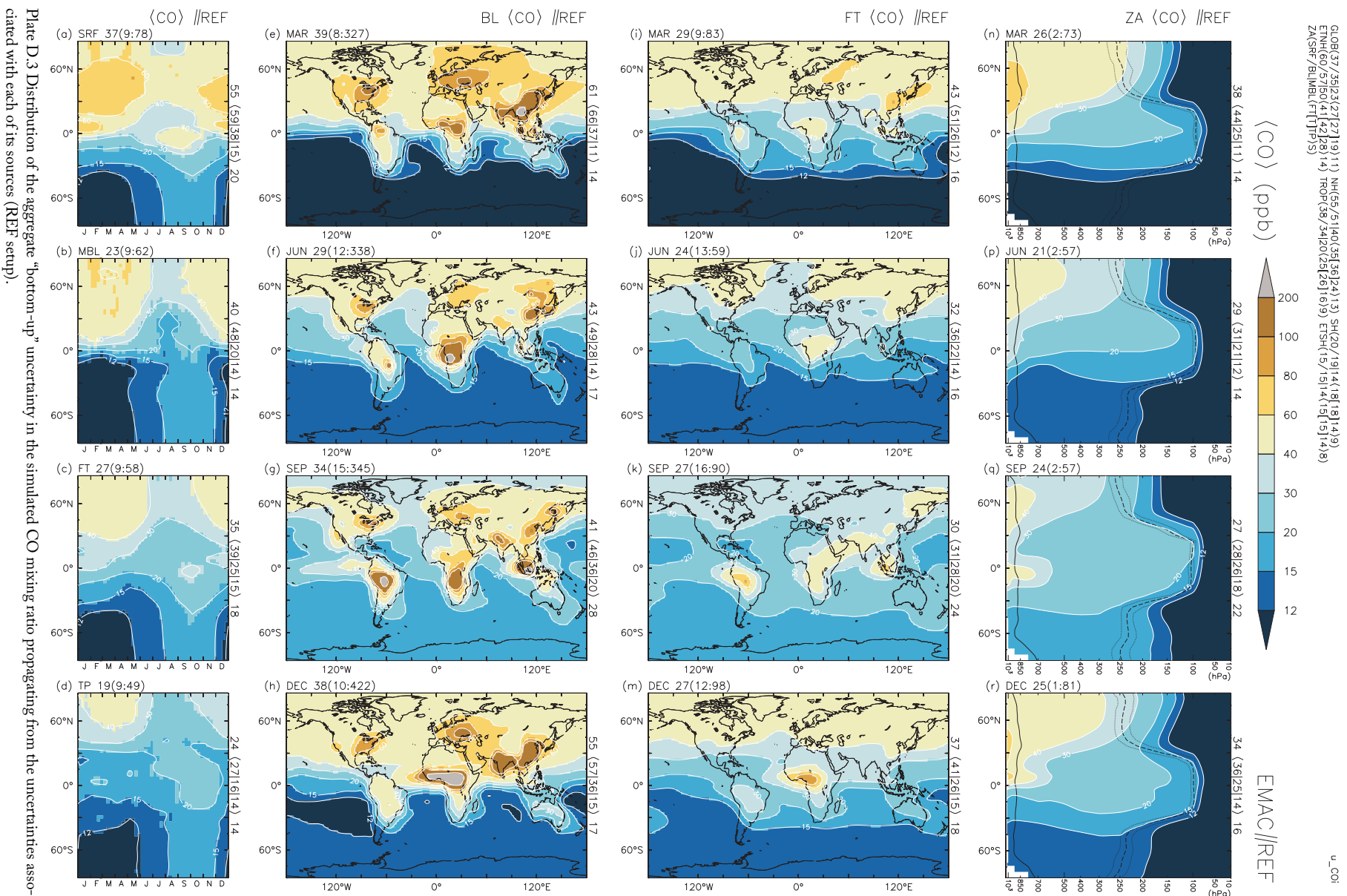




GLOB(-29.3/-29.5/-30.6/-30.6/-30.5/-32.4/-38.9) NH(-28.4/-28.5/-29.2/-29.6/-31.5/-37.6) SH(-31.2/-31.5/-32.7/-32.0/-31.9/-33.6/-40.5)
 ETNH(-28.3/-28.4/-28.7/-29.2/-29.1/-30.7/-36.5) TROP(-29.2/-29.5/-31.4/-30.8/-30.7/-33.7/-41.3) ETSH(-32.3/-32.3/-32.6/-32.6/-32.6/-33.5/-40.1)
 ZA(SRF/BLMBL(FT)TPS)

d13C0

EMAC/REF



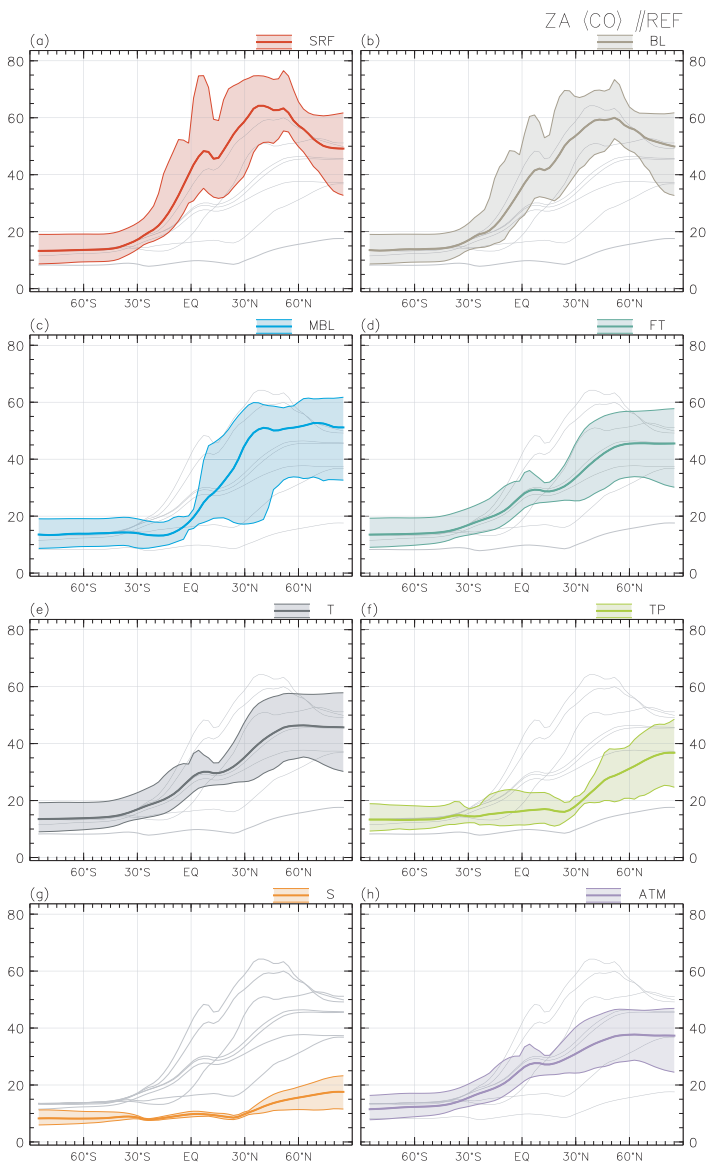
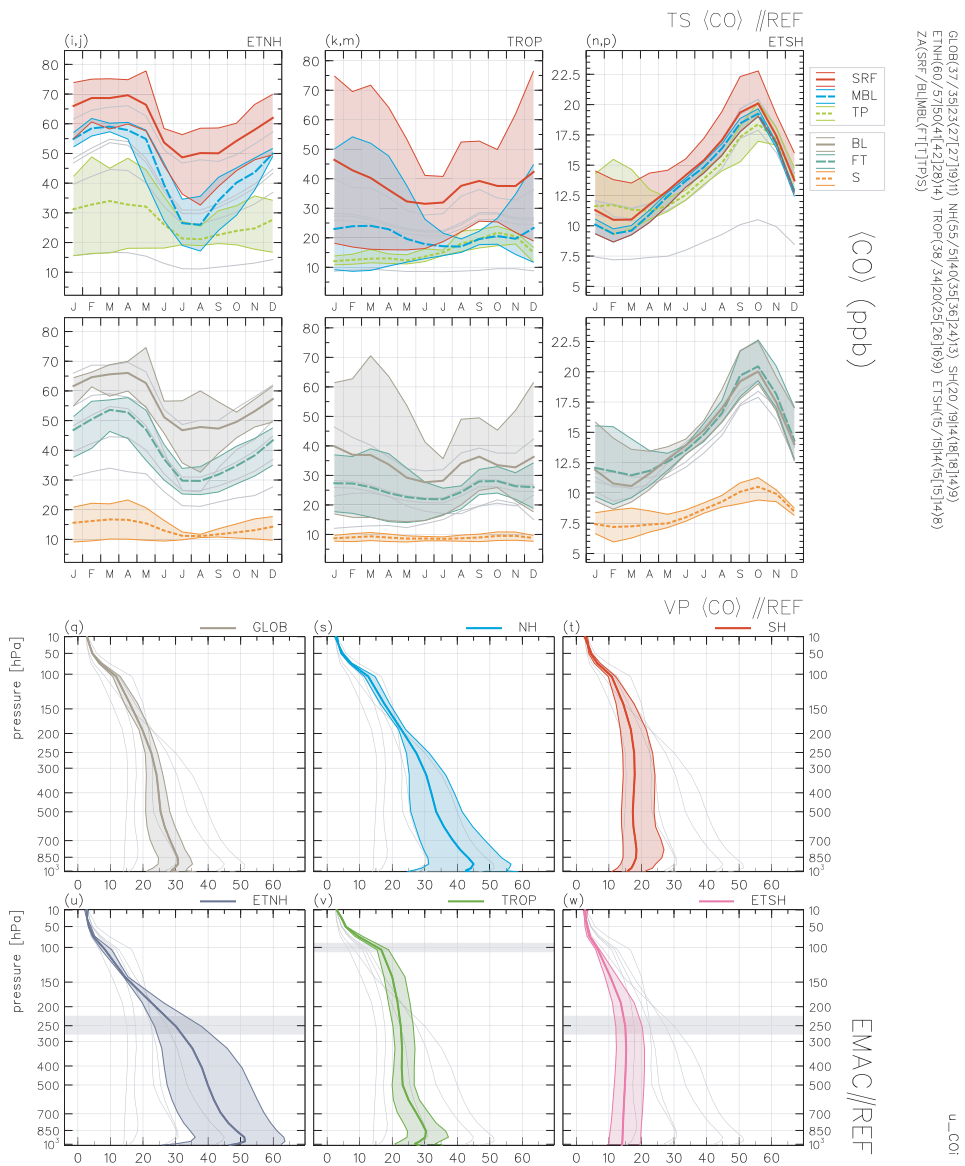
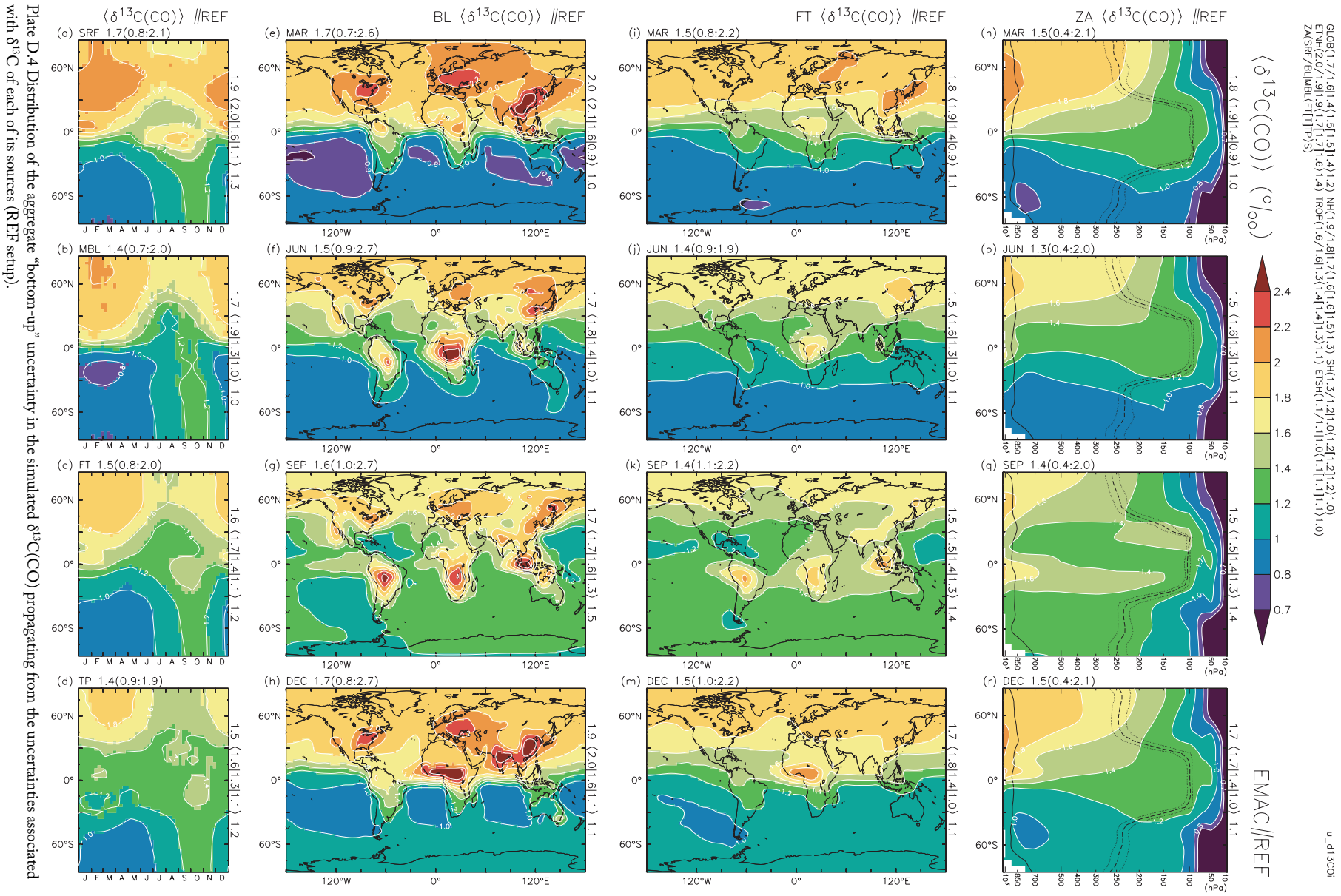
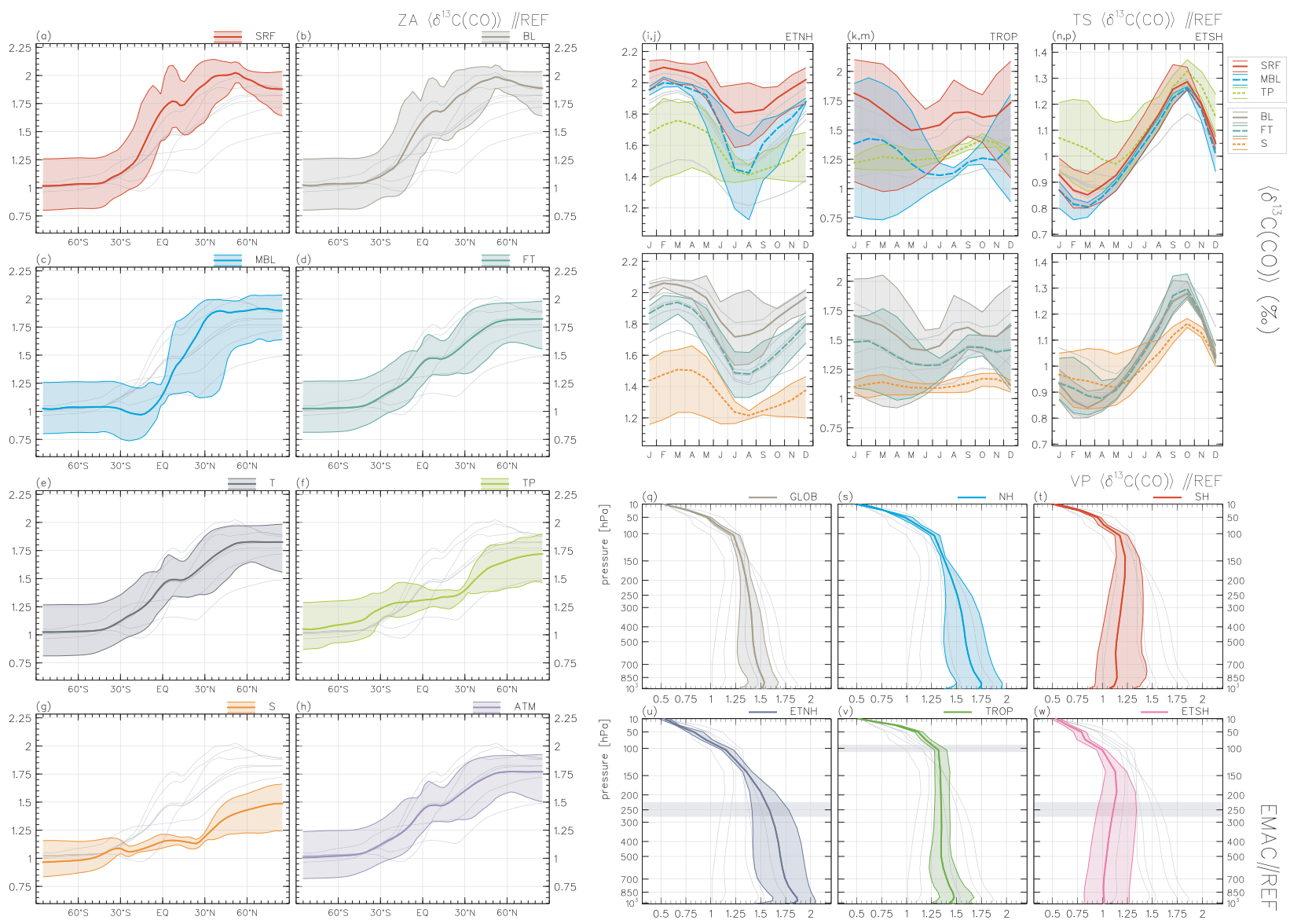
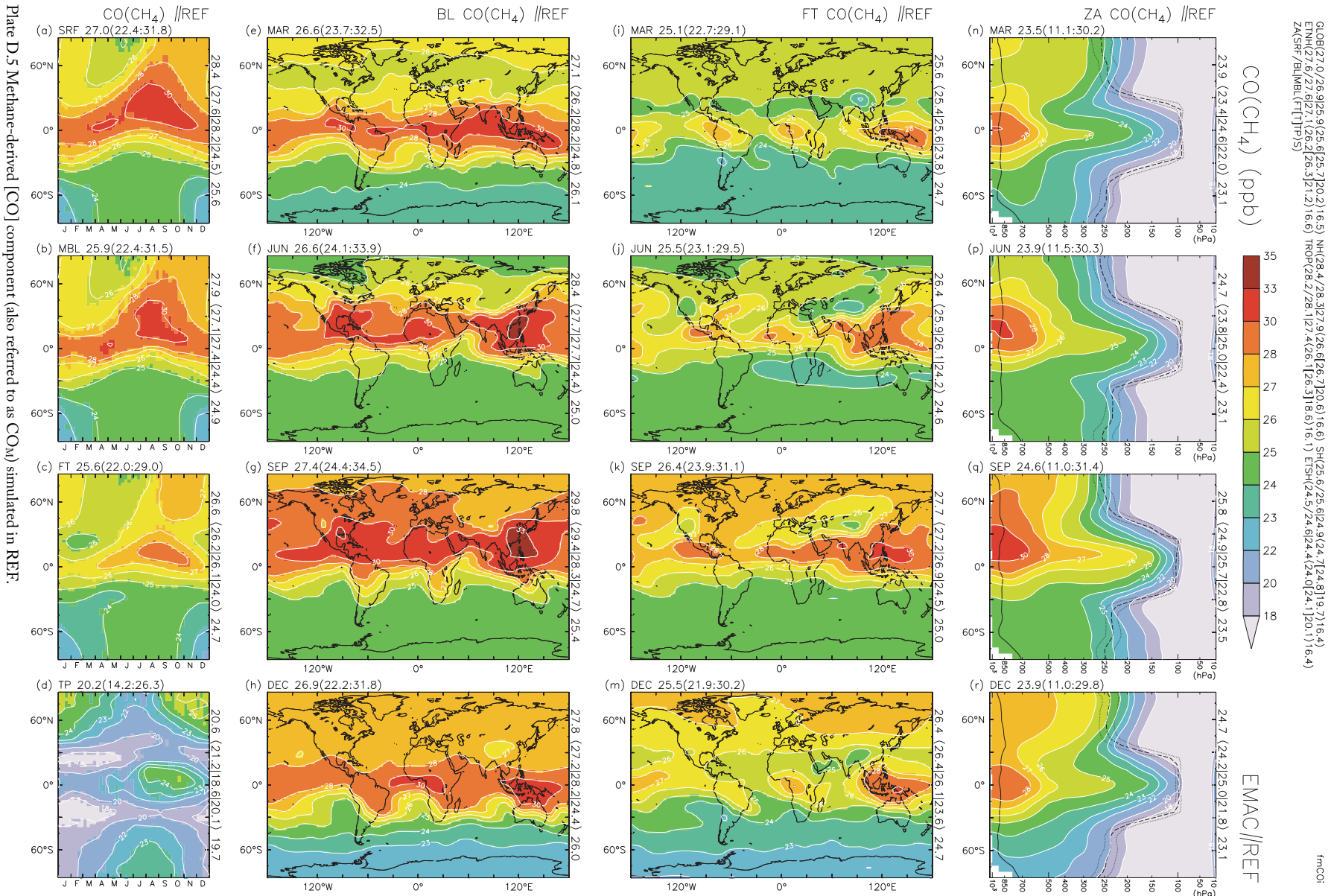


Plate D.3 (Continued).







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 ETNH(27.6/27.6)27.7(26.2)26.3(21.2)6.6) TROP(28.2/28.4)27.4(26.1)26.3(18.6)6.1) ETSH(24.5/24.6)24.4(24.0)24.1(20.1)6.4)
 ZA(SRF/BLMBL(FT)1)TP(S)

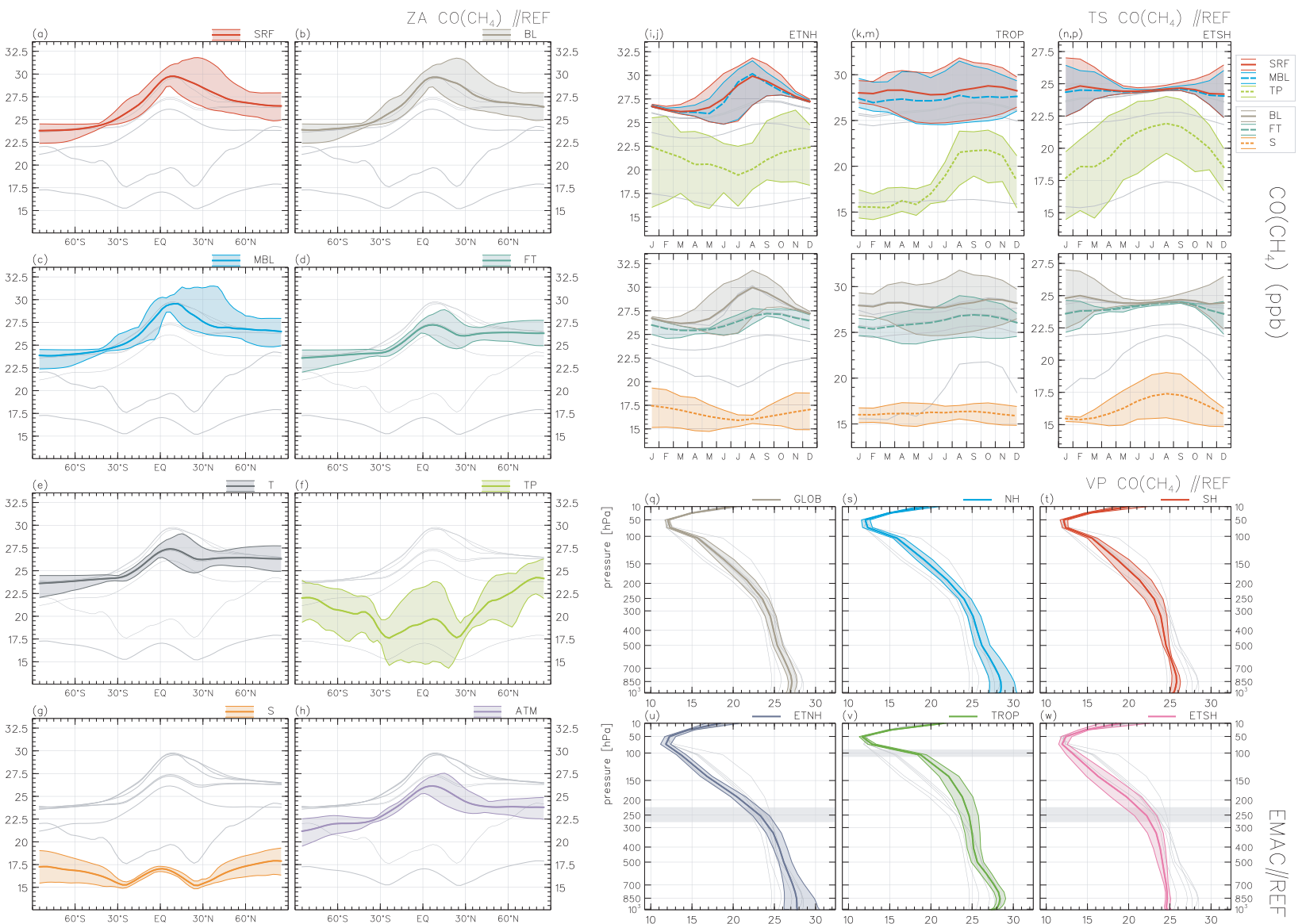
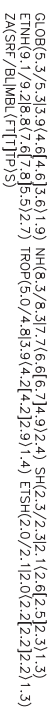


Plate D 5 (Continued).



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 ETNH(0.1/9.2/8.6/7.8/5.5/2.7) TROP(5.0/4.8/3.9/4.2/4.2/2.9)*4) ETSH(2.0/2.1/2.0/2.2/2.2/1.3)
 ZA(SRF/BLMBL(FT)TPS)

frCOI

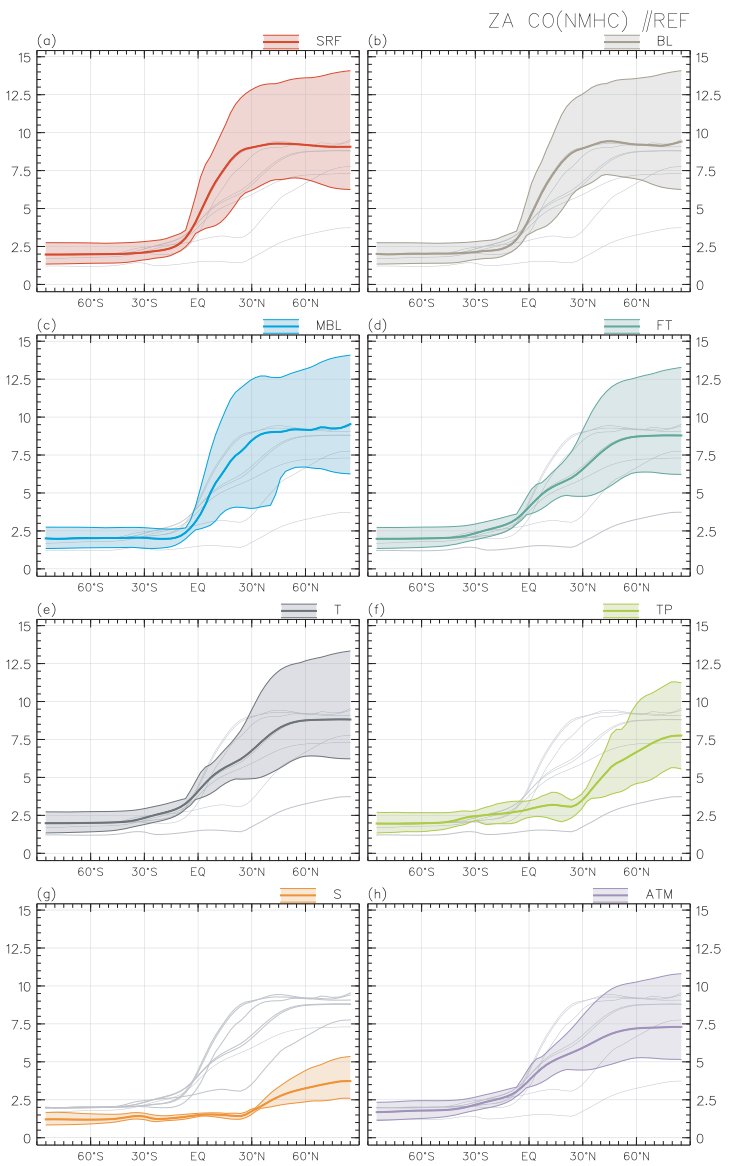
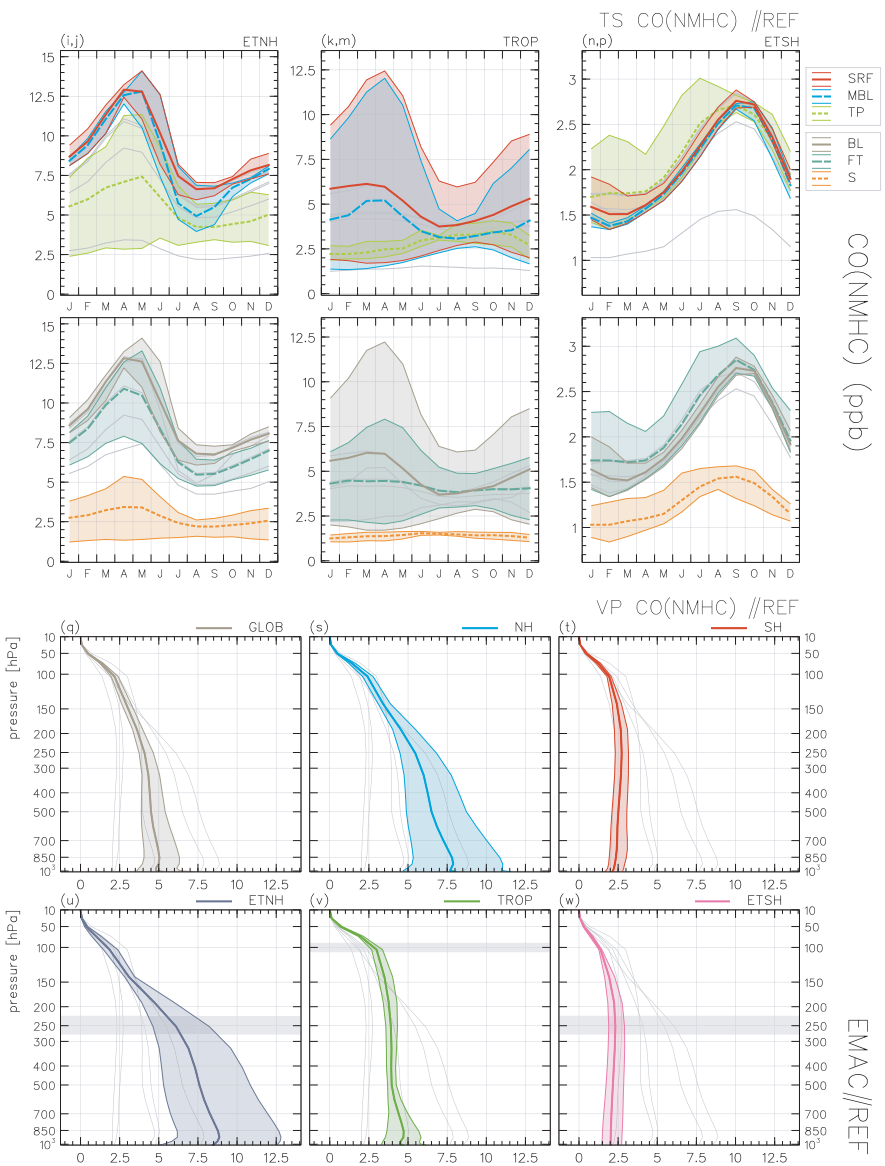
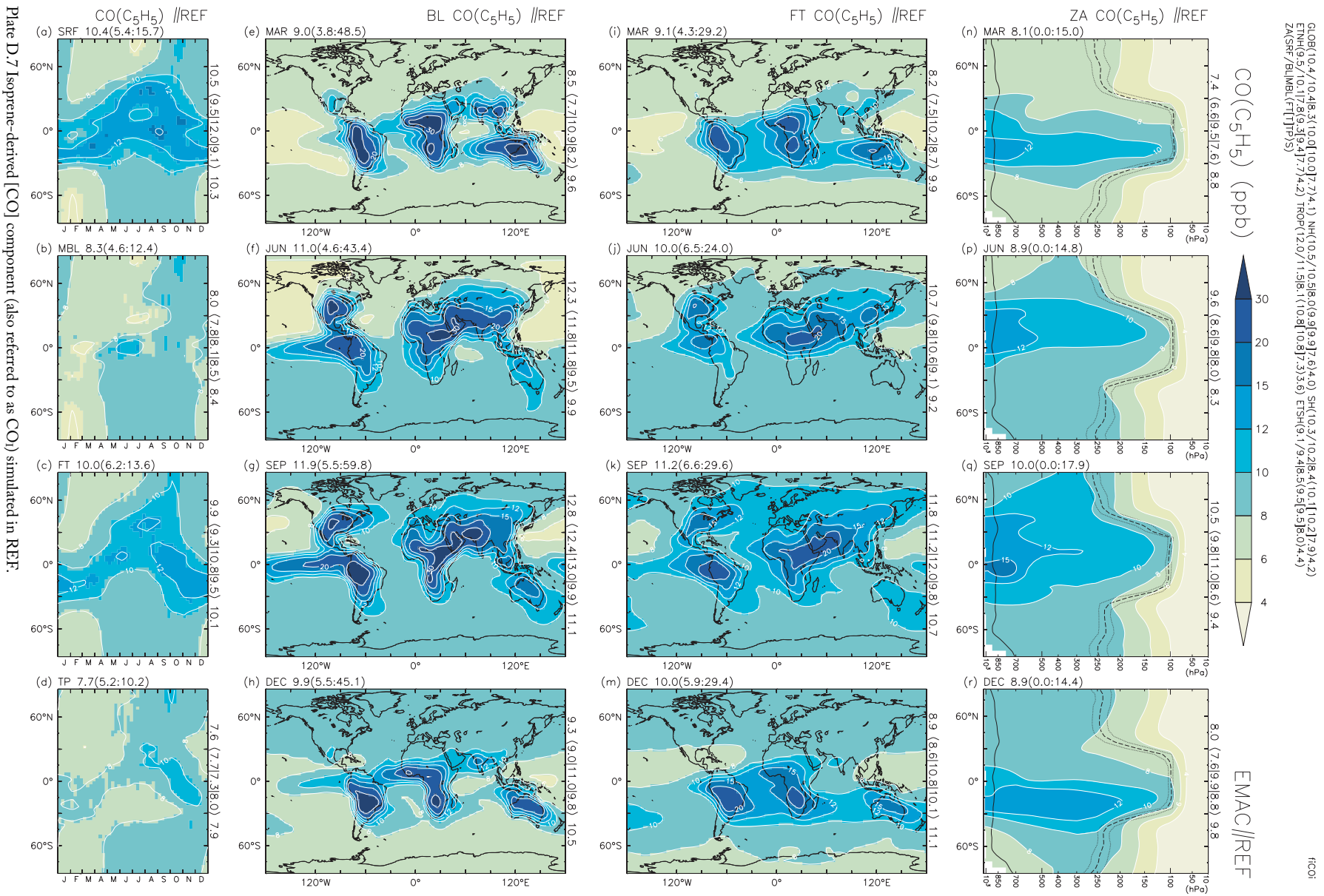
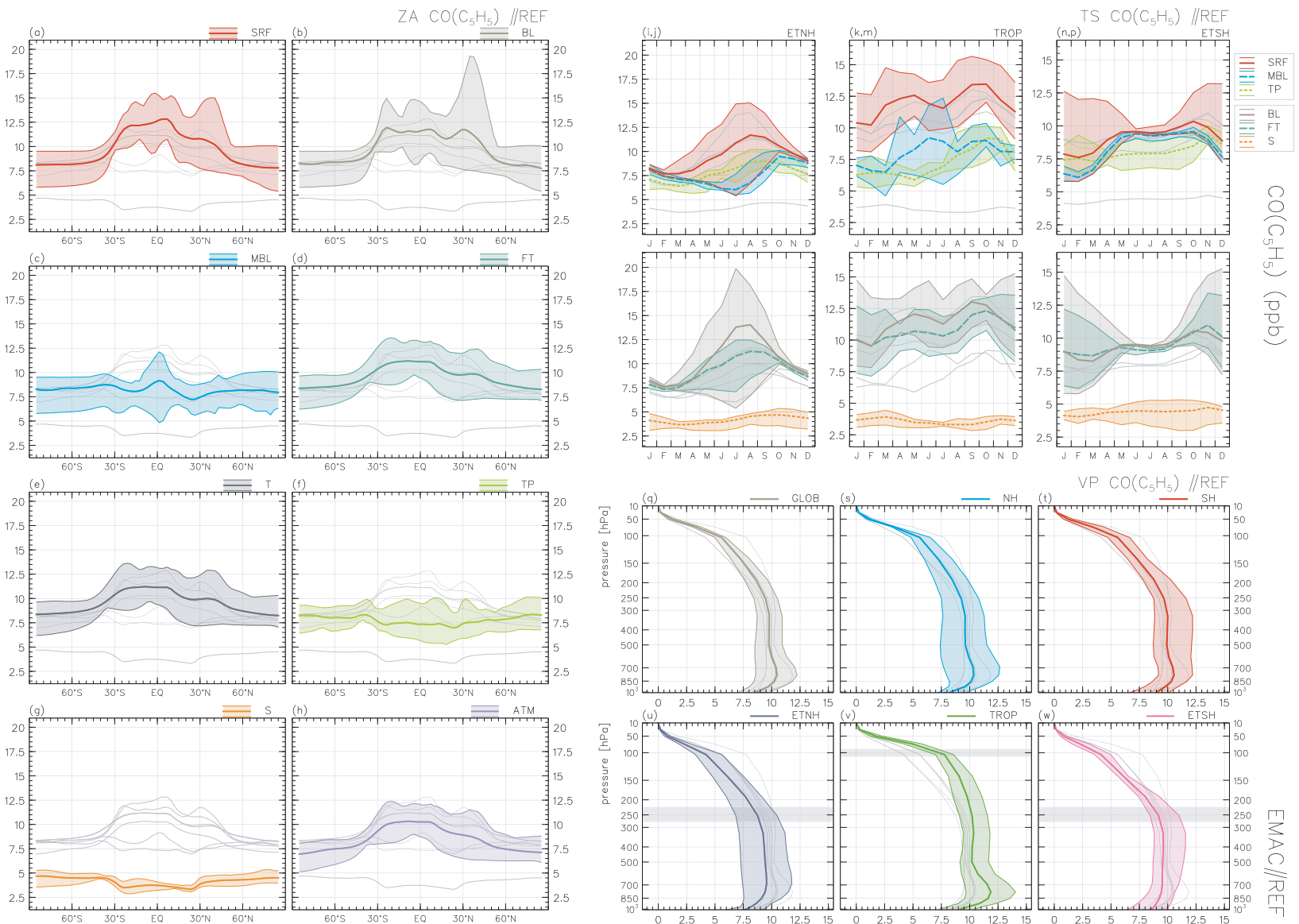
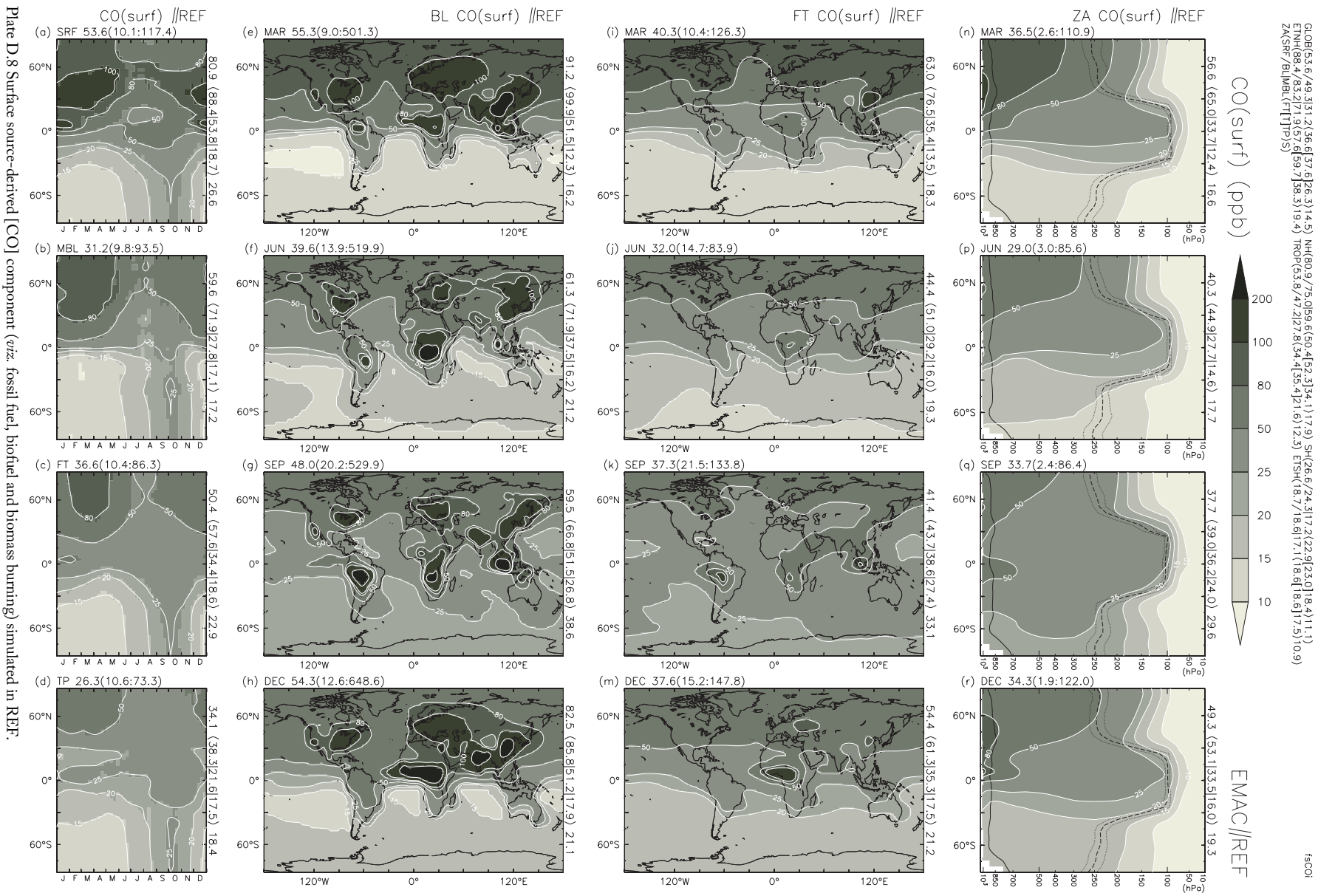


Plate D 6 (Continued).







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 ETNH(88.4/83.2)19.5(7.6)5.9)7)3.8(3)9.4) TROP(53.8/47.2)27.8(34.4)35.4)21.6)2.3) ETSH(18.7/18.6)17.6)18.6)17.5)9.9)
 ZA(SRF/BLMBL(FT)TPS)

fscOI

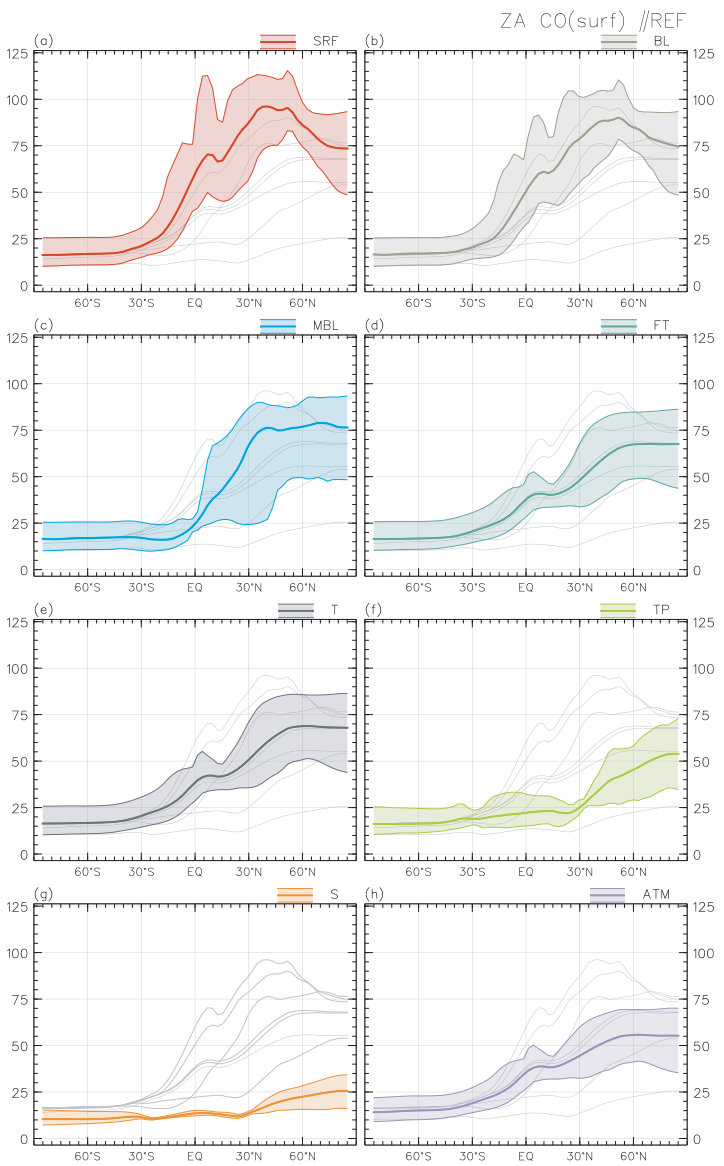
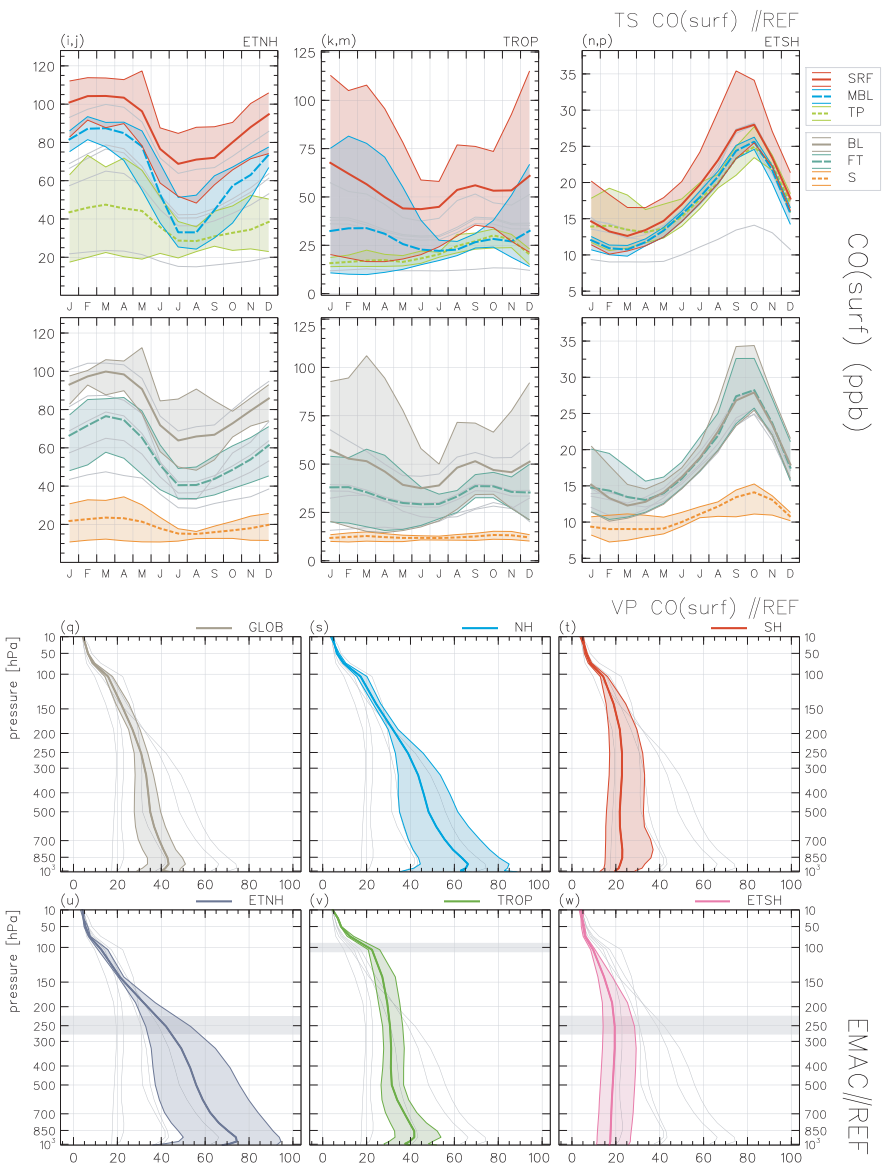


Plate D 8 (Continued).



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 ETNH(0.73/0.84/0.73/0.97[0.95]1.17)1.03 TROP(0.74/0.82/0.76/0.95[0.93]1.28)1.01 ETSH(0.62/0.74/0.68/0.96[0.93]1.21)1.04
 ZA(SRF/BLMBL(FT)1)1P5

$\lambda_{\text{CH}_4}(\text{CO})$ (m/c/m/c)

EMAC//REF

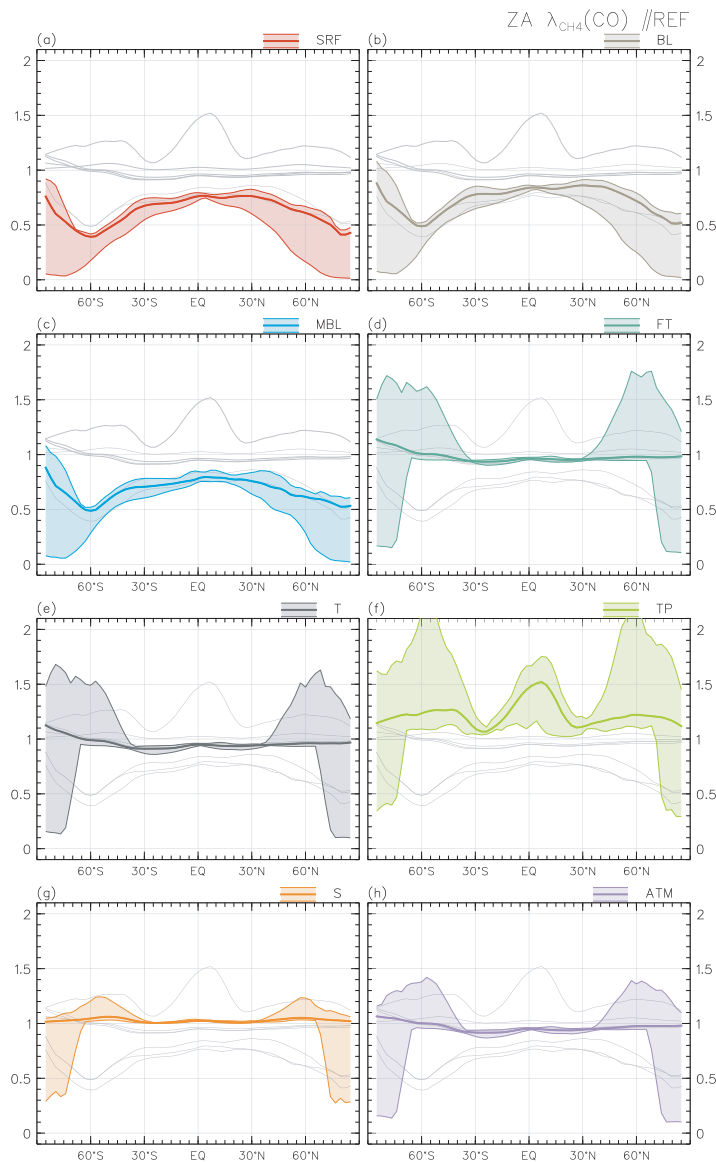
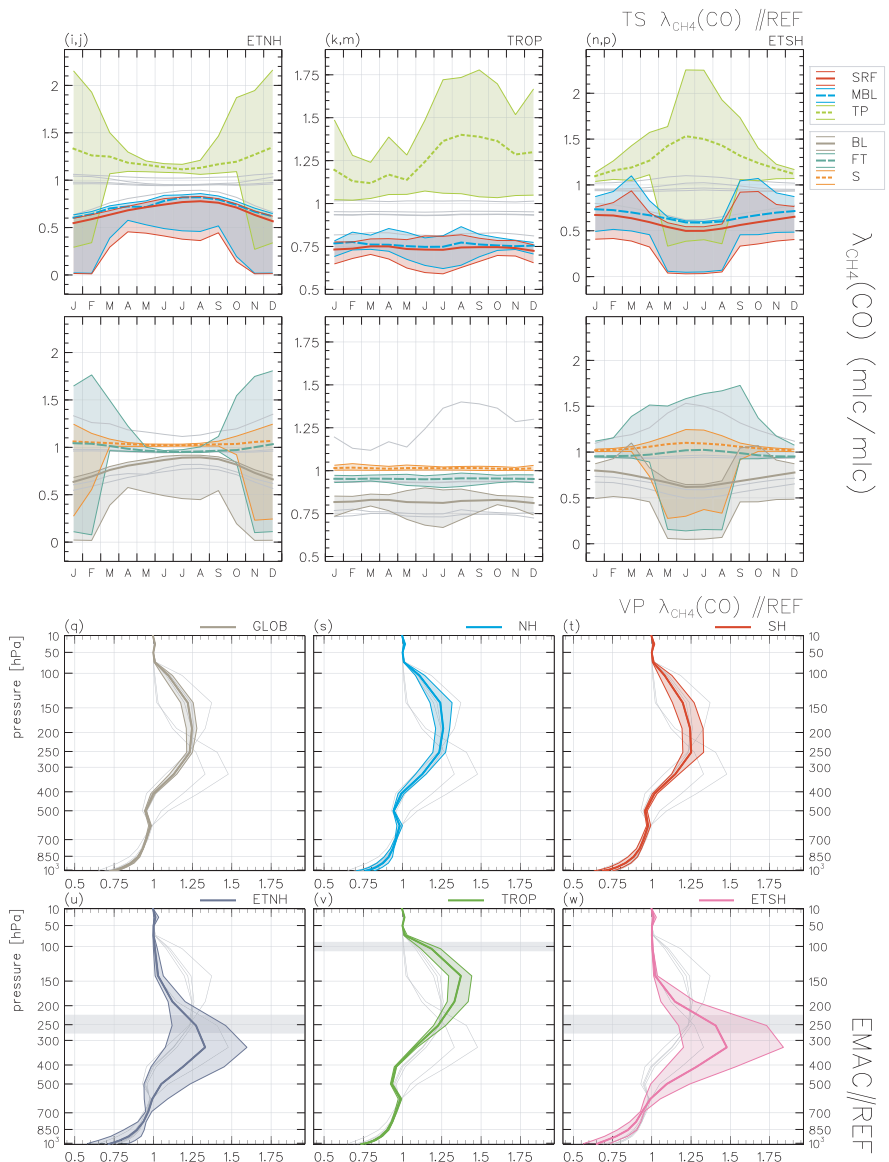
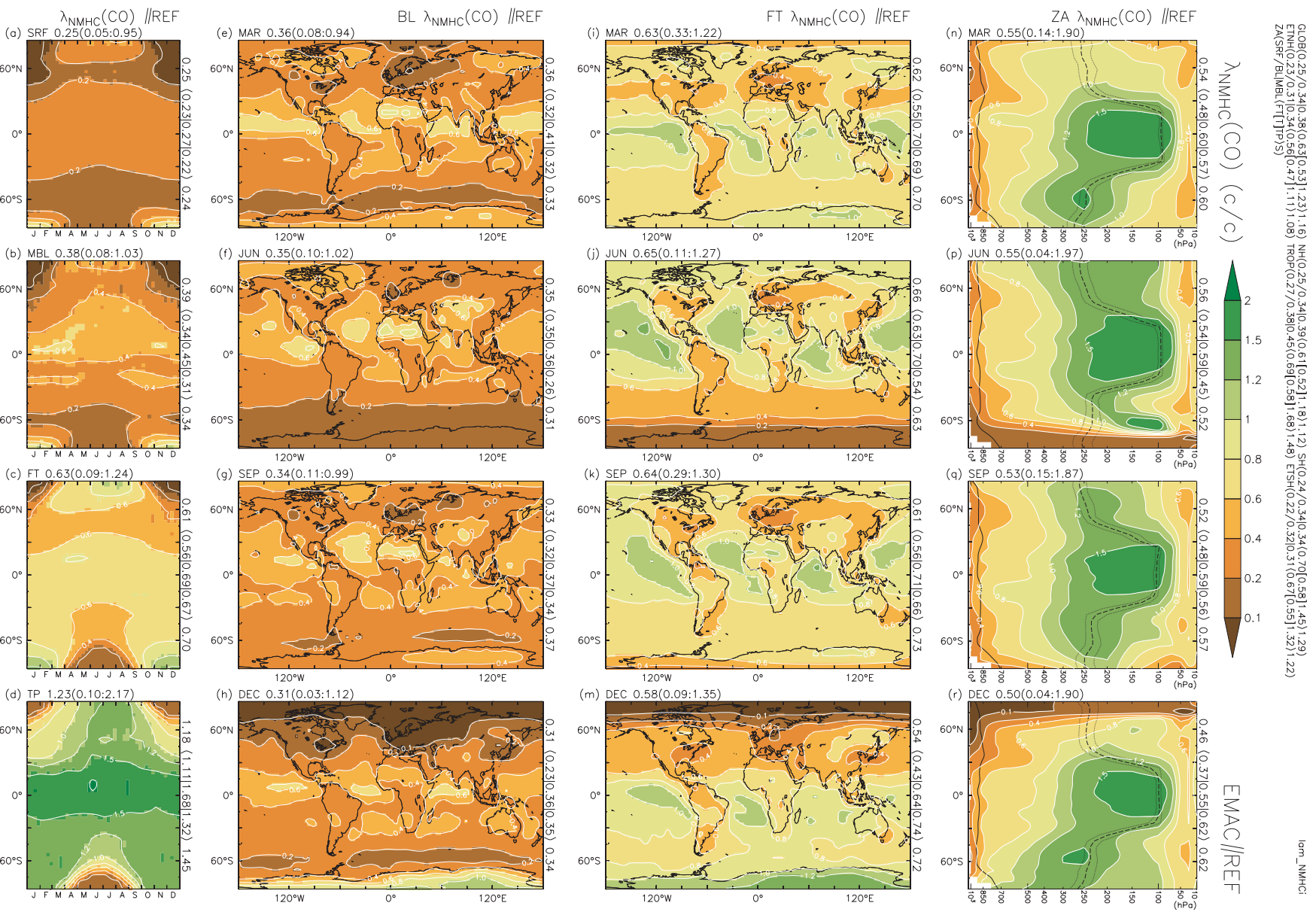


Plate D.9 (Continued).

[illegible]

lam_NMHCi

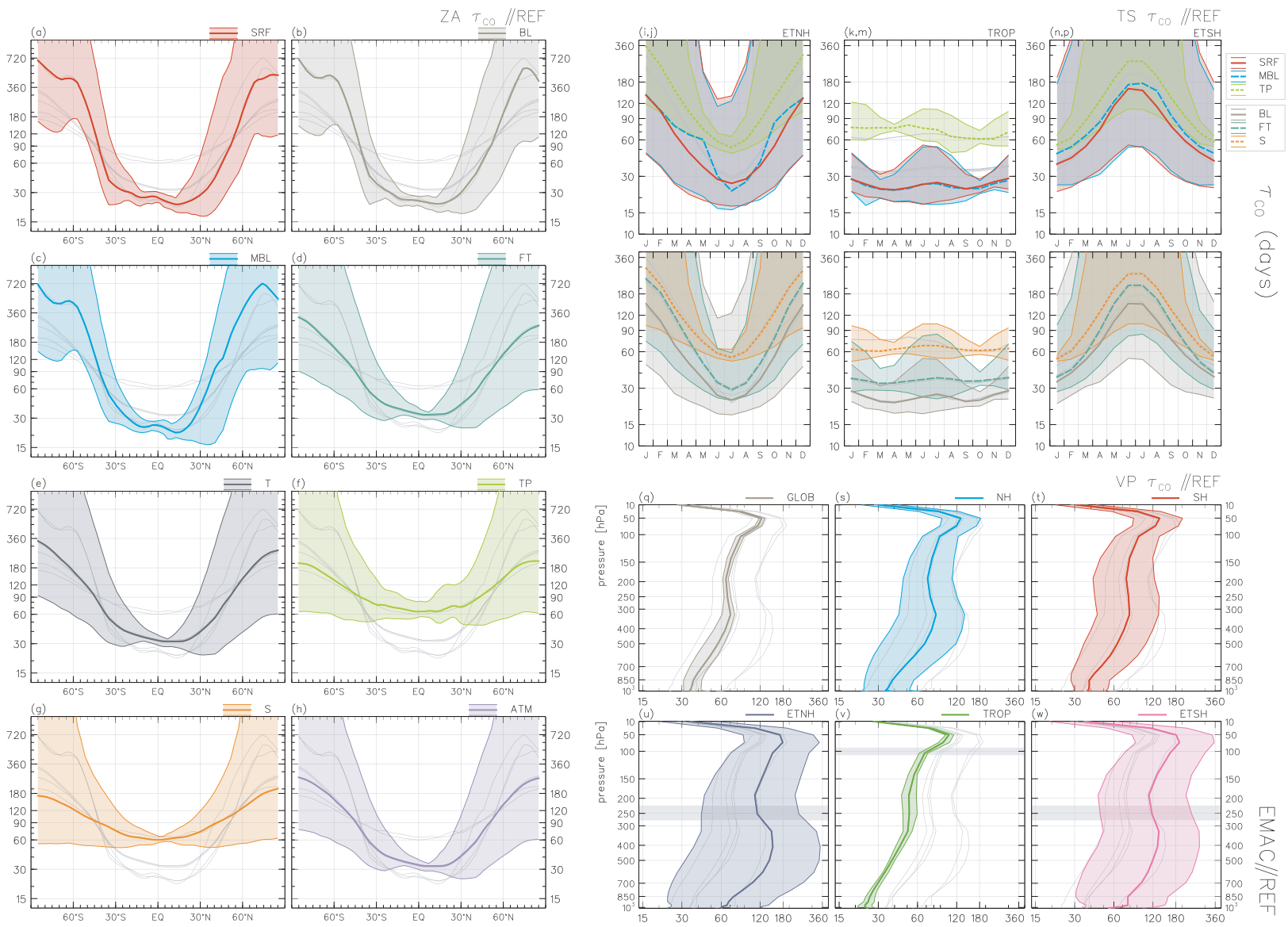

$$\lambda_{\text{NMHC}}(\text{CO}) \text{ (c/c)}$$

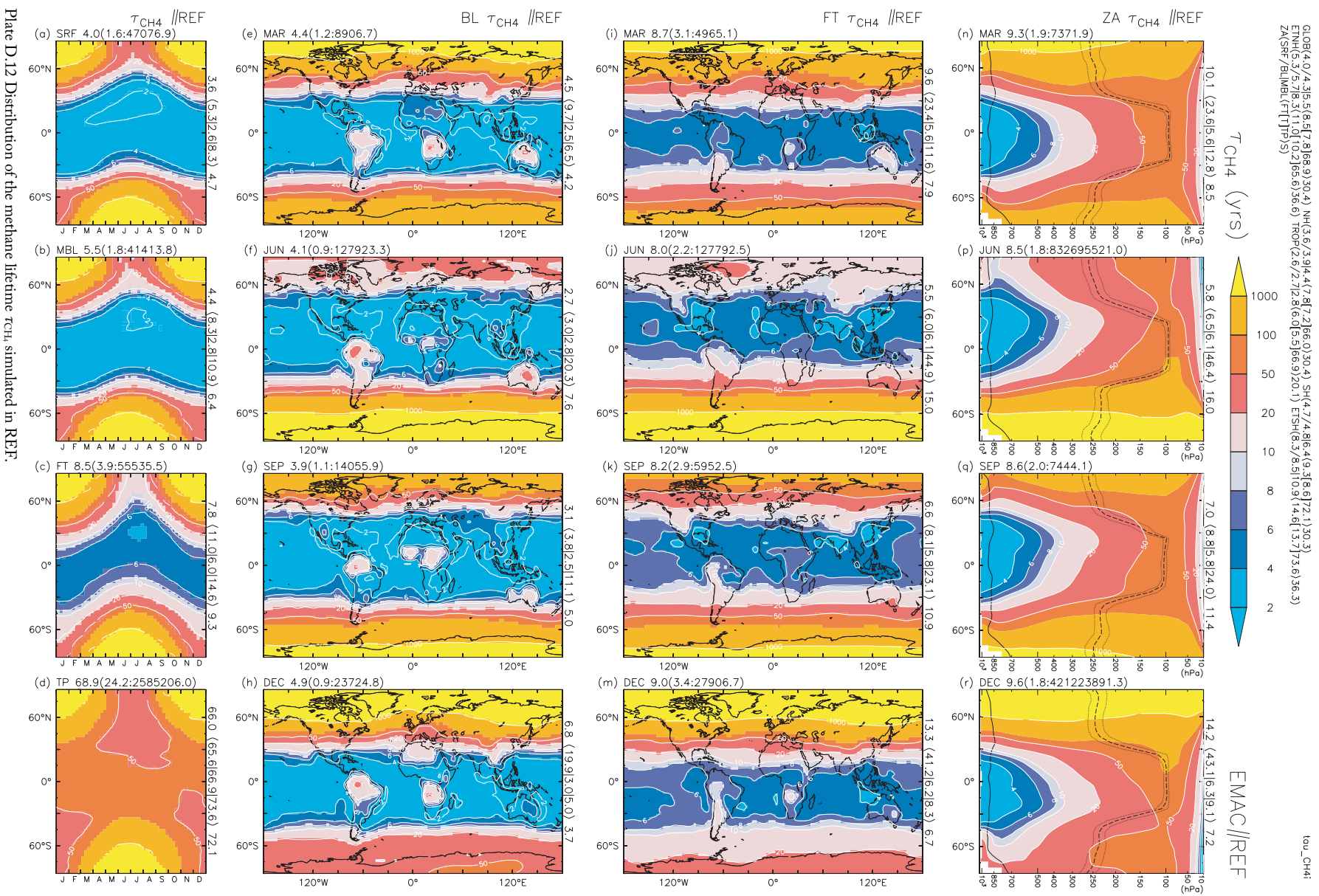
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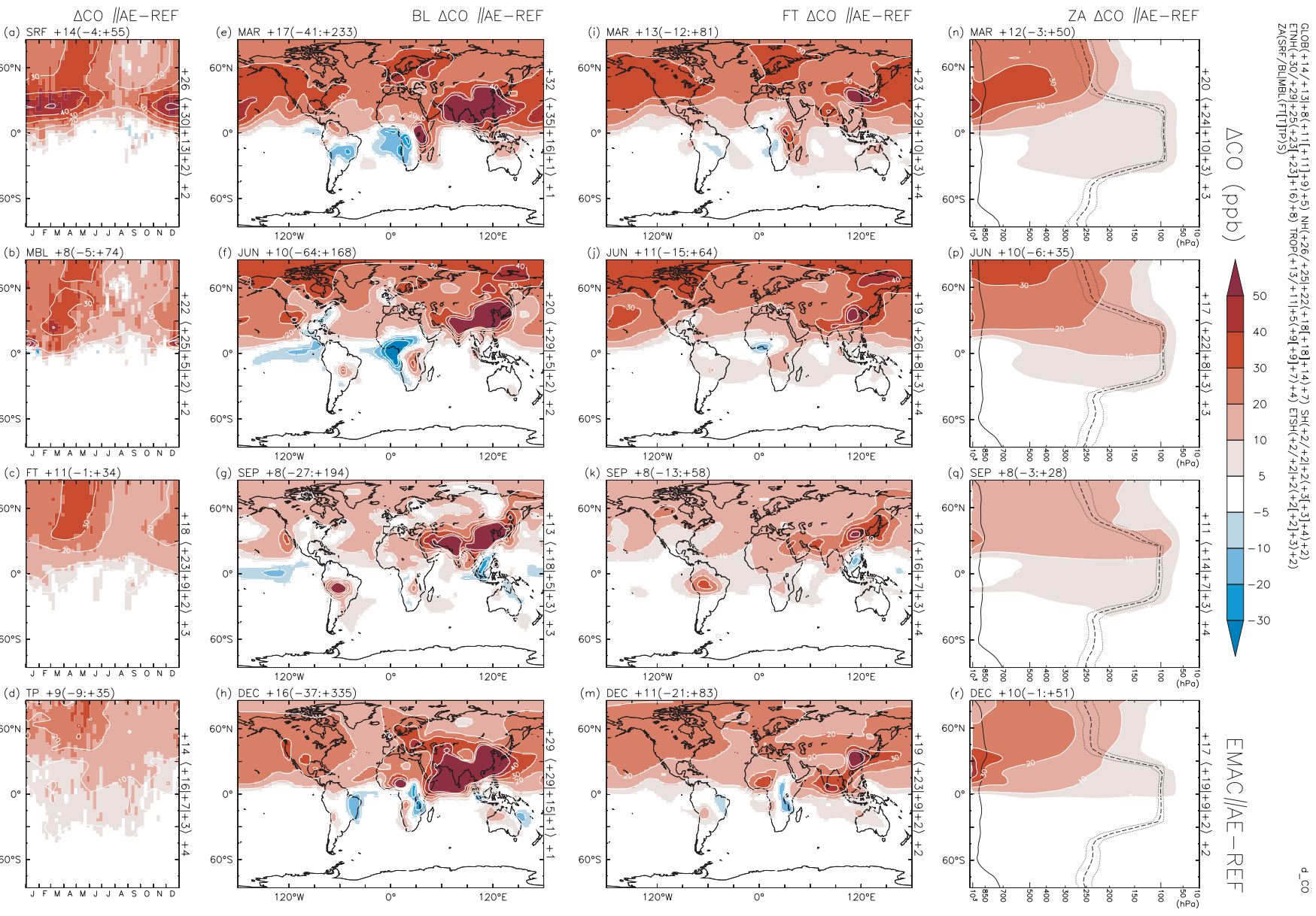
Plate D.10 (*Continued*).

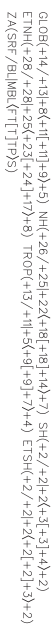


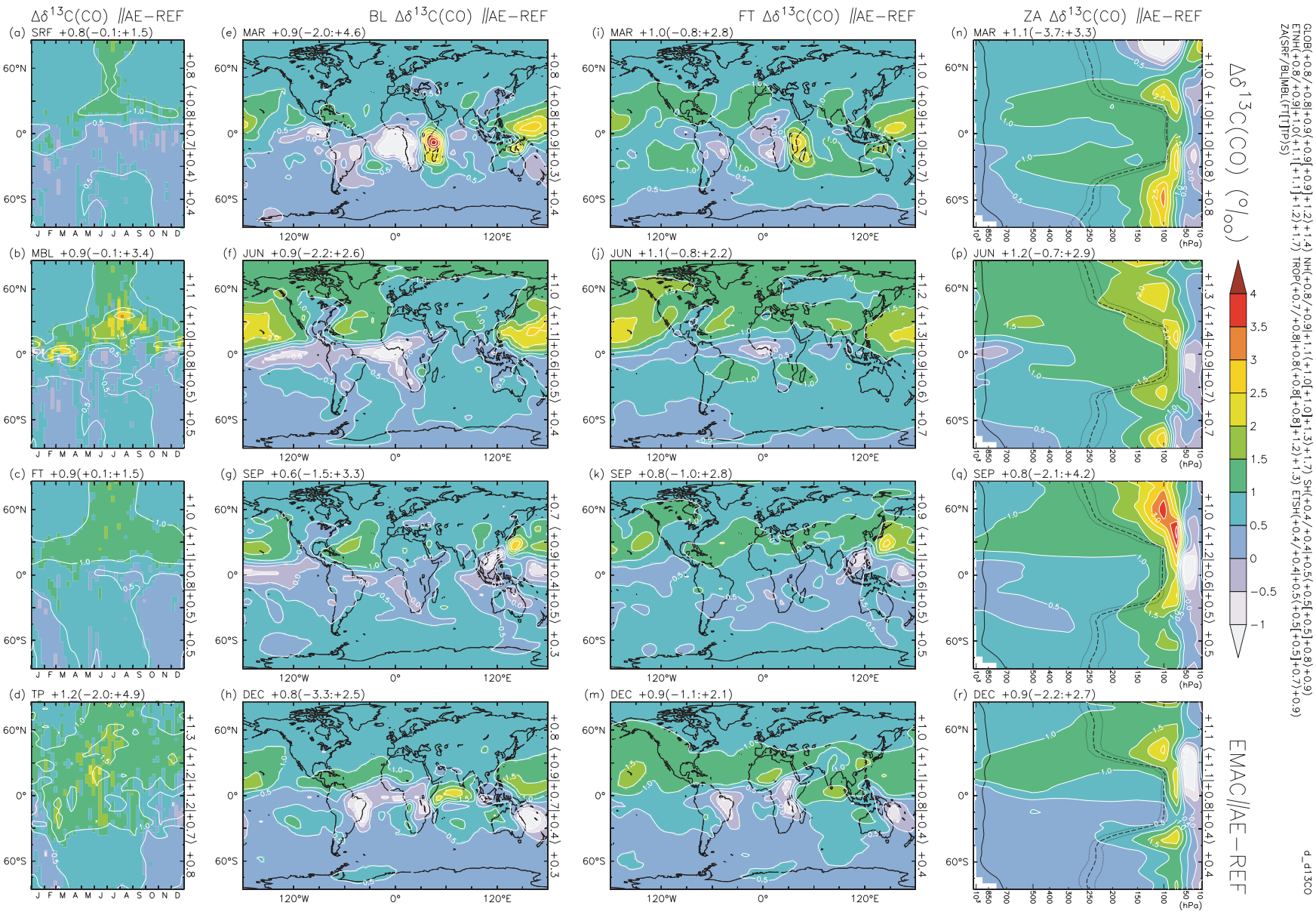
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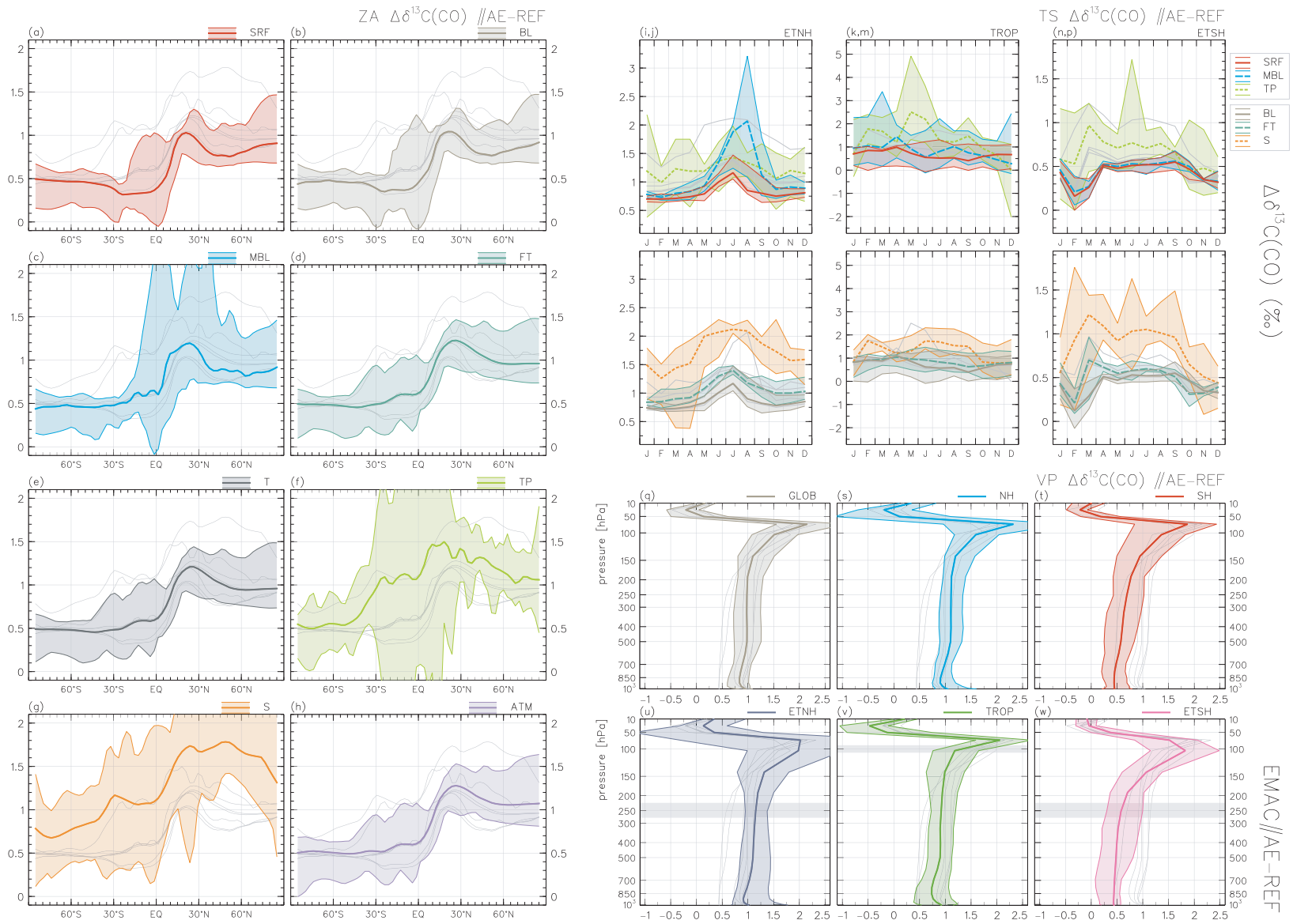


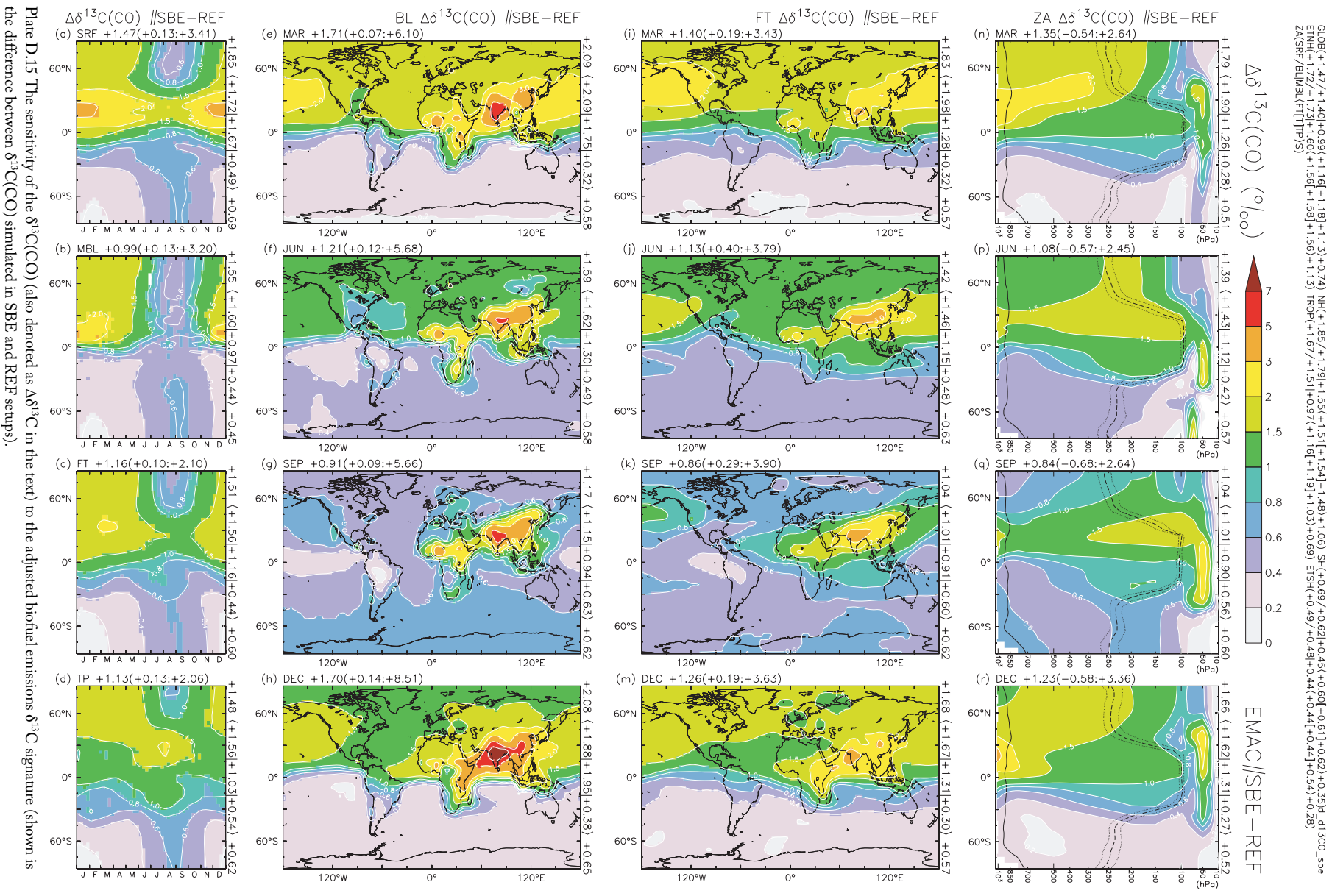


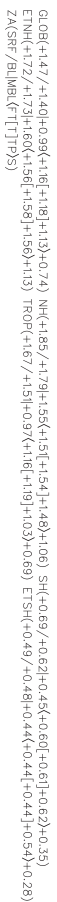


Plate D.13 (*Continued*).







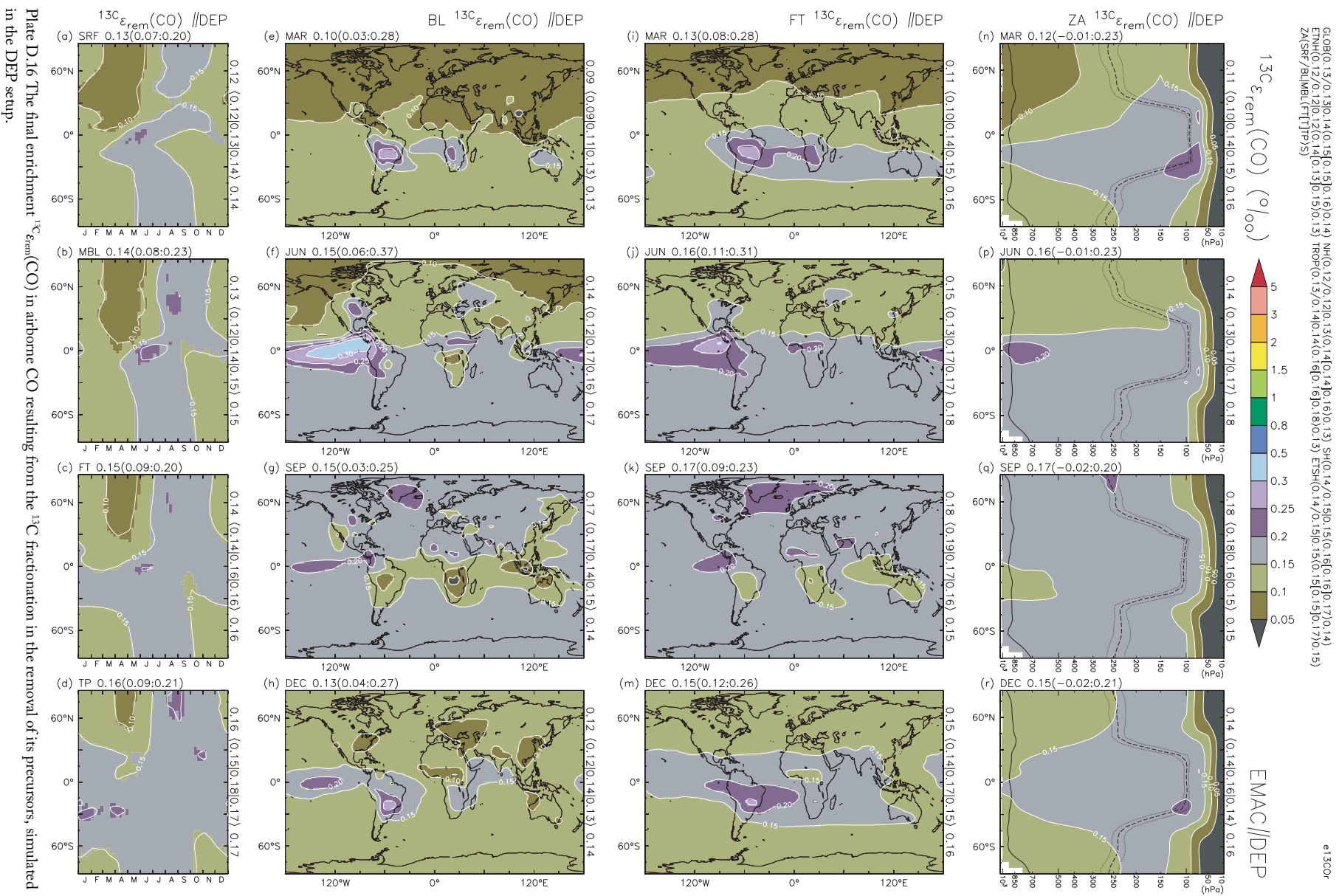


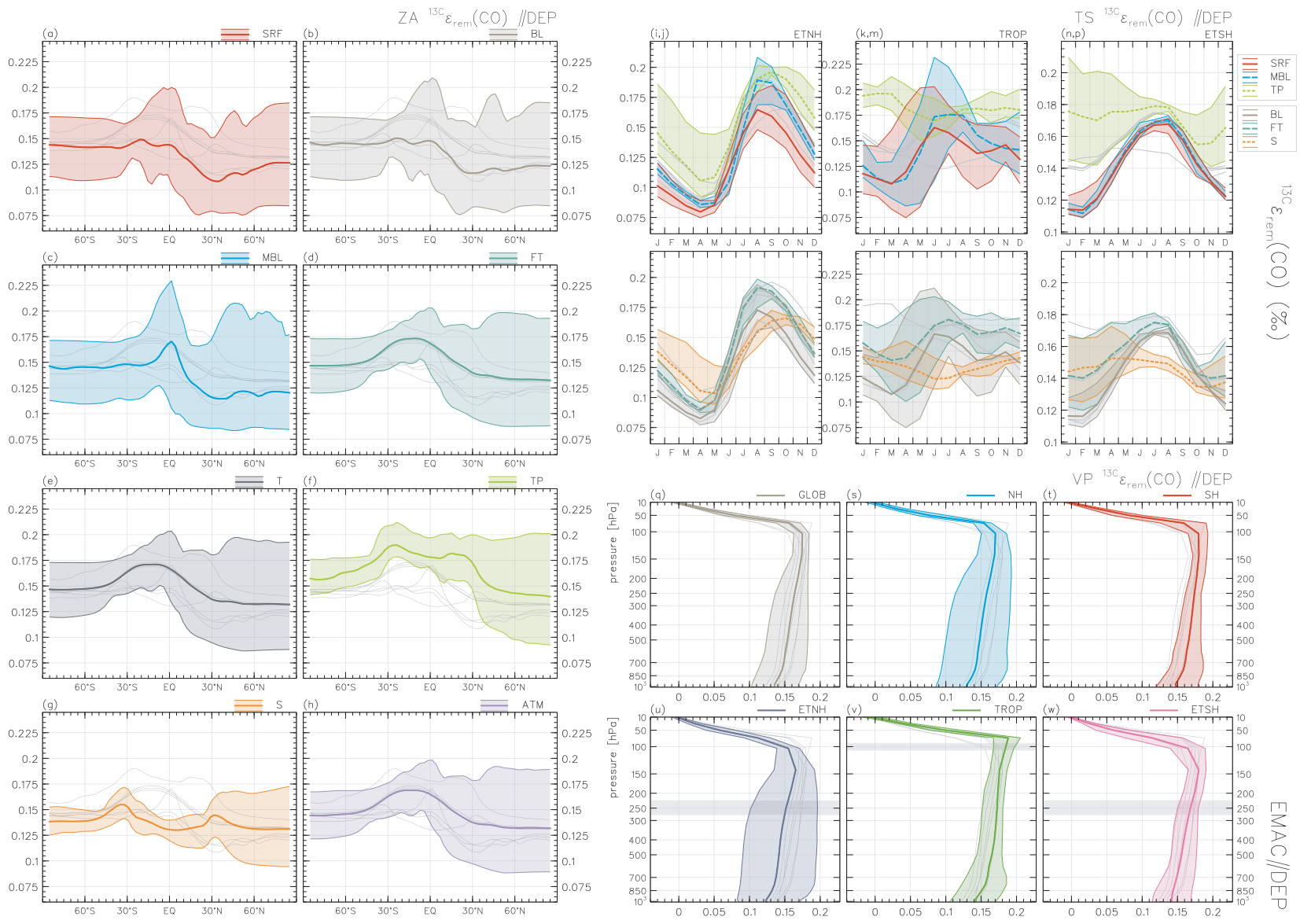
d_d13CO_sbe



EMAC//SBE-REF

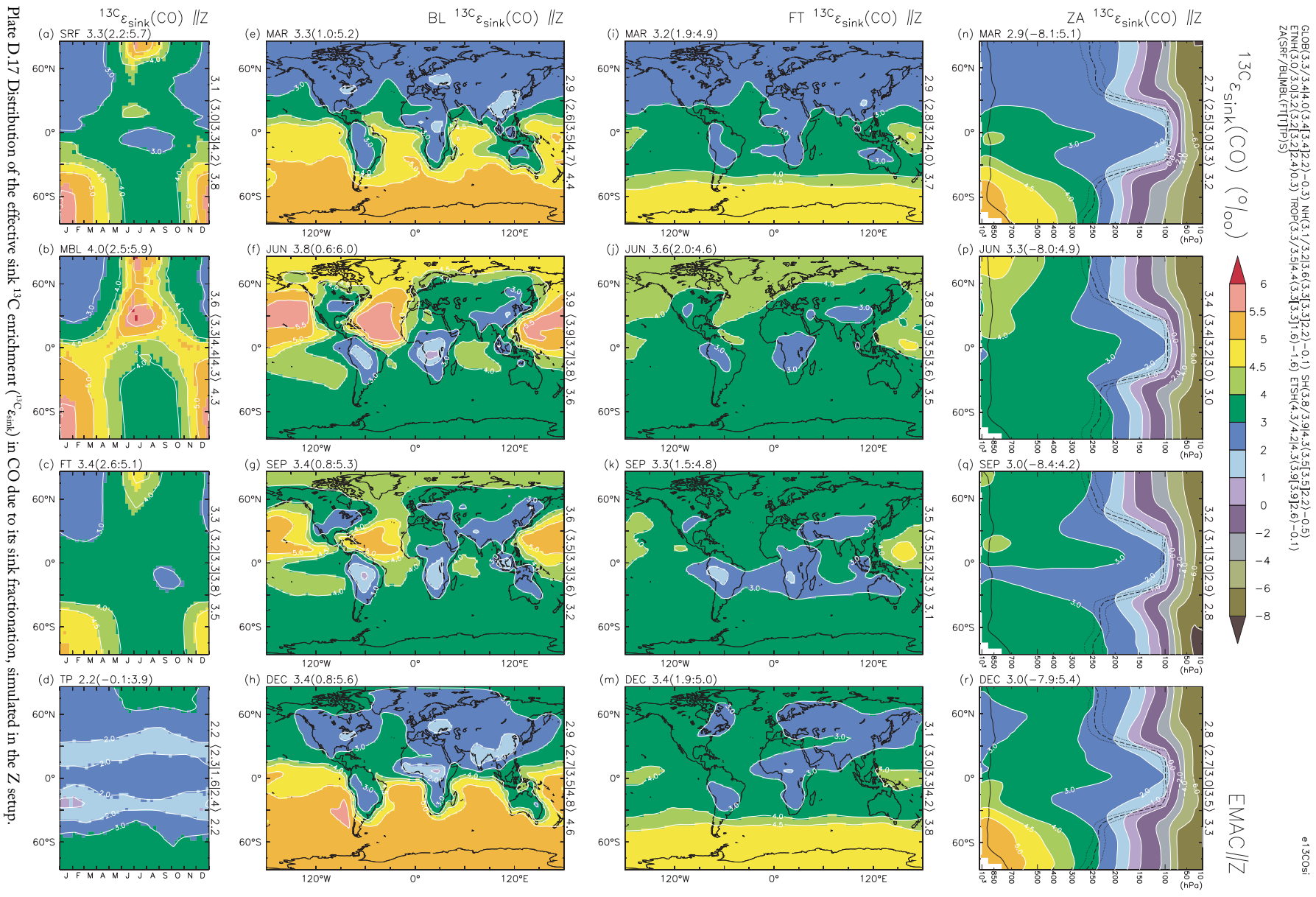
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 ETNH(0.12/0.1210.12/0.14/0.13/0.15/0.13) TROP(0.13/0.1410.16/0.18/0.13) ETSH(0.14/0.1510.15/0.17/0.15)
 ZA(SRF/BL/MBL/FT/TP/S)

e13Cor



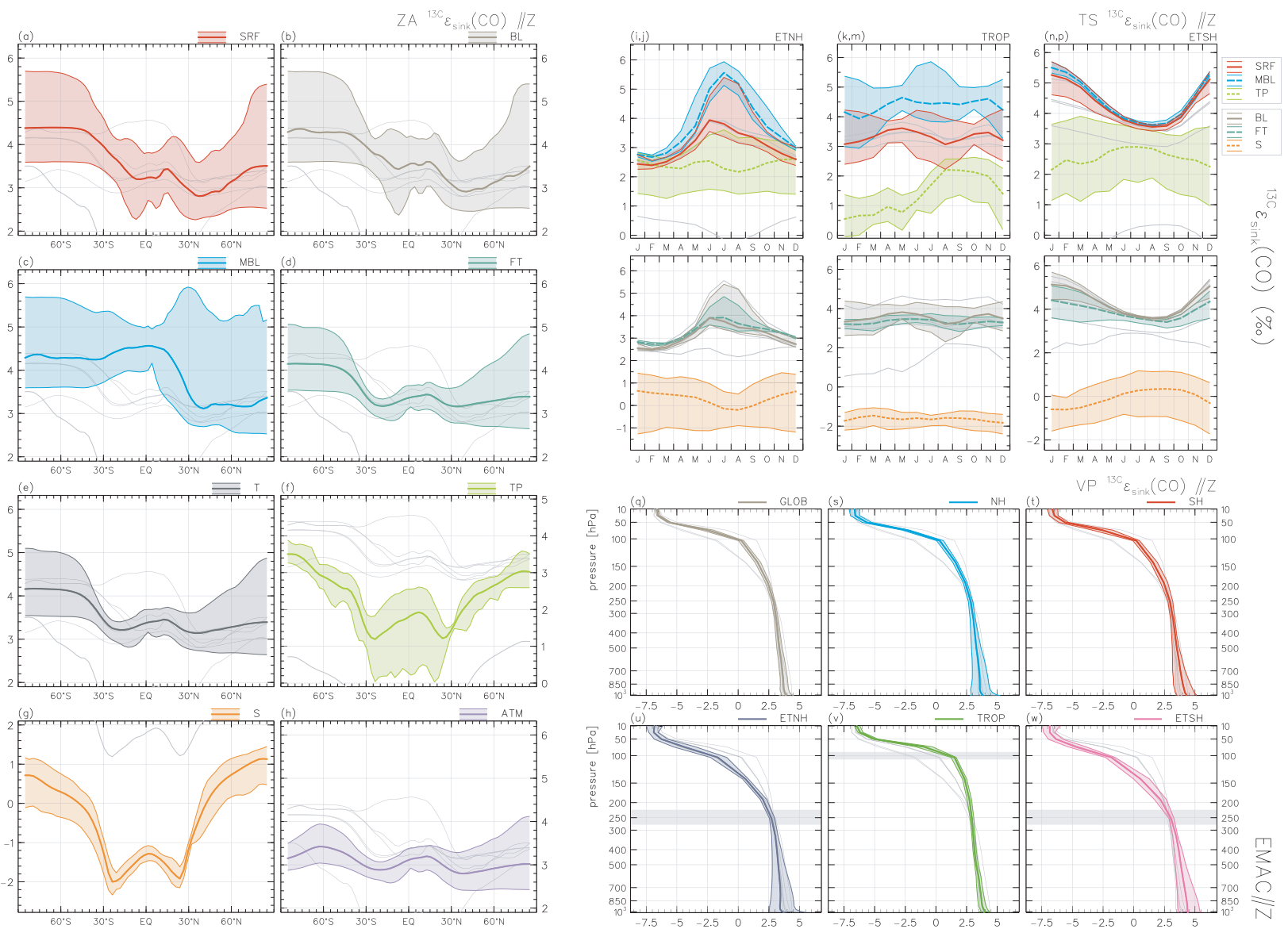
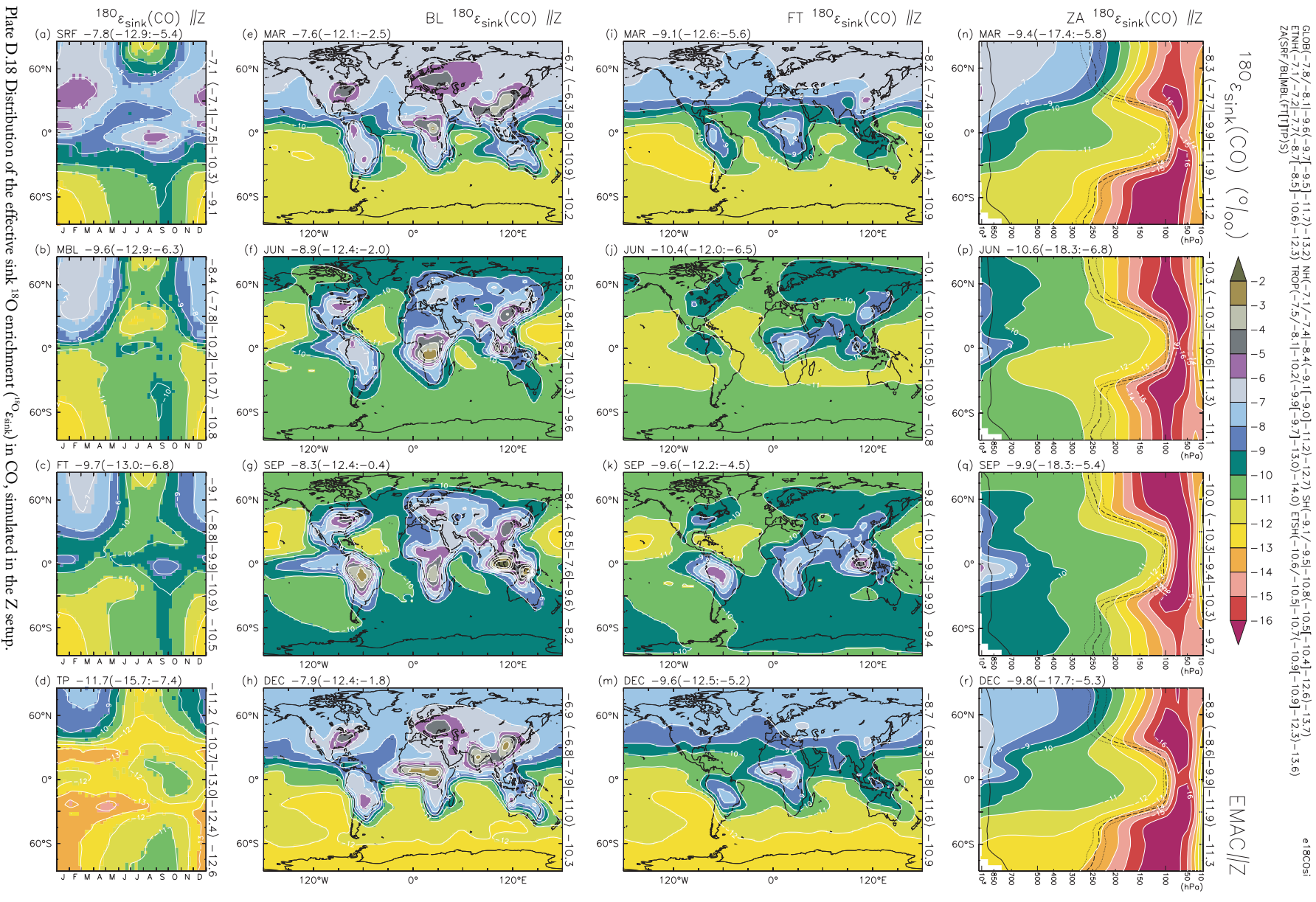
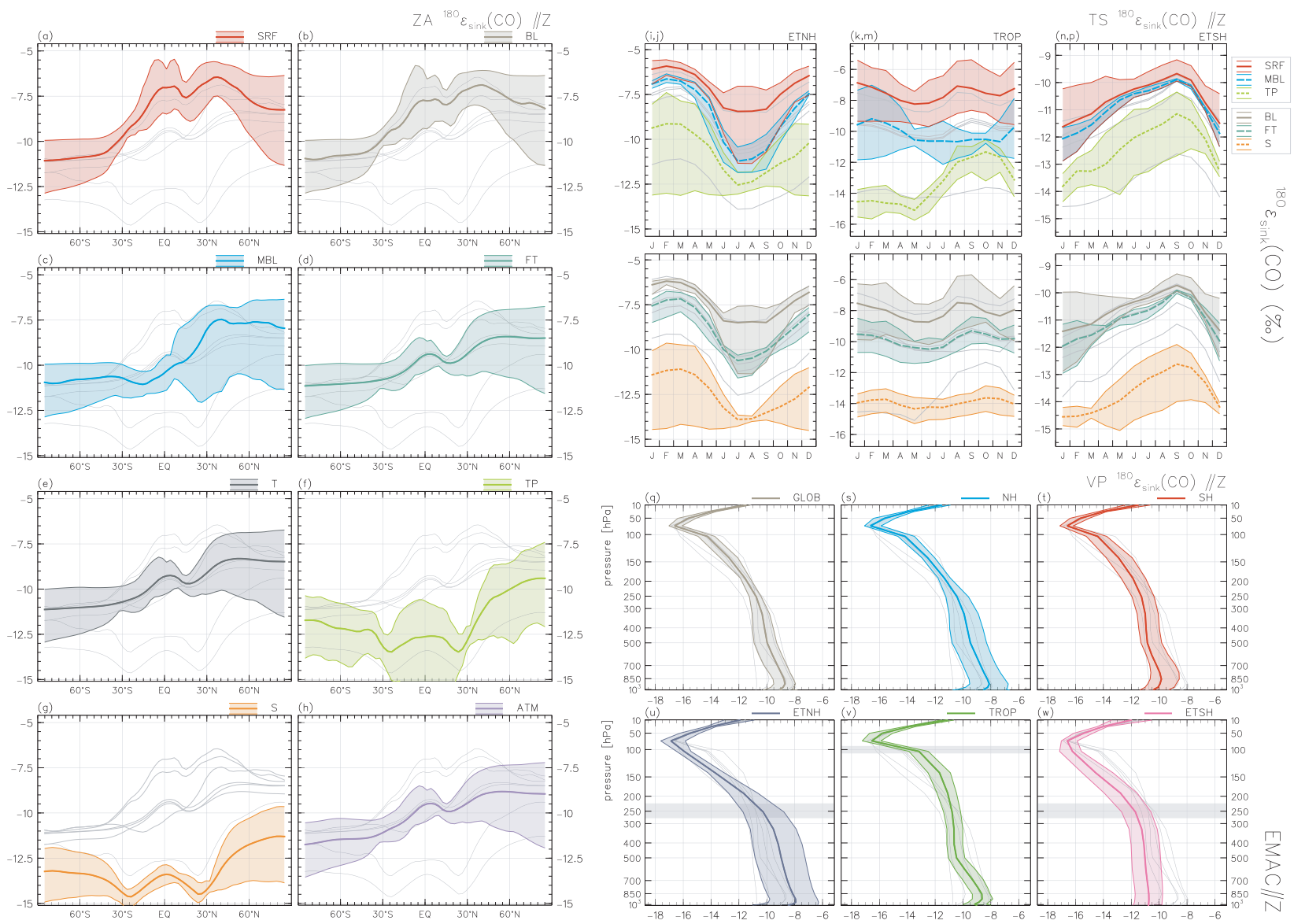
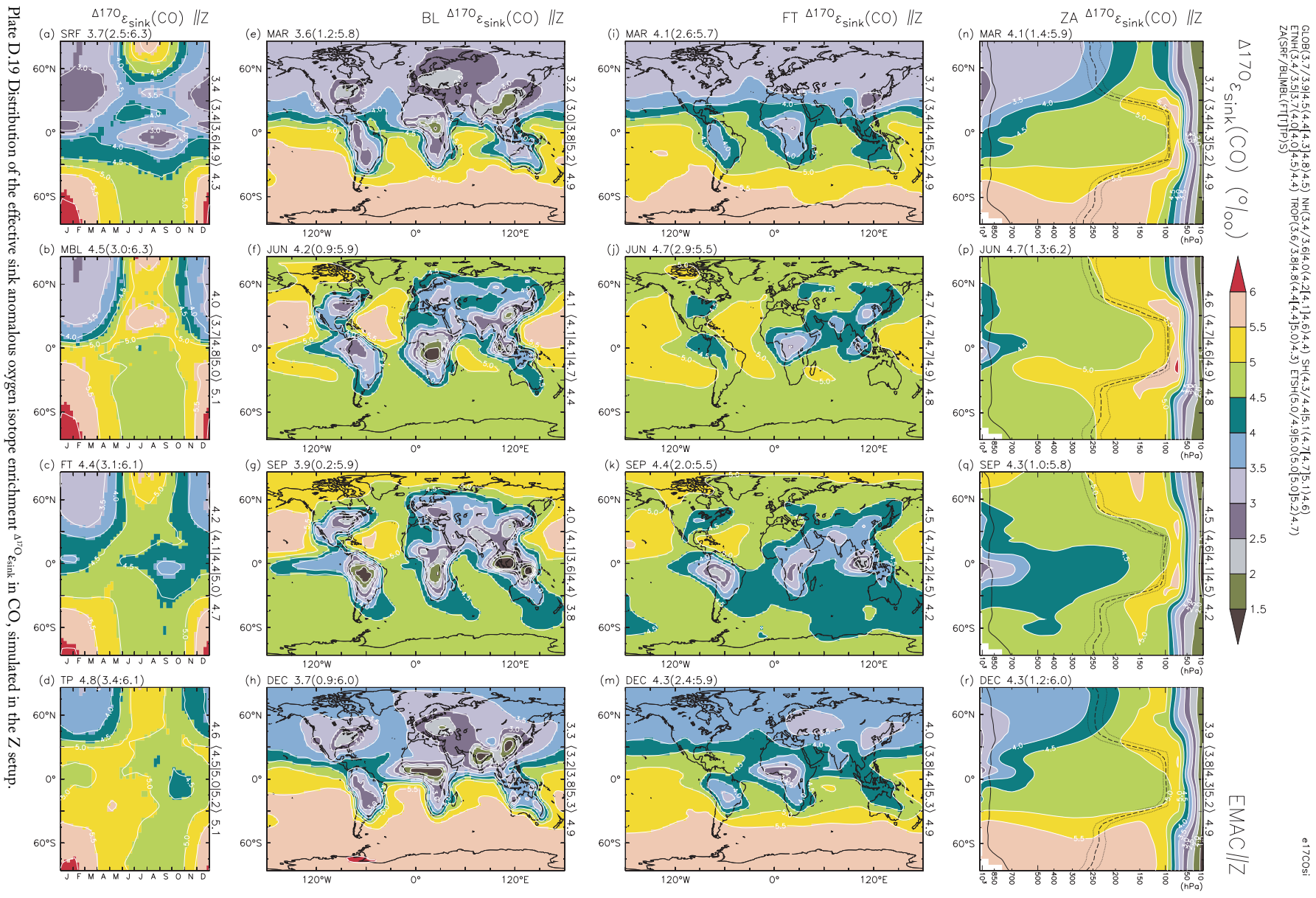


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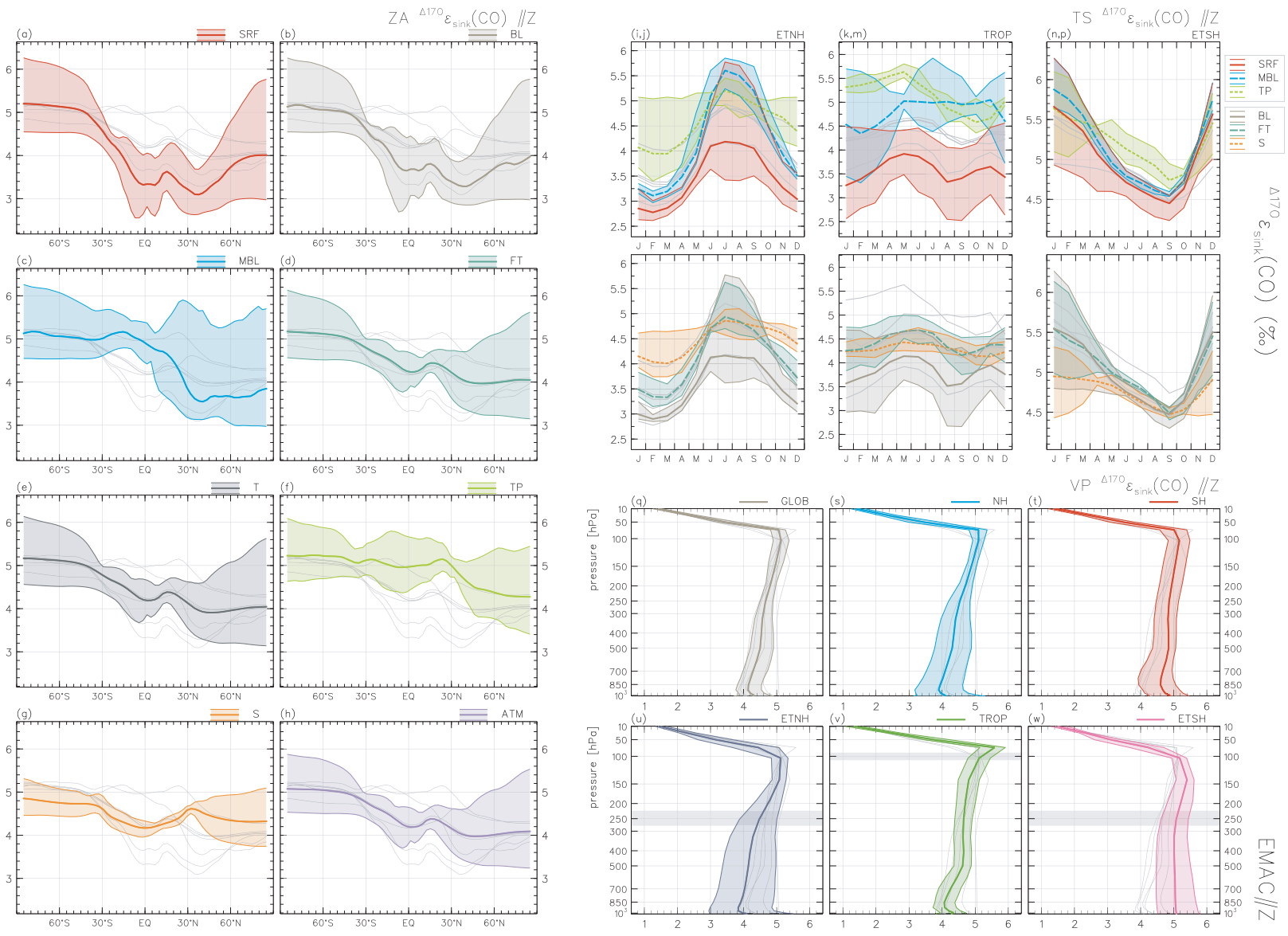


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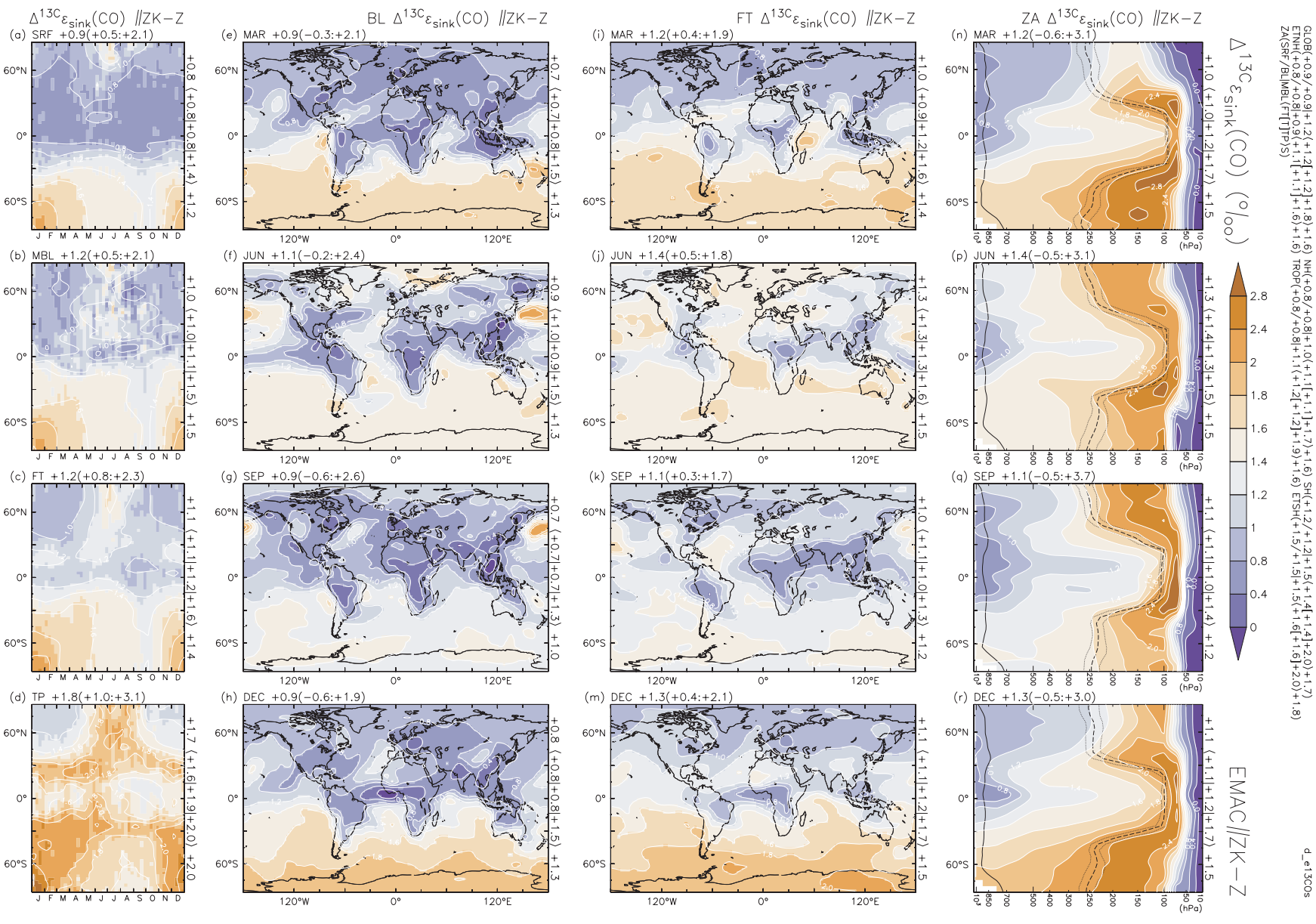
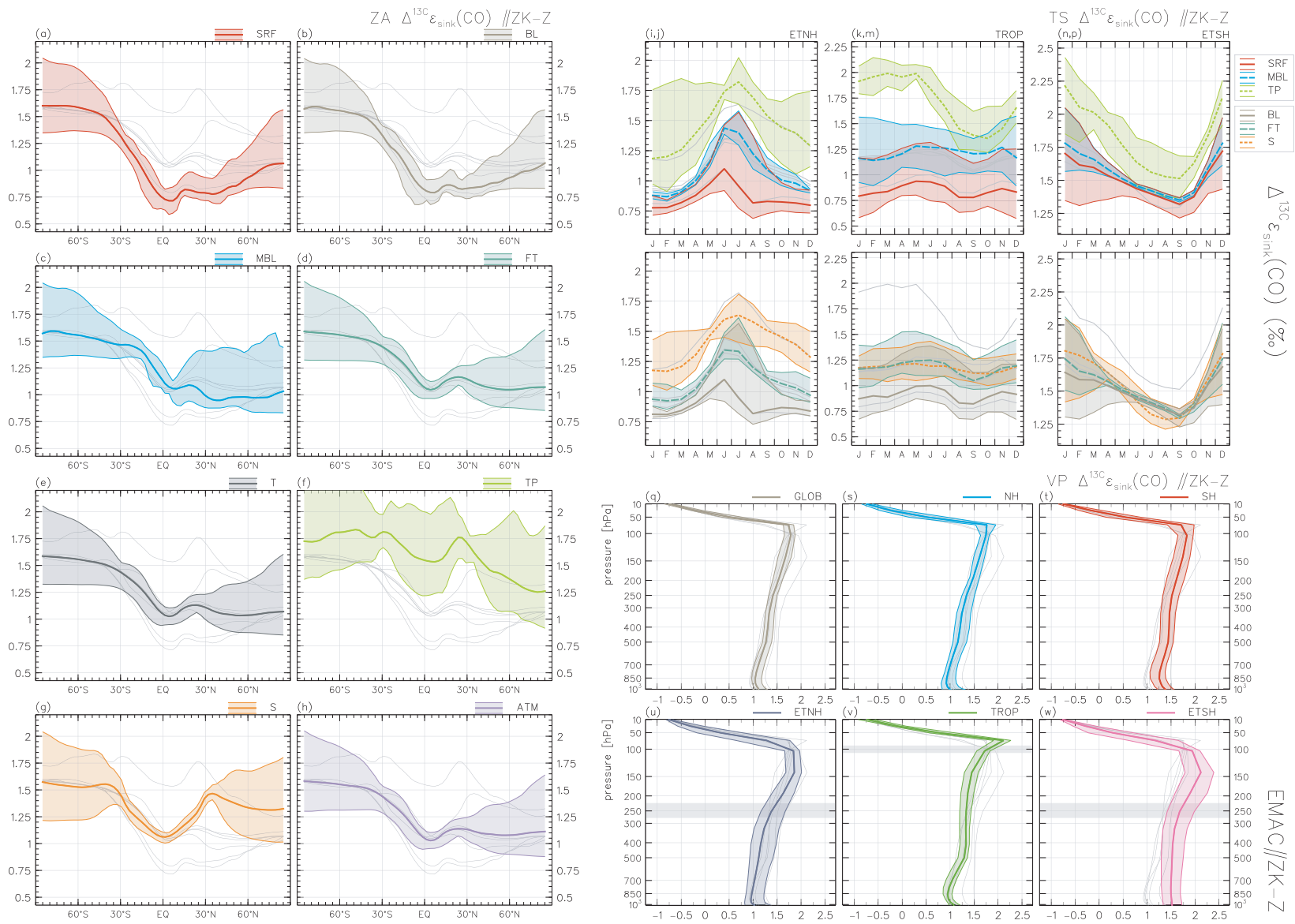
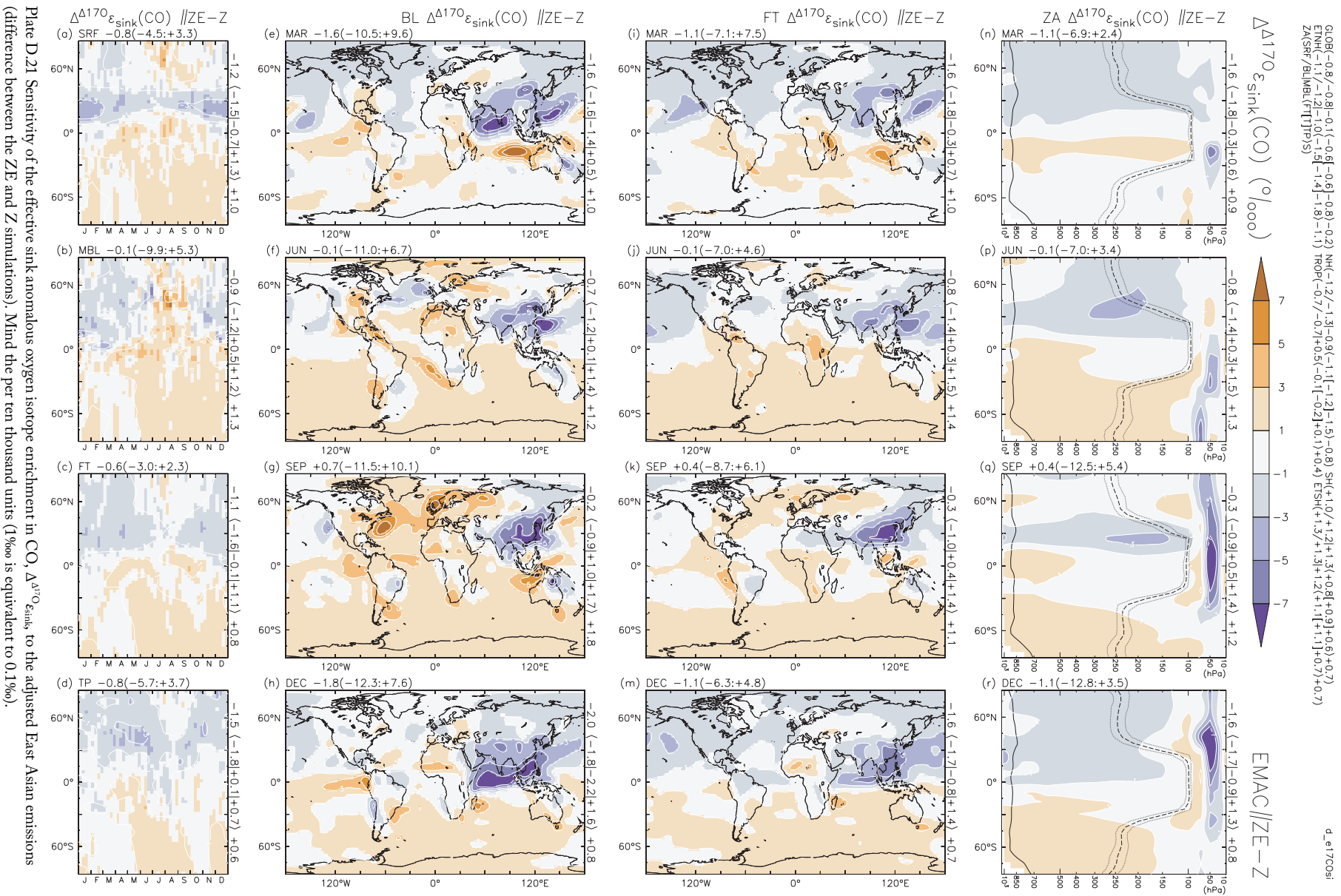


Plate D.20 Sensitivity of the effective sink ^{13}C enrichment in CO_2 , $\Delta^{13}\text{C}_{\text{sink}}$, to the changes in the parameterisation of the KIE in the $^{13}\text{CO}+\text{OH}$ reaction, simulated in the ZK-Z setups. The difference between the revisited and conventional approaches is shown.





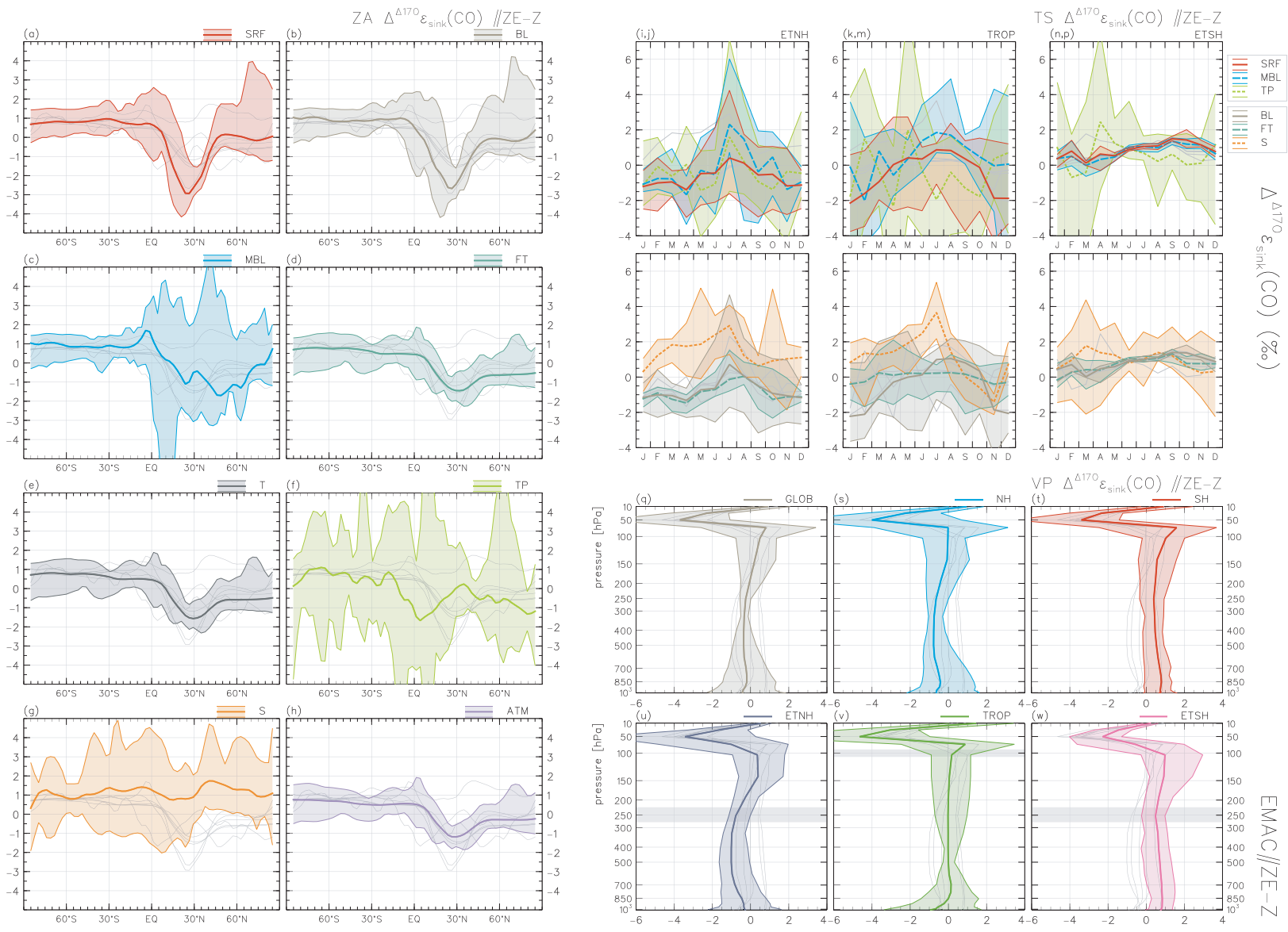


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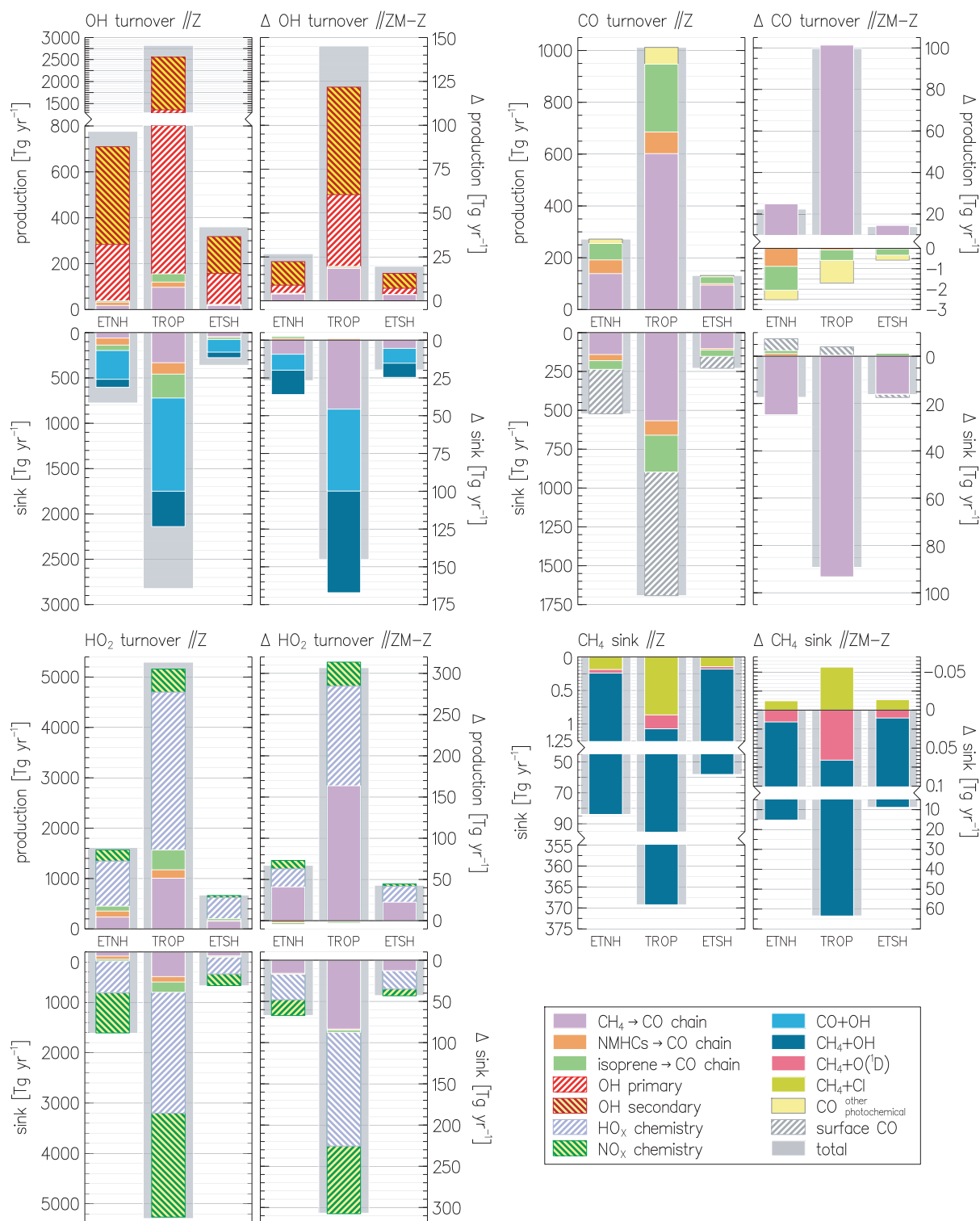
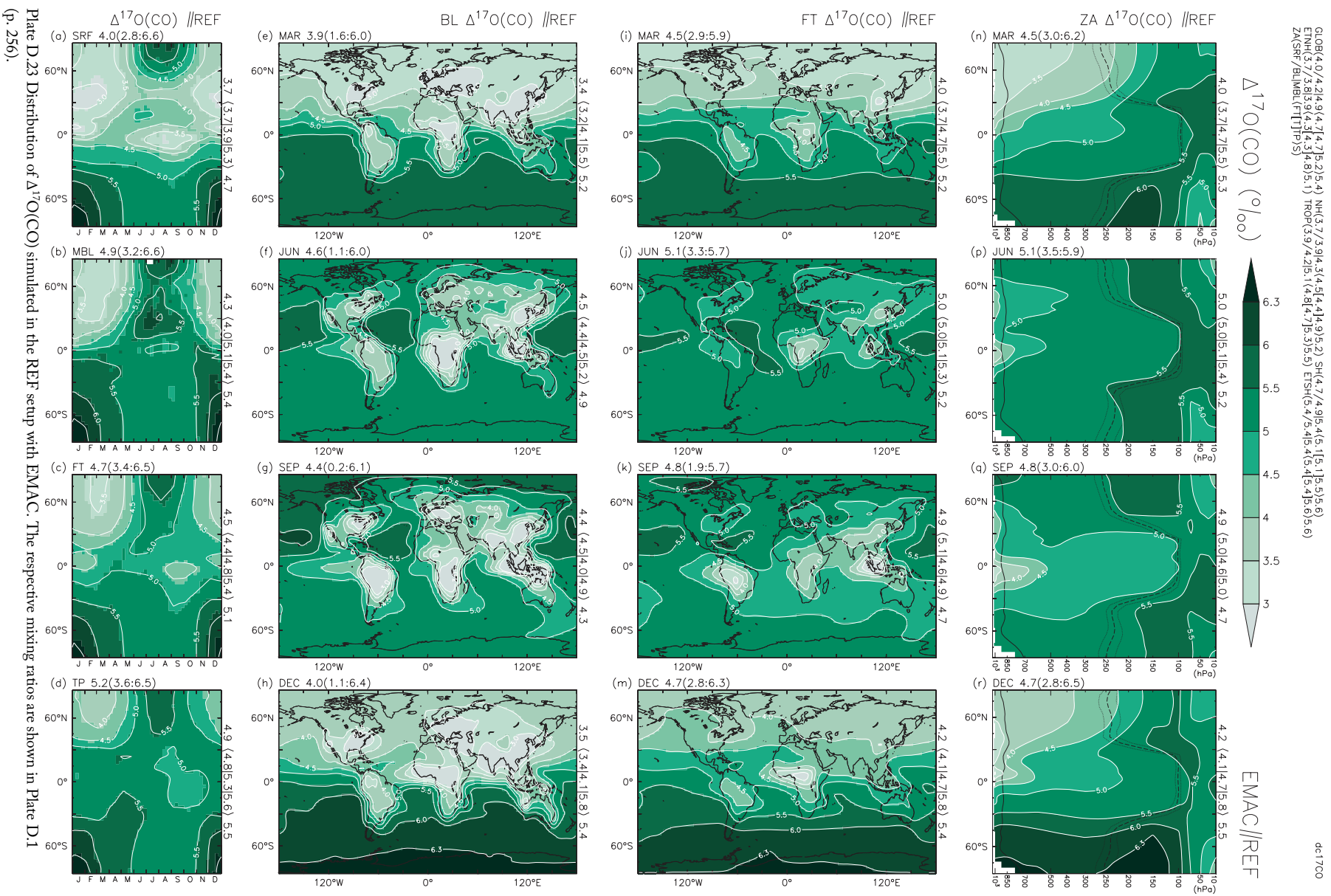


Plate D.22 Extended budgeting of OH, HO₂, CO and CH₄ photochemical turnover diagnosed in the Z (REF) and ZM setups simulations with EMAC. Each panel presents the component-wise in-situ production and sink simulated in Z (left), and their respective differences with those simulated in ZM (right) for the given species. For OH, the sinks shown in the CO production chains do not include those in the OH+CO and OH+CH₄ reactions; the production terms include the reactions of H₂O with O(¹D) (denoted primary) and HO₂ with O₃, NO and NO₃ (denoted secondary), respectively. The HO_x and NO_x chemistry terms amount to the aggregate production/sink of HO₂ in the reactions referenced in the MECCA mechanism as G2100–G2112 and G3100–G3224, respectively (see Appendix A, Table A.1, p. 225). For CH₄, only the sink terms are shown. Other (not shown) photochemical CO sources refer to the CO produced from HCHO and CH₃O₂ stemming from dimethylsulphide, methyl halogens (Cl, Br), and their oxidation/intermediate products. The discrepancies between the total and component-wise budgets pertain to the latter as well. Annual tropospheric integrals are shown. Mind the broken axes for the OH, CO and CH₄ plots. See Figure 6.10 (on p. 177) for the extended budgeting of the AE (ZE) setups simulations.

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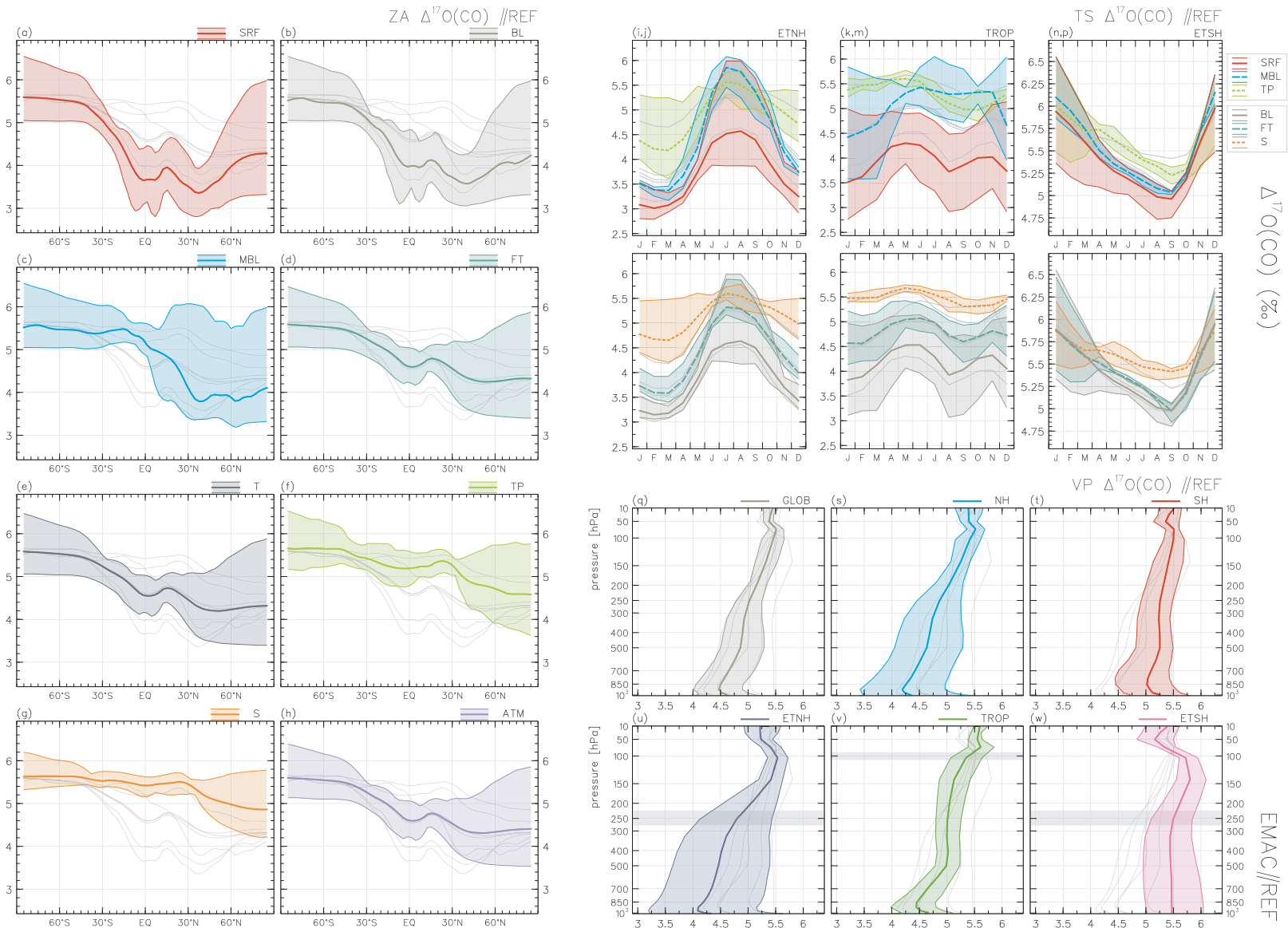
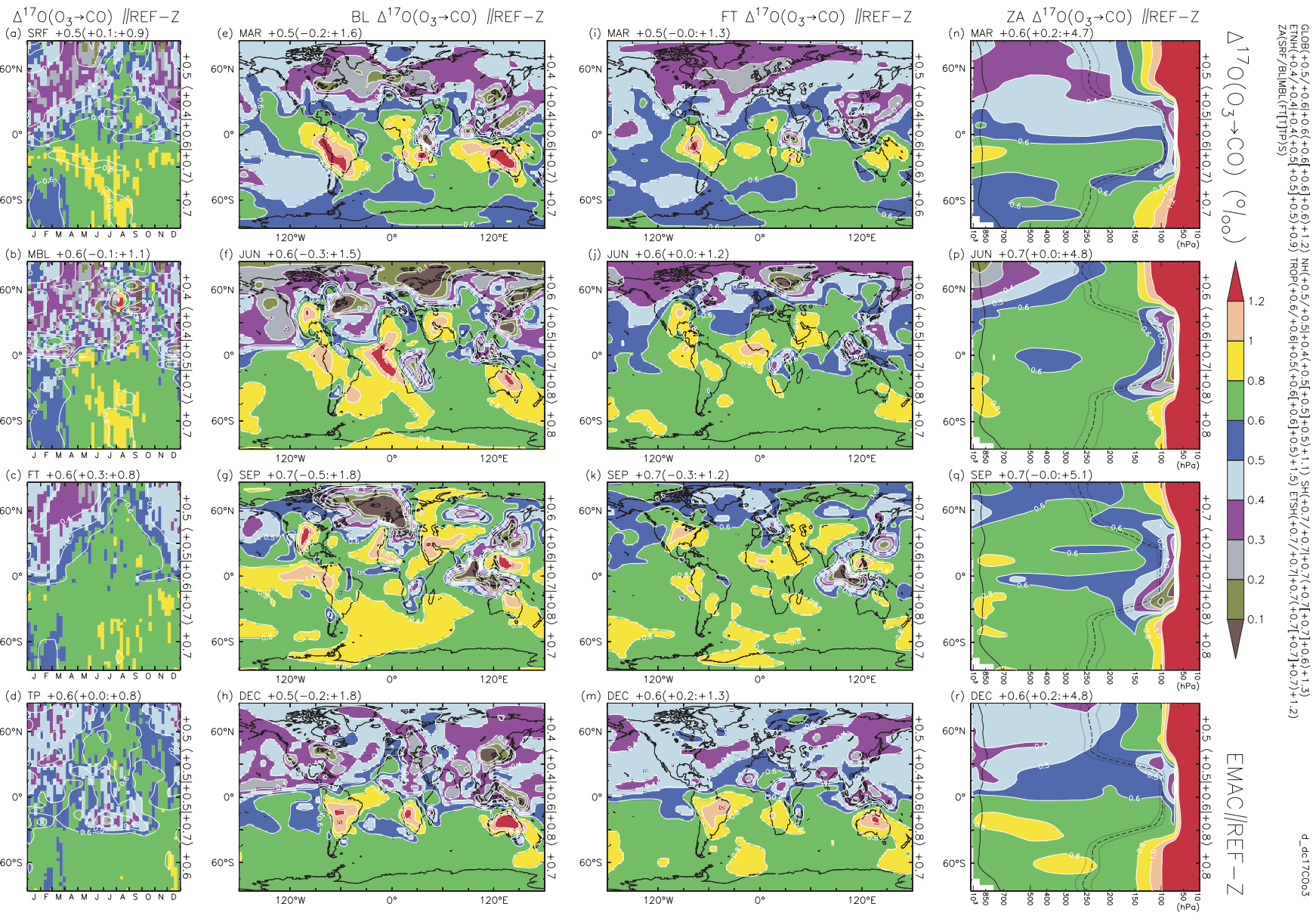
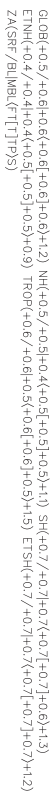
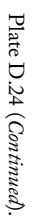


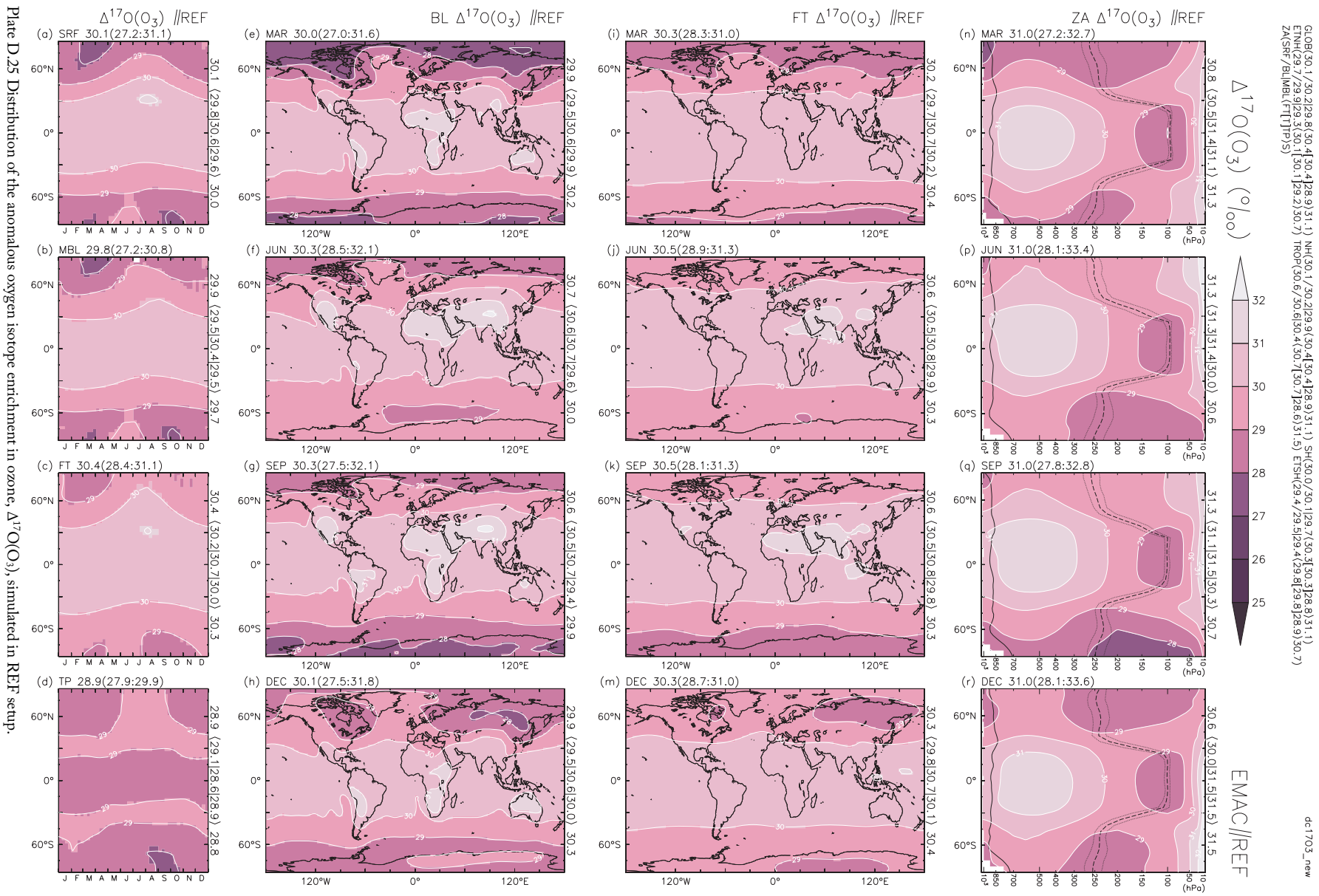
Plate D.24 Contribution of the ozone MIF signal to $\Delta^{17}\text{O}(\text{CO})$ inferred from the Z-REF setups simulations.




$$\Delta^{17}\text{O}(\text{O}_3 \rightarrow \text{CO}) \text{ (‰)}$$

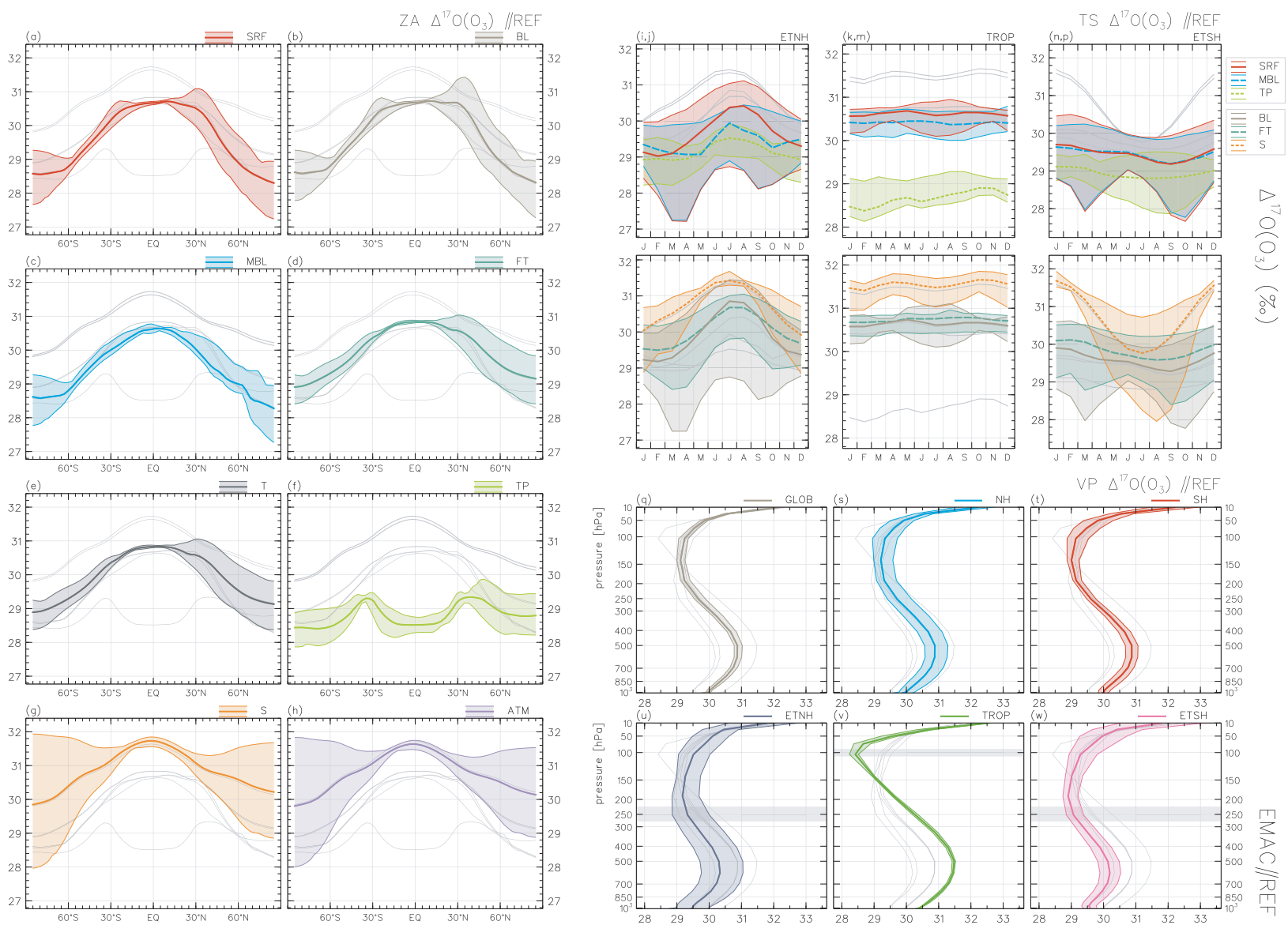
EMAC//REF-Z





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dc1703_new



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 ZASRF/BLMBL(FT)TPS

dc1703_new

List of abbreviations and acronyms

Acronym	Meaning	Reference (Sect.)
3D	three-dimensional	
AC-GCM	Atmospheric Chemistry GCM	
BB	biomass burning	
BF	biofuel (usage)	
(C)BL	(continental) boundary layer	
C1/C2	Phases One/Two of CARIBIC	4.2/Appendix C
CAM	Crassulacean Acid Metabolism	5.2.4.1
CARIBIC	Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container	4.2
CMS	Chlorine methane sink	6.1.1.2, 6.2.7.3
CTM	Chemistry-Transport Model	
DOC	Dissolved Organic Carbon	5.2.4
EMAC	ECHAM5/MESSy Atmospheric Chemistry model	
ENSO	El-Niño/Southern Oscillation activity	
ETNH/ETSH	Extratropical NH/SH	
EVAL	EMAC model Evaluation Setup	
FF	fossil fuel (usage)	
FT	free troposphere	
GCM	General Circulation Model	
HO _x	reactive hydrogen species (= HO ₂ +OH)	
IE	Isotope Effect	
IMV	Intra-Monthly Variation	6.2.1
IOR	Indian Ocean routes	4.2
IQR	interquartile range	note ⁴⁸ (p. 76)
ITCZ	Inter-Tropical Convergence Zone	
KIE	Kinetic IE	2.3.3
KPP	Kinetic Pre-Processor	2.2, 3.1
LHS/RHS	left/right hand side	
LMS	Lowermost Stratosphere	
MBL	marine (background) BL	
MCF	Methyl Chloroform (CH ₃ CCl ₃)	
MCM	Master Chemical Mechanism	3.1
MDF	Mass-Dependent Fractionation	3.2, 3.3.2
MECCA	Module Efficiently Calculating the Chemistry of the Atmosphere	2.2, 3.1
MESSy	Modular Earth Submodel System	
MIF	Mass-Independent Fractionation	3.2, 3.3.2
MIM	Mainz Isoprene Mechanism	3.1
MOZART	Model for Ozone and Related chemical Tracers	3.4.2, 6.1
NH/SH	Northern/Southern Hemisphere	
NMHC	Non-Methane Hydrocarbon(s)	
NO _x	Nitrogen oxides (= NO+NO ₂)	
NO _y	Reactive nitrogen (= NO _x + its oxidation products, incl. nitric acid)	
ODE	Ordinary Differential Equation	
ppm, ppb, ppt	mixing ratio in [μmol/mol], [nmol/mol], [pmol/mol], respectively	
RP _s	removal processes	
SD	standard deviation	
SIE	Solubility IE	5.1.5.2
STP	Standard Temperature and Pressure (273.15K, 10 ⁵ Pa)	
STE	Stratosphere-Troposphere Exchange	
UTLS	Upper Troposphere/Lowermost Stratosphere	
VOC	Volatile Organic Compound(s)	
ZPE	Zero-Point Energy	
[A], ⟨B⟩	denote abundance of A and uncertainty of B	3.2, note ¹⁰¹ (p. 142)

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