

Biogenic volatile organic compounds from green and blue oceans

Investigating reactive trace gases throughout the tropical troposphere

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Abstract

The biosphere emits a diverse suite of biogenic volatile organic compounds (BVOCs) into the atmosphere. Although their atmospheric mixing ratios are typically below a few tens of ppb (parts per billion, 10^{-9}), they play pivotal roles in the Earth system: they modify greenhouse gas concentrations, contribute to aerosol and cloud formation, and drive stratospheric ozone depletion. Consequently, a quantitative understanding of BVOC emissions, transport and loss pathways is a prerequisite for assessing the present-day impact of human activities on the Earth system.

This dissertation presents a comprehensive investigation of three key BVOCs—chloromethane (CH_3Cl), dimethyl sulfide (DMS) and isoprenoids (isoprene, its oxidation products, and total monoterpenes)—using Fast GC-MS and PTR-TOF-MS instruments deployed on the HALO research aircraft, together with the EMAC (ECHAM5/MESSy2) atmospheric chemistry model. Data from 27 measurement flights spanning 0.2–14 km altitude above two contrasting tropical regions, the "green ocean" of the Amazon rainforest (CAFE-Brazil) and the "blue ocean" of the Pacific (CAFE-Pacific), are used to study emission patterns, atmospheric chemistry and transport of those compounds under near-pristine conditions.

A previously unaccounted humidity interference of the Fast GC-MS setup has been identified and corrected employing stable tropospheric background mixing ratios of Chlorofluorocarbons (CFCs) as internal standards.

CH_3Cl mixing ratios rise to 700 pptv near the Amazon surface and exceed 1000 pptv over the Papua New Guinea rainforest, well above the tropical background of roughly 550 ± 50 pptv, confirming both ecosystems as net sources. The markedly higher values over PNG reveal substantial variability among rainforests. When combined with ten earlier airborne campaigns, the data show that the tropics dominate global CH_3Cl emissions but exhibit strong longitudinal heterogeneity. Upper-tropospheric mixing ratios above the western Pacific are roughly 10% higher than ground-based estimates, implying a larger stratospheric chlorine input than presently assumed.

DMS measurements reveal frequent upper-tropospheric enhancements (up to 56 pptv) in marine convective outflows, while they rarely exceed the detection limit in Amazonian convective outflows. EMAC model-observation comparisons show that the Hulswar et al. (2022) marine inventory best reproduces the CAFE-Pacific data, while the sole global terrestrial inventory (Spiro et al. 1992) overestimates Amazonian emissions by a factor of three. Among convection schemes, the Tiedtke-Nordeng parameterisation yields the closest match to the observed vertical DMS

profile. These results point to the need for refined terrestrial DMS emissions and more realistic convection representations in global models.

Observations of isoprene, its oxidation products (isoprene-OP) and total monoterpenes provide the first continuous vertical and diel profiles throughout the Amazonian troposphere. Night-time deep convection transports substantial amounts of those compounds (mean $\pm\sigma$ of 860 $\pm$ 34 pptv isoprene, 560 $\pm$ 200 pptv isoprene-OP, 50 $\pm$ 20 pptv monoterpenes) into the upper troposphere, priming it for rapid photo-chemistry at sunrise. A sensitivity study with EMAC shows that a 75% reduction in isoprenoid emissions (simulating deforestation) raises lower-tropospheric hydroxyl radicals and ozone, thereby shortening the methane lifetime by 0.3–0.4 years, but reduces secondary organic aerosol, leading to a modest net warming effect.

Zusammenfassung

Die Biosphäre gibt eine Vielzahl biogener flüchtiger organischer Verbindungen (BVOCs) an die Atmosphäre ab. Obwohl ihre Konzentrationen in der Atmosphäre in der Regel unter einigen zehn ppb (parts per Million, 10^{-9}) liegen, spielen sie eine entscheidende Rolle im Erdsystem: Sie beeinflussen die Konzentrationen von Treibhausgasen, tragen zur Aerosol- und Wolkenbildung bei und sind für den Abbau des stratosphärischen Ozons verantwortlich. Folglich ist ein quantitatives Verständnis der Emissionen, Transportwege und Abbauprozesse von BVOCs eine Voraussetzung für die Erforschung der Auswirkungen heutiger menschlicher Aktivitäten auf das Erdsystem.

Diese Dissertation präsentiert eine umfassende Untersuchung von drei wichtigen BVOCs—Chlormethan (CH_3Cl), Dimethylsulfid (DMS) und Isoprenoide (Isopren, seine Oxidationsprodukte und Summe der Monoterpene)—unter Verwendung von Fast-GC-MS- und PTR-TOF-MS-Instrumenten an Bord des Forschungsflugzeugs HALO, sowie des Atmosphärenchemie-Klima-Modells EMAC (ECHAM5/MESSy2). Daten von 27 Messflügen in Höhen von 0,2 bis 14 km über zwei kontrastierenden tropischen Regionen, dem „grünen Ozean“ des Amazonas Regenwaldes (CAFE-Brazil) und dem „blauen Ozean“ des Pazifiks (CAFE-Pacific), werden genutzt, um Emissionsmuster, atmosphärische Chemie und Transport dieser Verbindungen unter nahezu ungestörten natürlichen Bedingungen zu untersuchen.

Eine bislang nicht berücksichtigte Interferenz der Fast-GC-MS-Messungen aufgrund von variabler Luftfeuchte wurde identifiziert und, mithilfe der stabilen troposphärischen Hintergrundmischungsverhältnisse von Fluorchlorkohlenwasserstoffen (FCKWs), die als interne Standards genutzt wurden, korrigiert.

CH_3Cl -Mischungsverhältnisse steigen in Bodennähe über dem Amazonas auf bis zu 700 pptv an, und überschreiten 1000 pptv über dem Regenwald von Papua-Neuguinea, was deutlich über tropischen Hintergrund-Konzentrationen von rund 550 ± 50 pptv liegt, und bestätigen damit beide Ökosysteme als Netto-Quellen. Die deutlich höheren Werte über PNG zeigen eine erhebliche Variabilität zwischen Regenwäldern. In Kombination mit zehn früheren Flugkampagnen zeigen die Daten, dass die Tropen die globalen CH_3Cl -Emissionen dominieren, jedoch eine starke longitudinale Heterogenität aufweisen. Mischungsverhältnisse in der oberen Troposphäre über dem westlichen Pazifik liegen etwa 10% über den Beobachtungen bodengebundener Messnetzwerke und deuten auf einen größeren Chlor-Eintrag in die Stratosphäre hin, als derzeit angenommen.

DMS-Messungen dokumentieren häufige Anreicherungen in der oberen Troposphäre (bis zu 56 pptv) in marinen konvektiven Ausströmungen, während sie in konvektiven Ausströmungen über dem Amazonas überwiegend unterhalb der Nachweisgrenze lagen. Vergleiche zwischen

EMAC-Modell und Beobachtungen zeigen, dass der marine Emissionsdatensatz von Hulswar et al. (2022) die CAFE-Pacific-Daten am besten reproduziert, während der einzige globale terrestrische Datensatz (Spiro et al. 1992) die Amazonas-Emissionen um einen Faktor drei überschätzt. Unter den Konvektionsschemata liefert die Tiedtke-Nordeng-Parametrisierung die beste Übereinstimmung mit dem beobachteten vertikalen DMS-Profil. Die Ergebnisse verdeutlichen den Bedarf an verfeinerten terrestrischen DMS-Emissionen und realistischeren Konvektions-Parametrisierungen in globalen Modellen.

Beobachtungen von Isopren, seinen Oxidationsprodukten (Isopren-OP) und der Summe der Monoterpene liefern die ersten kontinuierlichen vertikalen und tageszeitlichen Profile über die gesamte Amazonas-Troposphäre. Nächtliche tiefe Konvektion transportiert erhebliche Mengen dieser Verbindungen (Mittelwert $\pm\sigma$: 860 ± 34 pptv Isopren, 560 ± 200 pptv Isopren-OP, 50 ± 20 pptv Monoterpene) in die obere Troposphäre und bereitet sie für eine rasche Photochemie beim Sonnenaufgang vor. Eine Sensitivitätsstudie mit dem EMAC-Modell zeigt, dass eine 75%-ige Reduktion der Isoprenoid-Emissionen (Simulation von Entwaldung) die Konzentrationen von Hydroxylradikalen und Ozon in der unteren Troposphäre erhöht, wodurch die Methan-Lebensdauer um 0,3–0,4 Jahre verkürzt wird, gleichzeitig jedoch die sekundäre organische Aerosolbildung reduziert wird, was zu einem moderaten Erwärmungseffekt führt.

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Chapter 1

Introduction

“For the first time in my life I saw the horizon as a curved line. It was accentuated by a thin seam of dark blue light—our atmosphere. Obviously this was not the ocean of air I had been told it was so many times in my life. I was terrified by its fragile appearance.”

Ulf Merbold (Physicist and Astronaut)

Although it represents only a negligible fraction of Earth’s total mass, life would be impossible without its gaseous shield—the atmosphere. It moderates temperature, blocks carcinogenic solar UV radiation, provides breathable air, and transports water from the oceans to the continents. For centuries, air was regarded as a single, unalterable element. Only in 347 BC did Aristotle suggest in *Meteorologica* that it might be a mixture of gases. We now know that the atmosphere is mainly composed of 78% nitrogen, 21% oxygen, 1% argon, and a variable amount of water vapour that changes with altitude. In addition, a myriad of trace gases and aerosols are present, ranging from relatively inert greenhouse gases such as carbon dioxide (CO₂) and methane (CH₄) to a diverse suite of highly reactive volatile organic compounds (VOC) and particles. The atmospheric composition is largely controlled by emission and uptake of the biosphere, Earth’s crust and its interior. Over geological time, the atmosphere has undergone dramatic transitions, evolving from a weakly reducing early state to the strongly oxidising atmosphere that characterises the planet today. (Seinfeld and Pandis, 2016)

Since the onset of the Anthropocene, the atmosphere has been undergoing unprecedented rapid change driven by human activity (Crutzen, 2002). Key drivers include, but are not limited to: fossil-fuel combustion, which has emitted vast quantities of CO₂ and sulfur dioxide (SO₂); the expansion of agriculture, accompanied by land-cover change and increasing emissions of CH₄ and nitrous oxide (N₂O); and industrial activity, which has released hazardous man-made chemicals such as chlorofluorocarbons (CFCs) and polyfluoroalkyl substances (PFAS). These perturbations have multiple consequences: higher CO₂, CH₄ and N₂O amplify the greenhouse effect and drive global warming (IPCC, 2001); SO₂ causes acid rain (Galloway et al., 1984) and alters cloud properties; CFCs would have nearly destroyed the ozone (O₃) layer were it not for international agreements curbing their emissions in the 1990s (Kim et al., 2011); and PFAS, toxic “forever-chemicals”, have spread throughout the entire Earth system and are now detectable in nearly every humans’ blood (Evich et al., 2022).

In the Anthropocene, these human impacts equal or exceed natural forcings on the Earth system at a global scale (Crutzen and Steffen, 2003). Consequently, understanding and predicting both the direct and indirect effects of human activities is essential for mitigating severe consequences for the planet, requiring coordinated efforts across multiple disciplines such as physics, chemistry, biology, geology, meteorology, and oceanography (Schellnhuber, 1999). Insights gained over decades from observations and experiments in these fields feed into Earth System Models (ESMs), which integrate numerical simulations of land, ocean, and atmospheric processes to support prediction and policy-making (Steffen et al., 2020). To assess anthropogenic perturbations such as global warming, present-day (PD) ESM simulations are contrasted with pre-industrial (PI)

simulations. Currently, one of the greatest uncertainties in these comparisons stems from poorly constrained natural emissions and related aerosols in the PI scenario (Carslaw et al., 2013). A key strategy for testing and improving ESM performance is inter-comparison with atmospheric measurements (Steffen et al., 2020), e.g., from permanent ground-based monitoring stations that track long-term trends or aircraft campaigns that provide high vertical and spatial coverage.

This dissertation is based on two extensive VOC datasets obtained during the Chemistry of the Atmosphere Field Experiment (CAFE) campaign series aboard the High Altitude Long Range (HALO) research aircraft. One mission sampled the tropical “green ocean” of the Amazon rainforest (CAFE-Brazil), and the other the remote “blue ocean” of the Pacific (CAFE-Pacific). In addition to the measurements, state-of-the-art ESM simulations were performed using EMAC (ECHAM5/MESSy2) for both settings. In these contrasting near-pristine environments the emission patterns, atmospheric fate, and model representation of three key biogenic VOCs—*isoprene*, *dimethyl sulfide*, and *chloromethane*—are examined.

The introduction aims to place this work within the broader context of the field and is organised as follows: first, the various types and origins of VOCs are presented; second, chemical and dynamical aspects of their fates in the atmosphere are discussed; finally, the thesis outline summarises the central scientific questions addressed throughout the dissertation.

1.1. Volatile Organic Compounds (VOC)

The term *volatile organic compounds* generally refers to all carbon-containing trace gases that exhibit sufficient vapour pressure to remain mainly in the gas-phase under atmospheric conditions. The three most abundant carbon-bearing gases— CO_2 , CO , and CH_4 —are usually excluded from this group, which has led to the expression “non-methane VOC” (NMVOC) frequently being used.

Although the presence of organic trace gases in the atmosphere was already recognised earlier (Gärtner, 1922), it was not until the early 1950s that advances in analytical techniques enabled identification of a rapidly expanding suite of VOCs (Eggertsen and Nelsen, 1958; Shepherd et al., 1951). This effort was initially driven by the need to explain the severe smog that plagued Los Angeles at the time (Haagen-Smit, 1952).

Precise analytical techniques now enable detection and quantification of VOCs at sub-parts per trillion (ppt; 1 in 10^{12}) levels (Williams, 2004). The number of currently identified VOC species is estimated at 10^4 – 10^5 , while the true number is likely orders of magnitude larger (Goldstein and Galbally, 2007). VOCs comprise a wide variety of gases, from simple hydrocarbons (e.g., alkanes, alkenes, aromatics) to compounds containing hetero-atoms: oxygenated species (OVOC; e.g., aldehydes, ketones, alcohols), nitrogen-bearing species (e.g., nitrates, nitriles), sulfur-bearing species (e.g., sulfides, thiols), and halocarbons (XVOC; e.g., organic chlorides, bromides, iodates). VOCs are emitted primarily by living organisms—animals, humans, plants, and microorganisms (Goldstein and Galbally, 2007). Current estimates attribute roughly 85% of global VOC emissions to biogenic

sources (BVOC; 860–1100 Tg (VOC) yr⁻¹), with tropical forests as the dominant source regions (Guenther et al., 2012; Sindelarova et al., 2014). The remaining ~15% (150–160 Tg (VOC) yr⁻¹), arise from anthropogenic activities, the bulk of which occurs in the Northern Hemisphere (Hoesly et al., 2018).

1.1.1. Anthropogenic VOC

The bulk of anthropogenic VOC emissions worldwide stems from fossil-fuel use for energy and transport, biomass burning, and industrial activities, including solvent use (Hoesly et al., 2018; Williams and Koppmann, 2007). A prominent class among anthropogenic VOC is the BTEX suite (benzene, toluene, ethylbenzene, and xylenes), which predominates in urban atmospheres (Cabrera-Perez et al., 2016; Hamid et al., 2019; Liu et al., 2025) and can therefore serve as a tracer for air masses with strong anthropogenic influence.

1.1.2. Biogenic VOC

Globally, terrestrial plants are the dominant biogenic VOC emitters (Sindelarova et al., 2014), with additional contributions from soil microbes (Bourtsoukidis; Behrendt, et al., 2018) and marine phytoplankton (Hulswar et al., 2022). Perhaps the most prominent group among BVOCs are the isoprenoids, emitted primarily by plants (Sindelarova et al., 2014). Other key BVOCs are dimethyl sulfide (DMS), which originates mainly from the oceans (Watts, 2000), and chloromethane (CH₃Cl), the most relevant biogenic XVOC (WMO, 2022). Although many other BVOC are relevant, this section concentrates on isoprenoids, DMS, and CH₃Cl, which are the protagonists of the present thesis and are introduced briefly below.

Isoprenoids

The term *isoprenoids* refers to compounds built from C₅H₈ (2-methylbuta-1,3-diene) units and includes isoprene (C₅H₈; ~70% of total BVOC), monoterpenes (C₁₀H₁₆; ~11%) and sesquiterpenes (C₁₅H₂₄; ~2%) (Sindelarova et al., 2014), together with a minor fraction of higher terpenes. Isoprenoids are emitted primarily by plants for whom they serve diverse functions such as defence against biotic and abiotic stress and plant-insect communication (Gershenzon and Dudareva, 2007). Because their release is linked to photosynthesis and respiration, isoprenoid emissions depend strongly on light and temperature (Kesselmeier and Staudt, 1999). The presence of multiple double bonds makes isoprenoids highly reactive toward atmospheric oxidants, influencing the methane budget and driving substantial secondary organic aerosol (SOA) formation, thereby affecting the Earth's radiative balance (see Section 1.2) (Claeys et al., 2004; IPCC, 2023).

Dimethylsulfide

Dimethyl sulfide (DMS) is the largest biogenic source of reduced sulfur to the atmosphere (M. O. Andreae, 1990). It is primarily released from ocean surface waters, where it is produced as a byproduct of phytoplankton metabolism, with smaller contributions from terrestrial sources such as plants and soils (Watts, 2000). The annual global budget of DMS is currently estimated at 39–52 Tg yr⁻¹ (Hulswar et al., 2022; S. Wang et al., 2019). Although accounting for only a small fraction (3–6%) of the global BVOC burden, DMS has received much attention over the past decades because of its role as a natural precursor to sulfate aerosol that acts as cloud condensation nuclei (CCN) in the marine atmosphere (Charlson et al., 1987; Quinn and Bates, 2011).

Chloromethane

Chloromethane (CH₃Cl) is the most important chlorine-bearing BVOC with a global emission strength of 4.7 Tg yr⁻¹ (WMO, 2022). The predominant source of CH₃Cl to the atmosphere is tropical vegetation (Xiao et al., 2010; Yokouchi et al., 2000), followed by biomass burning (Blake et al., 1996), oceans (Moore et al., 1996), salt marshes (Rhew et al., 2000), and wood-rotting fungi (Saxena et al., 1998; Watling and Harper, 1998). Because it is relatively inert to tropospheric oxidants, a substantial fraction of the emissions reaches the stratosphere, where photolysis releases chlorine atoms that significantly contribute to stratospheric ozone depletion (WMO, 2022). While at present roughly 17% of stratospheric chlorine originates from CH₃Cl, it was the dominant source in pre-industrial times (prior to the onset of anthropogenic CFC emissions in the 1930s) and is expected to regain dominance in the future as CFC concentrations continue to decline following the Montreal Protocol (UNEP, 1987; WMO, 2022).

1.2. Atmospheric Chemistry and Dynamics

The atmosphere is a crucial component of the Earth system, functioning as a vast chemical reactor that hosts gaseous, liquid, and solid species. After emission from the Earth's surface, these constituents undergo chemical transformations that alter their physical and chemical properties, are transported over long distances, and are eventually deposited on the surface again. Solar radiation supplies the energy driving these processes, while temperature and pressure gradients with altitude create distinct chemical and dynamical regimes in the five atmospheric layers (Figure 1.1).

The lowest layer, the troposphere (from the Greek *tropos*, “rotating”), is characterised by continuous vertical mixing driven by a negative lapse rate that induces convection. It contains ~80% of the atmosphere's mass, virtually all atmospheric water, and therefore hosts almost all weather phenomena (Seinfeld and Pandis, 2016). The upper boundary of the troposphere is the tropopause, a temperature minimum that also marks the base of the stratosphere. Tropopause height varies with latitude and season, ranging from ~7 km at the poles to ~17 km in the tropics (Reichle, 2023).

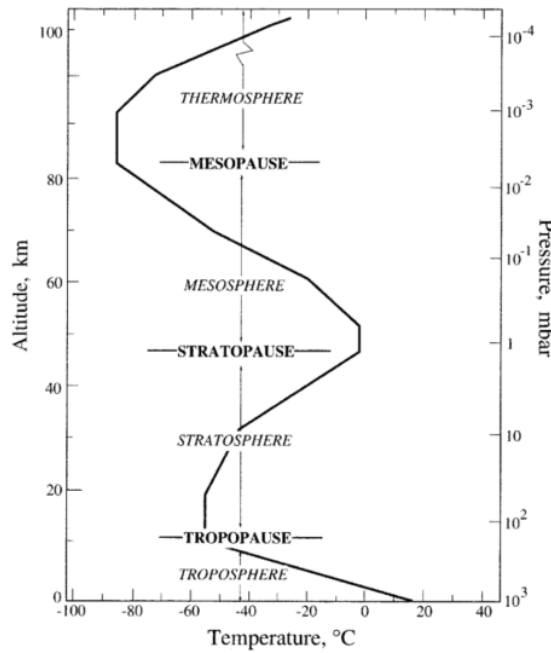


Figure 1.1.: Layers of the atmosphere, characterised by temperature and pressure variations with height. Illustration adopted from Seinfeld and Pandis (2016).

Above the tropopause lies the stratosphere (from the Greek *stratos*, “layer”), extending up to the mesopause. Its strong stratification results from a positive lapse rate: absorption of solar UV radiation by the ozone layer produces heat, creating a temperature increase with altitude (Seinfeld and Pandis, 2016). The next higher region is the mesosphere, where most meteoroids ablate, followed by the thermosphere, in which temperatures rise again because short-wave radiation is absorbed by the remaining air molecules, creating the ionosphere (Reichle, 2023). Finally, the outermost exosphere contains such sparse gas that molecules with sufficient energy can escape from the Earth’s gravity field, and the atmosphere gradually merges with interplanetary space (Seinfeld and Pandis, 2016). For the present work, the chemical and dynamical processes of the troposphere and stratosphere are most relevant and will be introduced in detail below.

1.2.1. Troposphere

The dynamics of the atmosphere are driven by heat exchange between warmer and colder air masses. Because the troposphere exhibits a negative lapse rate, a moist parcel that is warmed by the Earth’s surface becomes buoyant and rises, whereas a cooler parcel sinks—processes collectively termed convection. As the parcel ascends to lower pressure, it cools adiabatically. When the water vapour mixing ratio reaches saturation, condensation occurs, forming cloud droplets and releasing latent heat, which can further lift the parcel. Convection therefore shapes the tropospheric weather phenomena of clouds, winds, and thunderstorms. (Seinfeld and Pandis, 2016) In addition to transporting tracers vertically, deep convective clouds influence tropospheric chemistry by dimming UV radiation, scavenging water-soluble species, and generating nitrogen oxide (NO) radicals through lightning (C. Wang and Prinn, 2000).

From a dynamical viewpoint, the troposphere can be split into two sub-domains. The *planetary boundary layer* (PBL) occupies the lowest 100-3000 m and is directly coupled to the surface. It responds almost instantaneously to surface forcings (radiative heating, friction, emissions, uptakes, evaporation, transpiration), which maintain continuous turbulent mixing. The PBL height is highly variable depending on the surface temperature: it is greatest during daytime and over land, and smallest at night and over the oceans. Above the PBL lies the *free troposphere* (FT), where vertical motions mostly occur in distinct convective cells, and strong horizontal winds can transport air masses over long distances. (Stull, 2003)

The chemistry of the troposphere is strongly oxidising, sustained by O_3 and a suite of radicals—hydroxyl (OH), hydroperoxyl (HO_2), nitrate (NO_3), and halogens (Cl, Br, I and their oxides). The HO_x ($\equiv OH+HO_2$) cycle is the principal sink for most reactive trace gases (Ehhalt, 1999; Lelieveld et al., 2016; Levy, 1971), NO_3 radicals dominate nighttime oxidation (Brown et al., 2006), and halogen radicals provide a significant contribution in polar and marine regions (W. R. Simpson et al., 2015). Moreover, multiphase processes, including liquid-phase reactions in cloud droplets and surface reactions on aerosol particles, add further complexity (Ravishankara, 1997). Because of its role as the main tropospheric sink for the VOCs examined in this thesis, the focus lies on gas-phase chemistry related to the HO_x cycle in this section.

Primary OH production is initiated by the photolysis of O_3 , which yields singlet oxygen $O(^1D)$ (orange in Figure 1.2). The excited $O(^1D)$ atom reacts with water to form OH. OH oxidises VOCs mainly via two mechanisms—hydrogen abstraction from a C-H bond (illustrated in Figure 1.2) and addition to a C=C double bond or hetero atom—both of which generate a peroxy radical (RO_2). RO_2 can either react with other radicals (termination), forming an oxygenated VOC (OVOC) or, in the presence of NO_x ($\equiv NO+NO_2$), propagate further to produce an OVOC and HO_2 . HO_2 is then recycled to OH, which proceeds via three mechanisms: (i) the NO_x mechanism (blue), which leads to O_3 formation, favored in NO_x -rich urban and polluted environments; (ii) the ROOH-photolysis mechanism (red), dominant in high-VOC, low- NO_x settings such as forests; and (iii) the O_x mechanism (green), which consumes O_3 , important in remote marine regions with low VOC and NO_x levels. Globally, the abundance of OH is greatest in the tropics, where humidity and solar radiation are strongest, the latter due to the high solar zenith angle and a relatively thin O_3 layer. (Lelieveld et al., 2016, and references therein)

The resulting OVOC molecules possess physical and chemical properties that differ from their parent VOCs. Continued oxidation lowers their volatility, eventually leading to new particle formation (NPF) of SOA (Claeys et al., 2004; Curtius et al., 2024). These particles can act as CCN, thereby influencing weather and climate (Gordon et al., 2017; Merikanto et al., 2009). Finally, oxidised gases and particles are removed from the atmosphere by dry and wet deposition.

The oxidation of VOCs raises greenhouse gas concentrations either directly, by producing CO_2 and O_3 , or indirectly, by suppressing the atmospheric oxidation of CH_4 . Consequently, emission and oxidation of VOCs significantly influence the Earth system and modify its radiative budget in several ways, including the production and preservation of greenhouse gases and the formation of SOA. (IPCC, 2023)

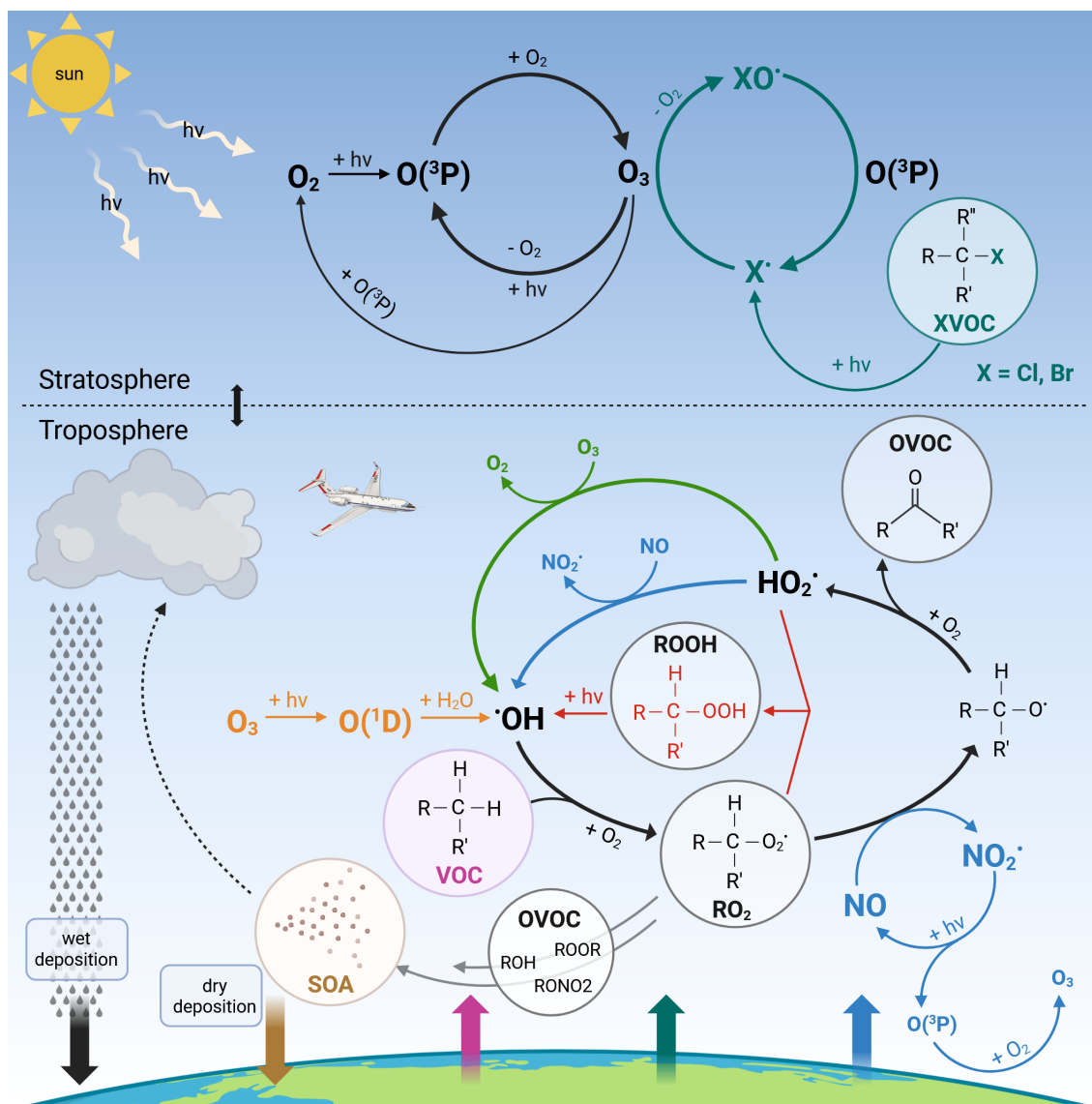


Figure 1.2.: Predominant atmospheric gas-phase chemistry mechanisms of troposphere and stratosphere.

Troposphere: VOCs are oxidised by the HO_x cycle. Orange – primary OH production; blue – catalysis and recycling by the NO_x cycle; green – recycling via O_x mechanism; red – recycling via photolysis of ROOH. Peroxy-radicals (RO₂) and oxygenated VOCs (OVOCs) can react further, eventually yielding secondary organic aerosol (SOA).

Stratosphere: black – Odd oxygen (O_x ≡ O + O₃) production and cycling in the Chapman mechanism produces O₃ layer; turquoise – halogenated VOC (XVOC) are photolysed and release halogen radicals (X), which catalytically decompose O_x.

Atmospheric lifetime

The timescales of their oxidation vary widely among VOCs—from hours for highly reactive species such as isoprene, over days for DMS, to a year for longer-lived compounds like CH_3Cl , and even up to 100 years for CFCs—and depend on temperature and, in some cases, pressure (Seinfeld and Pandis, 2016). A commonly used measure to compare the average residence time of different trace gases in the atmosphere is their *atmospheric lifetime*, derived from the balance of their production (P) and removal (R) rates (the derivation in this section follows Seinfeld and Pandis, 2016). The temporal change of the total atmospheric burden (Q) of a trace gas is:

$$\frac{dQ}{dt} = P - R \quad (1.1)$$

Assuming an equilibrium between production and removal (steady state), the atmospheric lifetime τ is defined as:

$$\tau = \frac{Q}{R} \quad (1.2)$$

When reaction with OH is the principal removal process, the removal rate can be written as:

$$R = k_{\text{VOC}+\text{OH}} * [\text{OH}] * Q \quad (1.3)$$

whereas $k_{\text{VOC}+\text{OH}}$ is the second-order rate coefficient specific to each VOC and $[\text{OH}]$ represents the average tropospheric OH concentration, typically estimated to be $10^6 \text{ molecules cm}^{-3}$ (Seinfeld and Pandis, 2016)). By inserting 1.3 in 1.2, the atmospheric lifetime with respect to OH is derived as:

$$\tau_{\text{OH}} = \frac{1}{k_{\text{VOC}+\text{OH}} * [\text{OH}]} \quad (1.4)$$

The lifetimes associated with other removal processes, such as reactions with additional radicals or photolysis, are calculated in the same way, and the individual lifetimes are summed to obtain the total atmospheric lifetime of a trace gas. By definition, the atmospheric lifetime is the time required for the gas's concentration to decay to $1/e$ ($\approx 37\%$) of its initial value. Lifetime strongly influences transport distance: short-lived species such as isoprene remain largely confined to the vicinity of their sources, whereas longer-lived compounds like CH_3Cl are mixed throughout the entire troposphere and even advected to the stratosphere.

1.2.2. Stratosphere

Exchange of air masses between the troposphere and stratosphere is driven by large-scale wave-induced forces, such as the breaking of Rossby and gravity waves (Holton et al., 1995), and intensifies as a consequence of global warming (Qie et al., 2022). Tropospheric air is primarily advected into the stratosphere in the tropics, while stratospheric air descends into the troposphere at the poles—a circulation pattern first proposed by and named after Brewer (1949) and Dobson (1956). After deep convection rapidly lifts air into the upper troposphere, the airmasses often spend weeks in the tropical tropopause layer (TTL) while being slowly uplifted into the stratosphere due to radiative heating (Fueglistaler et al., 2004). Approximately 80% of this troposphere-to-stratosphere transport (TST) occurs over the tropical western Pacific, where the tropopause is highest (and coldest) because of the region’s high sea-surface temperatures (Fueglistaler et al., 2004).

Due to the relatively long transport time from surface emission to the stratosphere, only gases that are comparatively inert to tropospheric oxidants reach the stratosphere in significant amounts. A prominent class of compounds with such long lifetimes are halogenated volatile organic compounds (XVOCs). Once in the stratosphere, they can be photolysed by high-energy UV radiation, releasing halogen atoms that catalyse O₃ destruction.

Stratospheric O₃ is produced by photolysis of molecular oxygen (O₂), which yields two ground-state oxygen atoms O(³P) (eq. 1.5). These atoms rapidly react with O₂ to form O₃ (eq. 1.6). Photolysis can convert O₃ back to O₂ plus either O(³P) or O(¹D), whereas the latter is almost instantly quenched to O(³P) by collisions with N₂ or O₂ (eq. 1.7). O₃ can also react with O(³P) to generate O₂ (eq. 1.8). Together, reactions 1.5–1.8 constitute the “odd-oxygen” cycle illustrated in Figure 1.2, in which O and O₃ are rapidly interconverted while absorbing a large fraction of the incoming solar high-energy UV radiation (Chapman, 1930).



Halogen atoms (X = Cl, Br) released by photolysis of XVOCs or CFCs efficiently catalyse the removal of O₃ via reaction 1.8, illustrated in turquoise in Figure 1.2. This mechanism, first described by Molina and Rowland (1974), caused the dramatic depletion of stratospheric ozone over Antarctica in the late 20th century, driven by anthropogenic CFC emissions (Farman et al., 1985; Stolarski et al., 1986). Consequently, CFC emissions were banned under the Montreal Protocol (UNEP, 1987), and their atmospheric abundances have been slowly declining since. Therefore, the

relative importance of other biogenic XVOCs—most notably CH_3Cl , which presently accounts for ~17% of stratospheric chlorine (WMO, 2022)—is expected to increase in the coming decades.

1.3. Research objectives and thesis outline

BVOCs play crucial roles in the Earth system, including the production and lifetime extension of greenhouse gases, the formation of secondary aerosol that scatters radiation and influences clouds, and the depletion of stratospheric ozone (IPCC, 2023; WMO, 2022). Consequently, understanding their emission patterns, atmospheric degradation, and transport is essential for developing, testing, and refining their representation in ESMs.

The primary objective of this work is to characterise the tropospheric spatial and vertical distributions of three key BVOCs—*isoprenoids*, DMS, and CH_3Cl —in two contrasting tropical regions, the “green ocean” of the Amazon rainforest and the “blue ocean” of the Pacific. As both regions experience frequent deep-convective events that can rapidly loft air from the planetary boundary layer to the upper troposphere (Bardakov et al., 2021), a central focus lies on quantifying the efficiency of VOC transport by deep convection. Airborne measurements (0.2–14 km) were obtained during the CAFE-Brazil and CAFE-Pacific campaigns with a Fast Gas Chromatography-Mass Spectrometry (Fast GC-MS) system and a Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS) aboard the HALO research aircraft. The observations are compared with, and complemented by, simulations from the global atmospheric chemistry-climate model EMAC to evaluate current emission and convection parametrisations and to gain further insights into the atmospheric impacts of the studied BVOCs.

The dissertation is organised as follows: first, the Fast GC-MS instrument is presented, and the data-correction procedures for humidity interferences are described; next, three chapters address each BVOC separately in order of increasing reactivity: CH_3Cl , DMS, and the *isoprenoids*; finally, the central conclusions are summarised.

Chapter 2: SOFIA. The System for Organic Fast Identification Analysis (SOFIA), a Fast GC-MS instrument, and its integration into the HALO payload have been previously described in detail (Bourtsoukidis; Helleis, et al., 2017; Voigt et al., 2022). During the present work, a previously unrecognised humidity interference, revealed by pressure fluctuations in the mass spectrometer, was identified and is discussed in this chapter. A correction for this effect was developed, following the approach of earlier studies (e.g., I. J. Simpson et al., 2001), and employs the highly stable background mixing ratios of CFCs throughout the troposphere as internal standards.

Chapter 3: Chloromethane. CH_3Cl is a long-lived BVOC with globally balanced sources and sinks, yielding a relatively constant atmospheric background of approximately 550 pptv, that contributes significantly to stratospheric ozone depletion (WMO, 2022). Although its concentrations are continuously monitored at numerous observatories worldwide (e.g., Prinn et al., 2018), the origin of roughly 20% of its annual emissions remains unidentified (Bahlmann et al., 2019). The

tropics constitute the principal global source region for CH₃Cl (Khalil and Rasmussen, 1999), with the main identified sources being tropical plants, biomass burning, coastal wetlands, oceans, and fungi (Xiao et al., 2010). Consequently, the first part of Chapter 3 focuses on identifying and quantifying the various CH₃Cl sources across both tropical study areas using latent-class analysis (LCA). In addition, previous airborne measurements have consistently reported elevated CH₃Cl mixing ratios in the upper troposphere at mid- and low latitudes compared to remote ground-based observations (Umezawa; Baker; Brenninkmeijer, et al., 2015; Umezawa; Baker; Oram, et al., 2014). To investigate this discrepancy, the second part of Chapter 3 combines the CAFE dataset with measurements from ten earlier aircraft campaigns to identify the principal source regions and vertical distribution of CH₃Cl in the tropics, and discusses the implications for its troposphere-to-stratosphere transport.

Chapter 4: Dimethyl sulfide. Dimethyl sulfide (DMS) is the largest biogenic source of reduced sulfur to the atmosphere (M. O. Andreae, 1990). Its oxidation drives the formation and growth of sulfate aerosol, a key source of cloud-condensation nuclei in marine regions (Charlson et al., 1987; Korhonen et al., 2008). DMS is emitted predominantly by phytoplankton in the oceans, with minor contributions from terrestrial plants and soils (Watts, 2000). Although numerous emission inventories have been developed (e.g., Hulswar et al., 2022; Kettle et al., 1999; Lana et al., 2011; S. Wang et al., 2019), DMS emissions remain a major source of uncertainty in ESMs (Carslaw et al., 2013). Consequently, model evaluation against observational data is essential. Although there have been numerous airborne measurements in marine environments (e.g., Conley et al., 2009; Marandino et al., 2013; Novak et al., 2021; Nowak et al., 2001; Thornton et al., 1997), in-situ observations of its deep-convective transport to the upper troposphere are scarce, and data on its vertical distribution above tropical rainforests are limited (M. O. Andreae and T. W. Andreae, 1988; M. O. Andreae; Berresheim, et al., 1990). Chapter 4 addresses these gaps by presenting observations of DMS over the “green ocean” (Amazon) and the “blue ocean” (Pacific). The chapter quantifies the uplift of DMS into the upper troposphere by deep convection in both regions and evaluates the performance of several marine and terrestrial emission inventories, as well as convection parametrisations, within the global chemistry-climate model EMAC.

Chapter 5: Isoprenoids. This chapter examines isoprene, its oxidation products, and monoterpenes over the Amazon rainforest, the world’s largest source of these highly reactive BVOCs (Guenther et al., 2012). Their comparably high abundance and rapid reaction with atmospheric oxidants strongly influence the Earth system by enhancing the concentrations of greenhouse gases (CH₄, O₃) and generating secondary organic aerosol (SOA) (IPCC, 2023). Recent studies based on model simulations and satellite observations have suggested that deep convection can transport these compounds vertically, especially efficiently at night when photochemical loss is limited, and highlighted their importance as precursors for upper tropospheric new particle formation (Bardakov et al., 2021; Palmer et al., 2022), yet in-situ measurements of isoprenoids and their oxidation products in convective outflows above the Amazon have been lacking. Chapter 5 provides the first observational record of their diurnal behaviour in the upper troposphere

and quantifies the efficiency of convective transport. In addition, measurements from pristine rainforest air are compared with those from a deforested area, and a sensitivity analysis with the global chemistry-climate model EMAC evaluates how changes in isoprenoid emissions due to deforestation affect the Earth system.

Chapter 6: Conclusions. The main findings of this work are summarized, and remaining research questions together with future perspectives are outlined.

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Chapter 2

SOFIA: configuration, characterisation and data processing of a Fast GC-MS system

Abstract. This chapter introduces the System for Organic Fast Identification Analysis (SOFIA), a Fast Gas Chromatography-Mass Spectrometry (Fast GC-MS) instrument, deployed aboard the High Altitude Long Range (HALO) research aircraft. SOFIA comprises a custom-built cryogenic pre-concentration module and GC oven, coupled to a commercial quadrupole MS. This chapter details SOFIA's configuration during the CAFE-Brazil and CAFE-Pacific campaigns, with emphasis on instrument characterisation performed and data processing procedures developed in this work.

2.1. Instrumental Setup

Gas Chromatography-Mass Spectrometry (GC-MS) has been a well-established standard technique for volatile organic compounds (VOC) measurements in laboratories worldwide for ~70 years (Eggertsen and Nelsen, 1958). A gas chromatograph typically employs a capillary column to separate a mixture of gas molecules into a time-dependent sequence of its individual component species based on their interactions with the stationary phase within the column. Each molecule exhibits a distinct retention time, reflecting its physicochemical properties. Because this separation is temperature-dependent, the column is housed in a temperature-controlled GC oven. Heating this oven can expedite the elution of the peaks. After separation, the molecules are transferred sequentially to the MS, where they are ionised by electron impact (EI) and mass-selectively detected. Each molecule is characterised by a unique combination of retention time and ion mass-to-charge ratio (m/z) fragmentation pattern, enabling unequivocal identification. Pre-concentration of samples allows for quantification of relatively low mixing ratios, reaching sub parts per trillion (pptv, 10^{-12}) levels for certain species. The Fast GC-MS system SOFIA was designed to achieve a total runtime of 3 minutes per sample, significantly faster than the 30 to 60 mins typically required by commercial benchtop GC-MS instruments. A high measurement frequency is essential for operation on fast-moving aircraft to ensure adequate spatial coverage. This high time resolution is enabled by two key custom-built components: the pre-concentration unit and the GC oven. Since the setup and its implementation in HALO's payload have been described in detail elsewhere (Bourtsoukidis et al., 2017; Voigt et al., 2022), only essential features are presented here. A schematic overview of relevant gas lines of the system is given in Figure 2.1.

2.1.1. Inlet system

When employed aboard HALO, SOFIA was connected to the forward-facing Trace Gas Inlet (TGI, EnviroScope GmbH, Germany) via a 2 m long 1/4" PFA inlet line, which was maintained at 40 °C to minimise line losses. Before entering the inlet system, the air passed through a PTFE membrane (Type 11842, Sartorius, Germany) and a sodium-thiosulfate-coated quartz filter (Type Q3400, Sartorius, Germany) to prevent interference from particles and ozone, as demonstrated by Ernle et al. (2023). The total residence time of ambient air in the inlet, from the TGI to the sampling point, was approximately 15 s.

The inlet system was designed to maintain constant pressure and flow conditions (1 atm, 200 sccm) throughout the aircraft's pressure altitude range between 140 and 1000 hPa. This was accomplished using four PFA diaphragm pumps (NMP 850KNDC, KNF Global Strategies AG) in combination with a 500 sccm mass flow controller (F-201-DV-AAD-22-V, Bronkhorst, Netherlands). All inlet system gas lines were made of uncoated stainless steel tubing.

Blank samples were generated from ambient air by removing VOCs through catalysed thermal decomposition. This ensured ambient equivalent humidity and was achieved by passing the air through a custom-made zero air generator, consisting of a 3/4" stainless steel tube heated to 350 °C

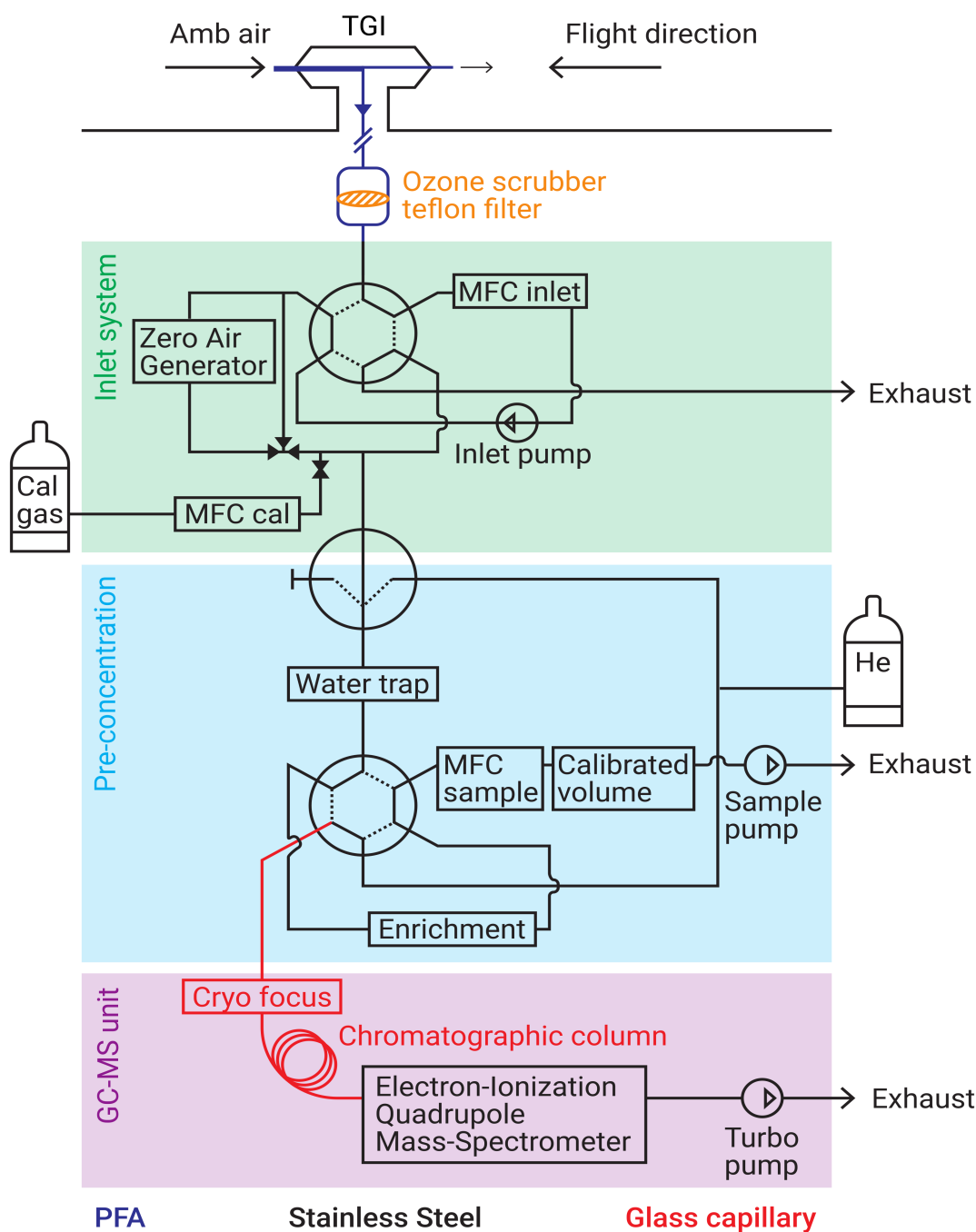


Figure 2.1.: Schematic overview of SOFIA's relevant gas lines. Blue lines denote PFA tubing, black lines indicate uncoated stainless-steel tubing, and red lines represent glass capillaries. Solid connections inside the multi-port valves show the configuration during sample collection. Graphic prepared by Dominic Jack, based on a drawing by Bianca Krumm.

and filled with platinum pellets (Pt on Al₂O₃, 3.2 mm pellets, Sigma Aldrich, Germany). Five-point calibrations were performed by adding 0.5–5.0 sccm of a calibration gas standard (Apel Riemer Environmental, USA) via a 5 sccm mass flow controller (F-200CV-002-AAD-22-V, Bronkhorst, Netherlands) to the generated zero air.

2.1.2. Pre-concentration

Samples were drawn at 40 sccm from the inlet line at the sample multi-port valve. The sample stream first passed through a water trap, a cold trap maintained at -10 °C, which removed most of the humidity to prevent possible interferences, such as damage to the GC column, ice blockages, or elevated MS background signals. Subsequently, samples were cryogenically enriched at -160 °C on the enrichment trap for one minute. The enriched sample was then released by rapid heating (200 °C) within a few seconds and transferred to the cryofocus trap (-160 °C), where the sample was focused onto a small volume before injection onto the GC column. All three cold traps are made of stainless steel tubes cooled with liquid nitrogen and heated electrically. All transfer lines and valves of the pre-concentration unit were maintained at 70–90 °C to minimise wall effects.

2.1.3. GC-MS Unit

The injected VOCs were separated on a GC capillary column (10 m x 0.25 mm x 1.40 µm, DB-624 UI, Agilent Technologies) housed in a custom-built GC oven. The temperature program was as follows: 30 °C for the first 50 s, followed by a ramp up from 30 °C to 200 °C at 1.8 °C/s, and then held constant at 200 °C until the end of the run after 144 s.

After separation, the VOCs were transferred through a heated (120 °C) transfer line to a quadrupole mass spectrometer (MS, Agilent Technologies 5973MSD), which operated in selected ion monitoring (SIM) mode. In SIM mode, the MS scans only a limited set (<15) of predefined m/z values simultaneously. SIM mode offers significantly greater sensitivity compared to full scan mode, in which all m/z values within a specified range are detected. Figure 2.2 presents an example chromatogram of the GC-MS method, optimised to separate more than 50 VOCs by unique combinations of retention time and m/z . A full list of all covered VOCs is given in the appendix of this chapter (Table 2.4).

2.1.4. V25 controlling unit

The in-house developed control unit (V25) continuously monitored sensor readings and regulated all electronically controlled components. The entire measurement cycle, including sample preparation, sampling, focusing, GC oven temperature control, and MS triggering, was fully automated. Sequences of sample types (ambient, calibration, and zero) could be pre-programmed and executed in a defined order. The V25 logged all relevant parameters, including temperatures,

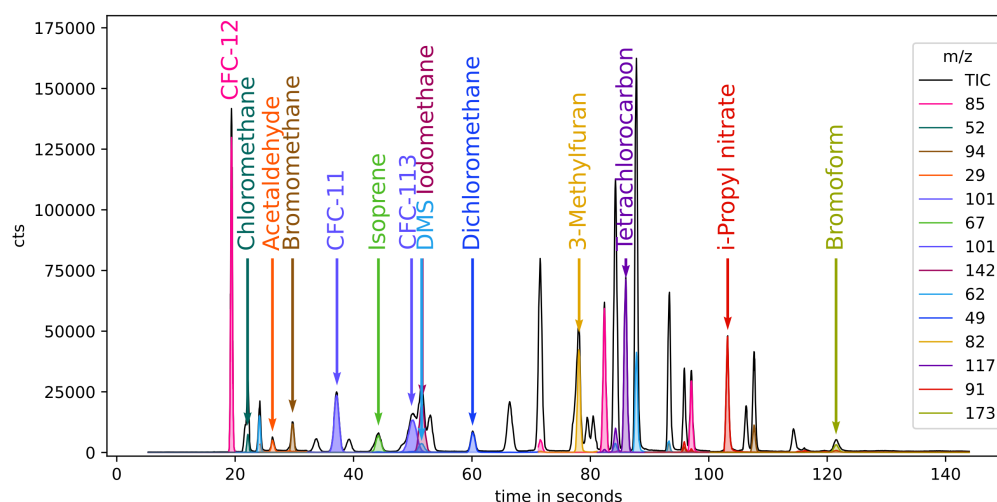


Figure 2.2.: Example calibration chromatogram. The coloured lines represent individual m/z of selected compounds, the grey line shows the total ion count (TIC). A full peak list is given in Table 2.4.

flows, pressures, and sampled volume, at a frequency of 1 Hz. Date and time synchronisation with other instruments aboard HALO was maintained via the BAHAMAS timeserver (Section 2.1.5).

2.1.5. BAHAMAS

Basic meteorological parameters (e.g. pressure, temperature, humidity, wind speed), along with the aircraft's altitude and position, were recorded by the Basis HALO Measurement and Sensor System (BAHAMAS). Latitude and Longitude were determined relative to the WGS 84 ellipsoid, and the pressure altitude was obtained from the nose boom pressure sensor. All scientific instruments on board HALO synchronised their time with the BAHAMAS timeserver to maintain temporal consistency. The latest available version of BAHAMAS data (V01 or V02, depending on the respective flight number) as of May 2025 was obtained from the HALO database (Re3data.Org, 2016).

2.2. Execution of measurements

Instrument preparation for a research flight (RF) typically began four hours before takeoff, with evacuation of the MS and filling of the liquid nitrogen dewar. Two hours before takeoff, the aircraft was towed from the hangar to the apron. At this point, the instrument was fully activated, and the inlet was flushed with apron air during the remaining ground time. Multiple zero samples and a five-point calibration were performed. Immediately before takeoff, a repeating sequence of 3 zero, 20 ambient, 3 calibration, and again 20 ambient samples was initiated to monitor the background signal and instrument sensitivity during flight. On some flights, the in-flight operator adjusted the sequence to ensure continuous sampling over specific regions. Nevertheless, zero

and calibration samples were consistently performed at approximately two-hour intervals. After landing, another five-point calibration was performed while the aircraft remained on the apron.

Calibrations were performed using a gas standard (Apel Riemer Environmental, USA) containing all analytes in Table 2.4 at approximately 50 ppbv, except for monoterpenes and nitrates. Monoterpenes were calibrated separately in the laboratory in Mainz, using isoprene as a reference.

2.3. Data processing and correction

During data finalisation, several instrument interferences were identified, and appropriate correction procedures were devised and applied where feasible. This section outlines the standard data processing workflow, detailing the observed interferences and the corresponding correction steps implemented throughout the analysis.

2.3.1. Peak Integration

Chromatogram peaks were automatically integrated with an in-house developed IGOR (Wave-metrics) procedure (*FastGCEVal*, version 7). Briefly, peaks were fitted to the expected peak shape, determined from a reference chromatogram (typically a calibration sample), using a modified Levenberg-Marquardt algorithm based on the least-squares method. Peak integration was performed numerically by summing the products of the peak's width and height at each data point. The uncertainty of the peak area was determined by propagating the uncertainties of the fit parameters. A key feature of the procedure is the automatic identification and correction of retention time fluctuations by comparing the retention times of characteristic peak groups to those in the reference chromatogram. Additionally, a graphical user interface is included to facilitate the identification and correction of occasional errors in peak fitting or retention time adjustment. Peaks with non-optimal shapes were occasionally divided into two separate peaks rather than being recognised as a single feature (Figure 2.3 a). This mis-assignment compromised the calculated peak area, and consequently, such peaks were flagged as outliers.

2.3.2. Calibration

Calibration was performed using a set of Python scripts that were developed within this work. First, the raw peak areas were merged with the corresponding instrument parameters from the V25 log files and with the aircraft's position and altitude. Outliers were then identified and removed. For several compounds, the background exhibited an exponential decay during the flights; this trend was corrected by using an exponentially interpolated background. A correction factor was applied to compensate for the instrument's sensitivity to water vapour using Chlorofluorocarbon (CFC) peaks as an internal standard where possible. Finally, the calibration factors derived from

Table 2.1.: Molecular weights, dipole moments, and boiling points of compounds showing a memory effect after calibration samples. Values were taken from the CRC Handbook of Chemistry and Physics (Lide et al., 2005).

compound	molecular weight (amu)	dipole moment (Debye)	boiling point (°C)	# samples after Cal
Tetrachloroethylene	165.8	0	121.3	1
Bromodichloromethane	163.8	-	90	1
1,2-Dichloroethane	98.96	1.80	83.50	1
1,1,2-Trichloroethane	133.4	1.40	113.8	1
Trichloroethylene	131.4	0.8	87.21	2
Iodomethane	141.9	1.62	42.43	2
Dimethyl sulfide	62.13	1.55	37.33	2
Dibromomethane	173.8	1.43	97	2
Chlorobenzene	112.6	1.69	131.7	3
Bromoform	252.7	0.99	149.1	3

the in-flight calibration samples were used to convert the corrected peak areas into final mixing ratio values.

Preparations

First, the peak areas and their corresponding errors were normalised by the sample volume:

$$area_{norm} = \frac{area}{volume} \quad (2.1)$$

Next, samples were categorised into three groups (pre-flight, in-flight, and post-flight), using an altitude threshold of 180 m (respectively 100 m for CAFE-Pacific) to distinguish between ground and airborne conditions.

Outliers

Two distinct outlier groups were identified and removed from the main dataset. The first group comprises peaks that were incorrectly integrated (see Section 2.3.1), resulting in erroneous peak areas. The second group consists of samples measured immediately after calibration, which displayed a memory effect for certain compounds. This effect is attributed to adsorption of the analytes onto the uncoated stainless-steel inlet during calibration (exposure to 1.2 ppbv of each compound) and their delayed desorption over several minutes (see Figure 2.3 b). Table 2.1 lists the affected substances together with their molecular weight, dipole moment, boiling point, and the number of samples showing the memory effect after a calibration. Apart from dimethyl sulfide, these compounds are relatively heavy, moderately polar, and contain multiple halogen substituents, properties that likely promote adhesion to the stainless-steel surface.

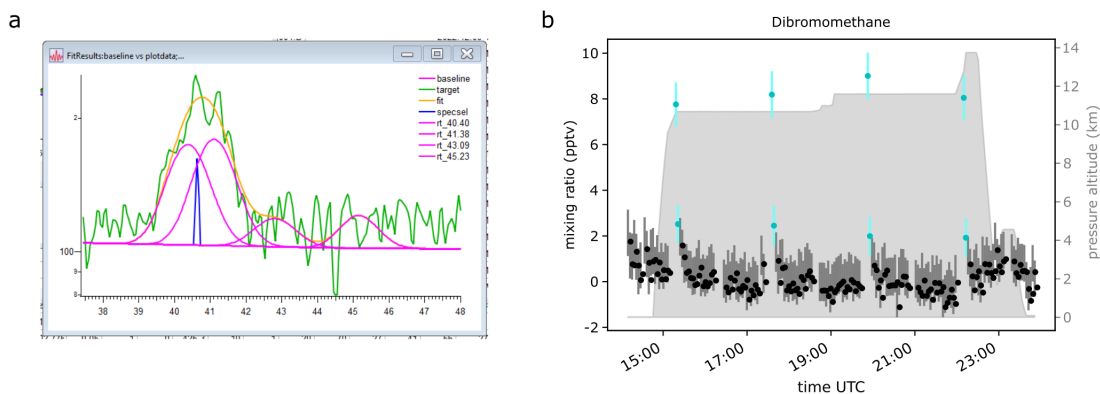


Figure 2.3.: Examples for both outlier categories: a) A screenshot from the integration procedure illustrating incorrect integration of an isoprene peak due to the assignment of two peaks instead of one. b) Timeseries of dibromomethane mixing ratios exhibiting a memory effect after calibration samples (turquoise points) during the CAFE-Brazil RF 12.

Background Interpolation

Another group of polar and/or heavy VOCs, which were particularly abundant in airport air, exhibited an exponential decay after takeoff over several hours. This behaviour was observed in all three sample types (ambient, background, calibration), indicating that it originated in the inlet system, most likely in the section downstream of the zero-air generator. During flight preparations on the ground, the inlet lines become saturated with VOCs from the polluted airport environment. Once the aircraft ascends and the lines are exposed to cleaner air, the adsorbed compounds desorb exponentially until a new equilibrium is reached. This decay pattern was observed for acetaldehyde, benzene, toluene, chlorobenzene, 1,2-dichloroethane, 1,1,2-trichloroethane, and bromoform. To correct for this effect, the background time series was fitted with a mono-exponential decay function, which was then used as the interpolated background $Zero(t)$.

$$Zero(t) = A * \exp(-b * t) + C \quad (2.2)$$

After landing, the instrument was again exposed to polluted air on the apron, causing the background levels to rise. Although ground-level ambient measurements after landing are not relevant for this work, an accurate background characterisation is essential because the complete five-point calibration was usually performed at this stage. In the absence of a more robust approach and given the limited number of zero air measurements available, the post-landing background was approximated by linear interpolation between the recorded points.

Figure 2.4 a illustrates peak areas of ambient and zero samples for acetaldehyde as an example. The ambient measurements exhibit a similar exponential decay as the background. Therefore, an exponential fit was applied to the zero samples, with occasional outliers excluded from the fit. The uncertainty of exponentially interpolated $Zero(t)$ was determined by propagating the fit

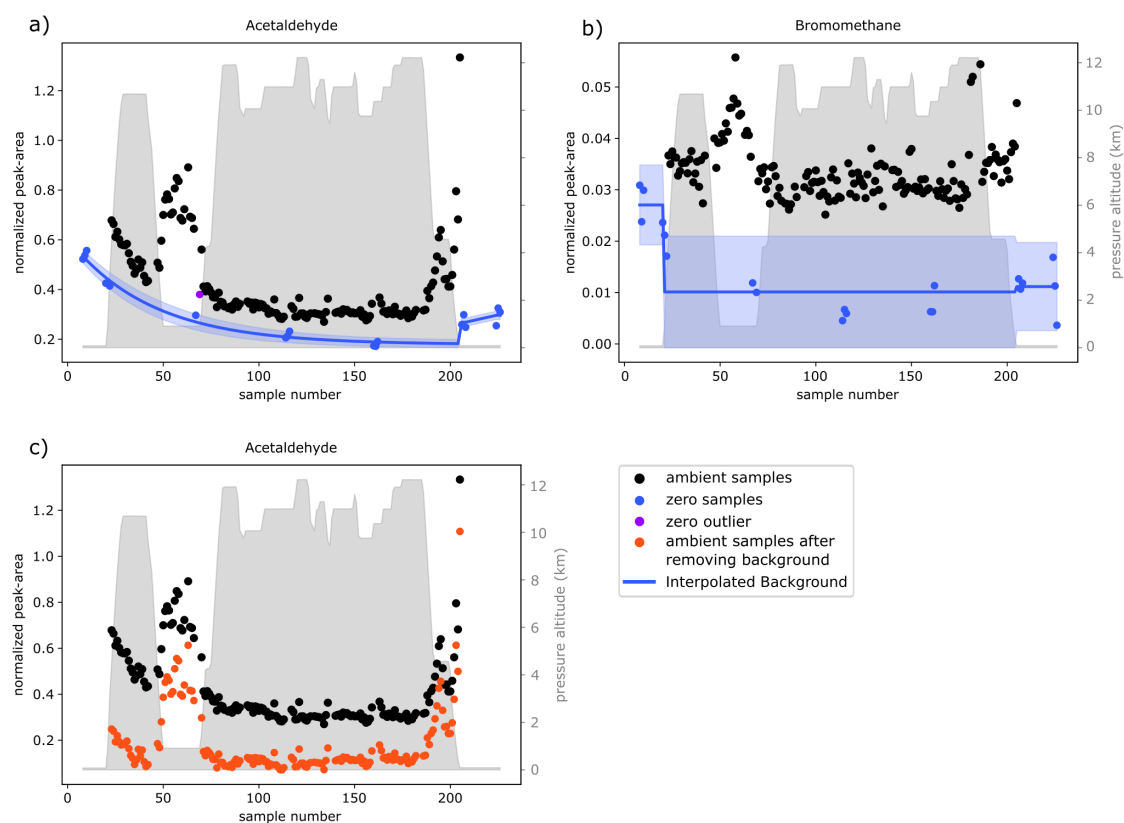


Figure 2.4.: Background interpolation for: a) an exponentially decaying background (e.g. acetaldehyde), and b) a constant background before, during and after flight (e.g. bromomethane). Panel c) shows a comparison of ambient samples before and after subtracting the exponentially interpolated background. The data is from RF 13 during CAFE-Brazil.

uncertainty, illustrated by the blue shaded area in Figure 2.4 a. The background-corrected values, obtained by subtracting the interpolated background, are presented in Figure 2.4 c.

This procedure was applied to all affected compounds across all RFs. However, for toluene, chlorobenzene, 1,1,2-trichloroethane, and bromoform, the zero values exceeded the ambient values, indicating additional issues that could not be corrected within the scope of this work (see Section 2.3.3).

For the remaining VOCs the background was assumed to be constant within each segment (pre-flight, in-flight, post-flight). Typically, the background was lowest during flight and slightly elevated during the pre- and post-flight periods on the ground, as illustrated for bromomethane in Figure 2.4 b. Accordingly, the background was calculated as the mean of all zero samples within the respective segment, with the uncertainty determined as twice the standard deviation (2σ).

CFC correction

A common strategy for reducing systematic and random errors in quantitative GC-MS analysis is the use of an internal standard, an added compound (absent from the original sample) at a known concentration, to monitor sampling biases and detector sensitivity drift. Isotopically labelled molecules (e.g., ^2H - or ^{13}C -labeled) are frequently employed. For instance, $^2\text{H}_8$ -toluene was used as an internal standard for ambient VOC measurements (Demeestere et al., 2008). We did not purposely introduce such an internal standard to our samples. Instead, we exploited the quasi uniform presence of long-lived CFCs in the troposphere and used them as an internal standard because their mixing ratios are spatially homogeneous. By normalising the VOC signals to the nearby CFC peaks, we corrected for variations in instrument sensitivity caused by CO_2 and humidity.

The typical variation of MS pressure during a chromatographic run is shown in Figure 2.5. The sharp peak at the beginning ($\sim 16\text{--}17\text{ s}$) corresponds to the elution of CO_2 , which is trapped in the -160°C enrichment trap together with all other VOCs. The subsequent, broader feature ($\sim 25\text{--}105\text{ s}$) is caused by water vapour. Both CO_2 and water are present at significantly higher concentrations than VOCs in the atmosphere. Although most of the sample's water was expected to be removed by the -10°C cold trap before enrichment, our results indicate that a substantial fraction of water vapour nevertheless survived this stage and entered the GC-MS system. The magnitude of the water feature was highly variable throughout a RF, closely linked to the flight altitude and the corresponding ambient humidity. Conversely, the MS pressure can be used as a proxy for the water abundance in the MS at a given retention time.

CFCs are highly volatile, chemically inert substances that were used industrially (e.g., as refrigerants) from the 1930s until their ban under the Montreal Protocol in the late 1980s because of their strong ozone-depleting potential (Kim et al., 2011). Their long atmospheric lifetimes (CFC-11: 43 yr; CFC-12: 88 yr; CFC-113: 72 yr) exceed the timescales of tropospheric mixing, resulting in uniform background mixing ratios throughout the troposphere. These background mixing ratios are continuously monitored by a global network of long-term stations, such as

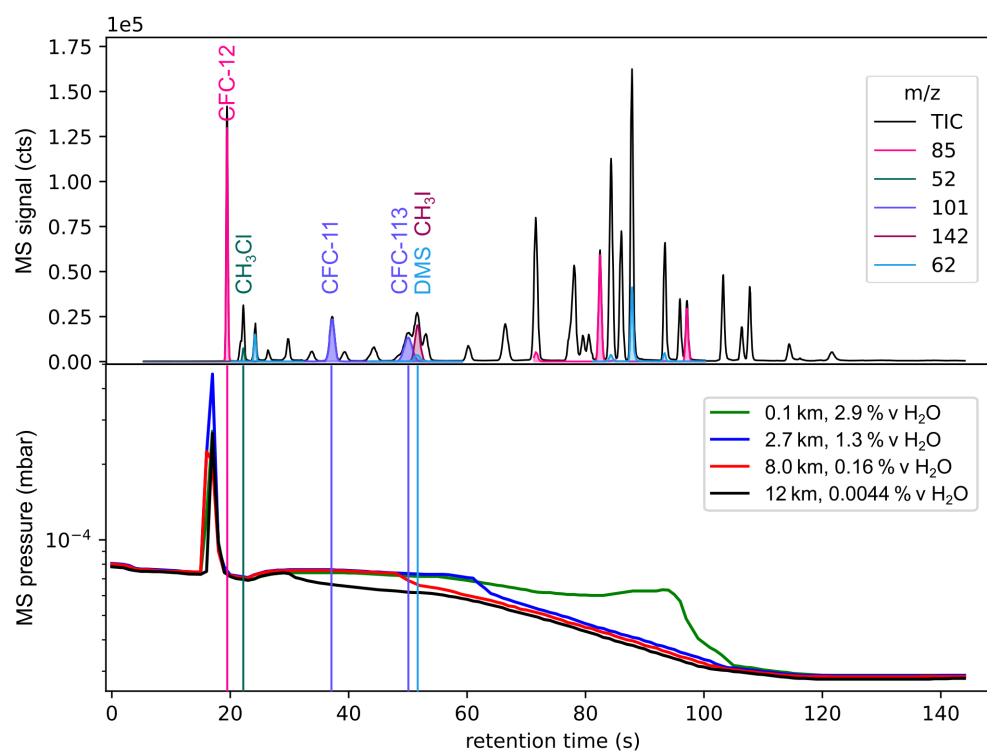


Figure 2.5.: Upper panel: Representative calibration chromatogram obtained with the Fast GC MS system. Lower panel: Corresponding MS pressure recorded throughout the chromatogram at different altitude and humidity conditions during RF7 of CAFE-Brazil.

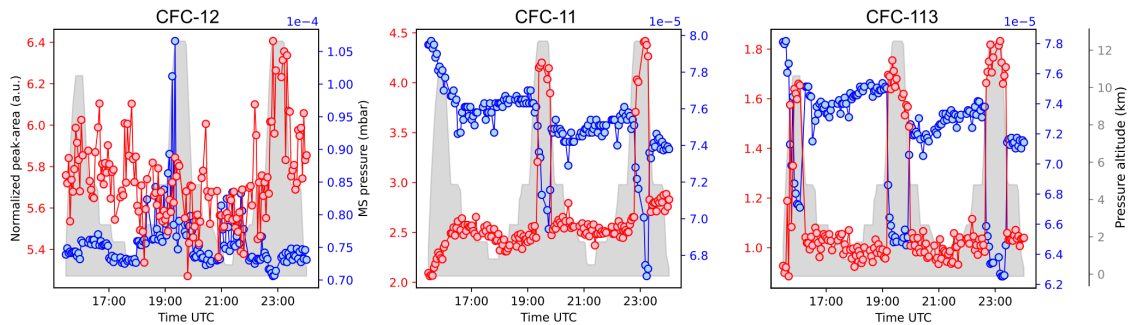


Figure 2.6.: Normalised peak areas of CFC-12, CFC-11, and CFC-113 from ambient samples measured during RF7 of CAFE-Brazil are shown in red (left y-axis). The right y-axis shows the pressure inside the MS at the approximate retention time of each compound, plotted in blue. Y-axis labels are the same for every panel, but are only shown in the first one for clarity. The grey area indicates the flight altitude, with the corresponding y-axis on the right side of the figure.

the Advanced Global Atmospheric Gases Experiment (AGAGE) (R. G. Prinn et al., 2018), making CFCs excellent tracers for assessing instrument sensitivity. CFC-12 (ret. time = 19.8 s, $m/z = 85$), CFC-11 (ret. time = 36.3 s, $m/z = 101$), and CFC-113 (ret. time = 47.7 s, $m/z = 101$) were included in our method. For the background mixing ratios, we adopted the following reference values:

- CFC-12: monthly averages of the high-resolution dataset by R. Prinn et al. (2025).
- CFC-113: averages derived from flask measurements by Stephen A. Montzka and Isaac Vimont.

Both datasets were obtained at the Kennaook/Cape Grim Baseline Air Pollution Station (Tasmania, Australia), which provides a well-characterised, clean air baseline for the Southern Hemisphere.

The time series of CFC-11, CFC-12, and CFC-113 recorded during the RFs (red curves in Figure 2.6) show pronounced variability, with each compound displaying a distinct pattern. For CFC-11 and CFC-113, the variability is especially large: recorded peak areas at high altitude can be up to a factor of two higher than at lower altitudes. This behaviour follows the changes in MS pressure at the retention times of their peaks, suggesting that increased water vapour in the ion source reduces sensitivity. A higher abundance of ionised H_2O molecules creates a denser space-charge cloud within the ion source, which can perturb ion trajectories and prevent efficient transmission of analyte ions out of the source (Cowen et al., 1993).

In contrast, CFC-12 exhibits lower variability ($\sim 10\%$), which appears not correlated with MS pressure (Figure 2.6). A similar space-charge effect may still be present because the tail of the CO_2 peak overlaps the CFC-12 retention window. The lack of an observable relationship could be partly due to the MS pressure being recorded at only 1 Hz, which is insufficient to resolve the rapidly changing pressure associated with the relatively narrow CO_2 peak. Moreover, the tropospheric variability of CO_2 concentrations is modest. For example, a CO_2 variability of up to 10% has been reported in the boundary layer above a tropical rainforest in Surinam (Williams et al., 2001), while variability above the boundary layer is expected to be considerably smaller. This magnitude is consistent with the observed CFC-12 variability.

Finally, additional factors that influence all compounds equally should be considered, such as the water dilution effect, which is explained in detail elsewhere (Harazono et al., 2015), and other instrumental effects like electrical drift of the MS.

To correct for these various influences on instrument sensitivity, we normalised each analyte peak to a nearby CFC peak. This approach rests on three assumptions:

1. The prevailing conditions in the MS at a given retention time affect the sensitivity to all compounds in the same manner.
2. Peaks that are close in retention time to each other (approx. 2 s apart from each other) experience the same sensitivity conditions.
3. Ambient CFC mixing ratios are vertically and spatially homogeneous throughout the troposphere (Zeng et al., 2022) and can be represented by the well-established background values reported in the literature.

Under these premises, the CFC peaks provide an internal reference that corrects for altitude-, humidity-, and instrument-related sensitivity variations affecting nearby VOC signals. Only VOCs whose retention times lie close to a CFC peak can be corrected with this method. In the present dataset, these are CH_3Cl , which was corrected with the CFC-12 signal, and DMS and CH_3I , which were corrected with CFC-113.

The first step of the correction was to flag any sample in which the MS pressure at the retention time of the CFC and the analyte differed by more than 2%. Such samples violate the second assumption (that both peaks experience comparable conditions) and were excluded from further analysis. For DMS, this criterion removed 6.5% of the CAFE-Brazil in-flight samples and 6.8% of the CAFE-Pacific samples, most of which were recorded during ascent or descent.

For the remaining samples, the background contribution was subtracted, after which correction factors for the calibration samples were derived. This was done by forcing the CFC calibration points onto a straight line through the origin and an arbitrarily chosen reference peak area ($area_{ref}$) at the corresponding background mixing ratio (MR_{lit} , denoted as cyan stars in Figure 2.7 b,f).

$$cf_{cal}(CFC) = (area_{norm} - Zero) * \frac{MR_{lit}}{MR_{calc} * area_{ref}} \quad (2.3)$$

$$\text{with } MR_{calc} = \frac{F_{cal}}{F_{inlet}} * MR_{calgas}$$

In the next step, correction factors were applied to the areas of the corresponding VOCs for each calibration sample:

$$area_{cal,corr}(VOC) = \frac{area_{norm} - Zero}{cf_{cal}(CFC)} \quad (2.4)$$

The final calibration parameters for CH_3Cl , DMS, and CH_3I were obtained as the mean slope of the corrected in-flight calibration points (*Slope*, blue line in Figure 2.7). For VOCs lacking a nearby

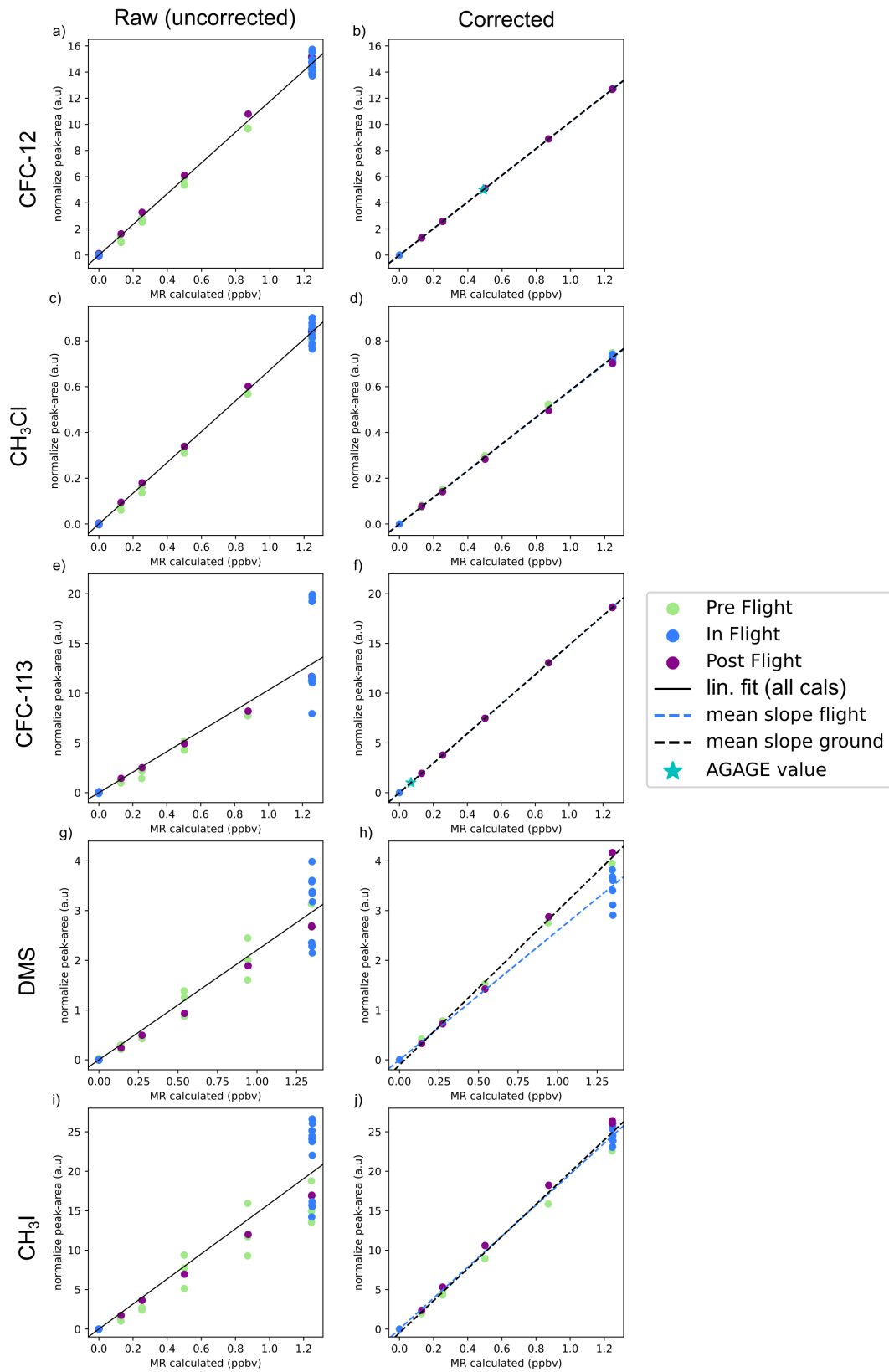


Figure 2.7.: Calibration samples from RF7 during CAFE-Brazil before and after applying the CFC correction.

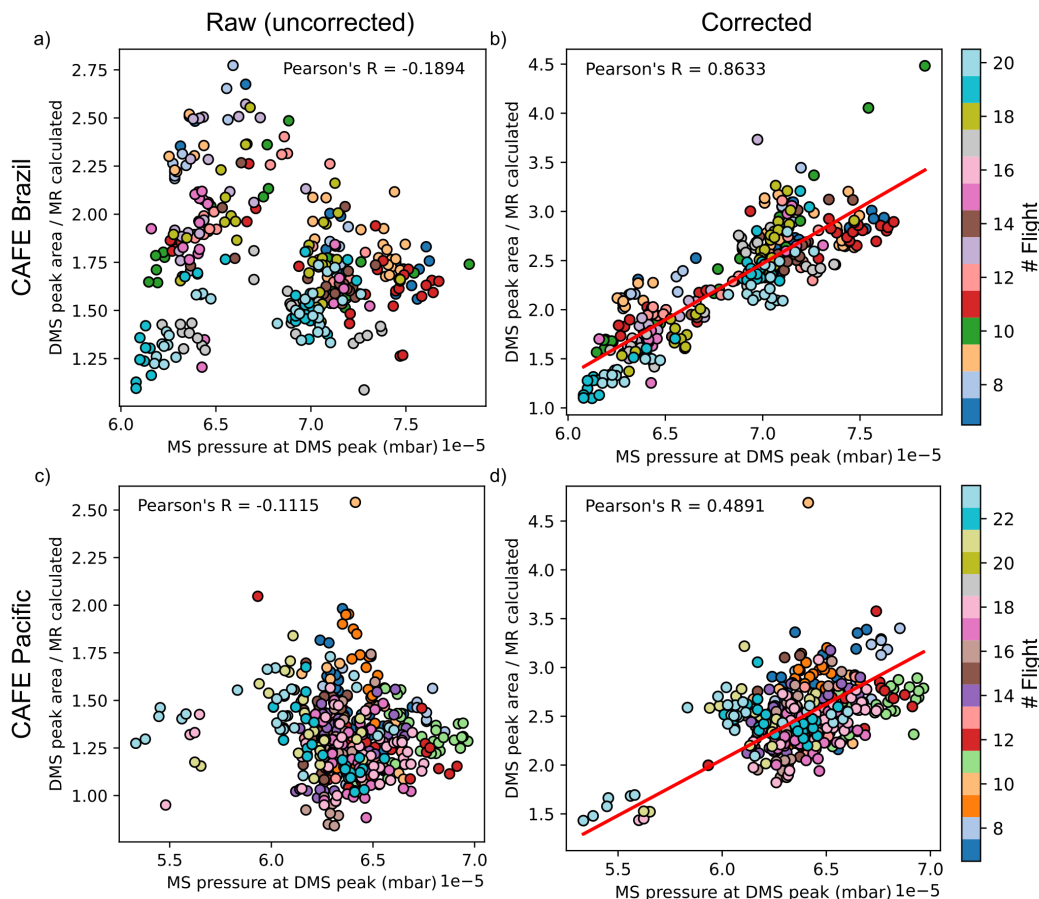


Figure 2.8.: Correlation between the instrument response (peak area divided by the injected mixing ratio) and the mass spectrometer pressure at the DMS retention time, shown before (a,c) and after (b,d) applying the CFC correction. The red line denotes the calibration parameterisation: a linear regression for CAFE-Brazil. Because only a few dry calibration points were available for CAFE-Pacific, the slope from the CAFE-Brazil calibration was retained, and the intercept was adjusted to best match the CAFE-Pacific data. See text for more details.

CFC peak, the uncorrected calibration points were taken instead. This adds extra uncertainty, which is discussed in Section 2.3.2.

As shown in Figure 2.7, the CFC correction significantly reduces the variability of the calibration points for all three analytes. For DMS, however, the corrected in-flight calibration points remain systematically lower than the ground-based calibrations. We attribute this discrepancy to an additional humidity effect in our inlet. Under more humid conditions, DMS may adsorb less efficiently to the stainless steel inlet lines, leading to enhanced transmission. This hypothesis is supported by the observation that, after correcting for the water-induced MS sensitivity loss, the DMS instrument response exhibits a linear relationship with MS pressure (see Figure 2.8), which is a proxy for the water vapour level in the inlet. Because the difference between high and low humidity conditions exceeds a factor of two for DMS, we used this linear relationship to correct the DMS signal.

Between the CAFE-Brazil and CAFE-Pacific campaigns, the platinum pellets in the Zero Air-Generator were replaced during routine maintenance, introducing an additional source of humidity into the calibration system. Consequently, only a few dry calibrations at high altitude were obtained during the later flights (RF18 onward) of CAFE-Pacific. Since the calibration points for CAFE-Brazil are more evenly distributed between wet and dry conditions, we retained the slope derived from the CAFE-Brazil calibrations for both campaigns and adjusted only the y-intercept for CAFE-Pacific to achieve the best fit. This adjustment was necessary because the foreline pump of the mass spectrometer was replaced between the campaigns, resulting in generally slightly lower MS pressure during CAFE-Pacific.

Calibration of ambient data

For the compounds that were corrected using a CFC reference (CH_3Cl , DMS, and CH_3I), the ambient-sample correction factor was derived from the ratio of the CFC peak area to the reference area:

$$cf_{amb} = \frac{area_{norm}(CFC)}{area_{ref}(CFC)} \quad (2.5)$$

The calibrated mixing ratios of the VOCs were then calculated with Equation 2.6. For the remaining species, where the CFC correction could not be applied, the correction factor was set to unity.

$$MR_{obs} = cf_{amb} * \frac{area_{norm} - Zero(t)}{Slope} \quad (2.6)$$

Limit of detection

The limit of detection (LOD) was calculated according to the IUPAC definition (Gold, 2019) as follows:

$$LOD = \frac{k * s_{blank}}{Slope} \quad (2.7)$$

where $k = 3$ was selected, corresponding to a confidence level of over 95%, as recommended by Long and Winefordner (1983). Here, s_{blank} demotes the standard deviation of zero samples. Only zero samples recorded during flight were included in the calculation, as higher zero levels observed in the polluted environment on the apron would otherwise lead to an overestimation of the LOD. The LOD was calculated separately for each RF and, by dividing by the *Slope* of the calibration curve (see above), expressed as a mixing ratio.

Table 2.2.: Uncertainties of all relevant parameters (as percentages of each parameter) and their respective sources.

Parameter	Variable	Uncertainty (%)	Source
Peak area	$\Delta area_{norm}$	0.1–10	Integration procedure output
Sample volume	$\Delta volume$	0.5	Maximum error estimation
Inlet flow	ΔF_{inlet}	2.5	MFC documentation, Bronkhorst
Cal gas flow	ΔF_{cal}	2–15	MFC documentation, Bronkhorst
Gas standard	ΔMR_{calgas}	5	Certification report, Apel Riemer
CFC lit. MR	ΔMR_{lit}	5.0	Estimate, see text

Uncertainty

The total uncertainty of the ambient mixing ratios was calculated by Gaussian error propagation using the uncertainties of each parameter involved, as summarised in Table 2.2.

The uncertainty of the integrated peak area was obtained from the fit uncertainty of each peak in the IGOR procedure described above. It was highly variable, depending strongly on peak shape and size, i.e. drastically increased for peak sizes approaching the noise level. The sample volume was calculated using the pressure difference ($P_{end} - P_{start}$, in mbar) measured in a calibrated volume (V_{calvol}) between the start and end of the sampling period at a known temperature (T_{calvol} , in °C), based on the ideal gas law:

$$volume = \frac{P_{end} - P_{start}}{1000} * \frac{273.15}{273.15 + T_{calvol}} * V_{calvol} \quad (2.8)$$

Uncertainties were estimated as 1 mbar for the pressure measurement and 0.1 °C for the temperature sensor¹. It is worth noting that the uncertainty of the calibrated volume does not affect the uncertainty of the obtained mixing ratios, as it equally impacts the normalisation of all samples. The flow-dependent uncertainties of the mass flow controllers were obtained from the manufacturer’s documentation. The uncertainties of the individual component mixing ratios in the gas standard were provided by the supplier’s certification report. The additional uncertainty associated with the assumption of a uniform CFC background mixing ratios made during the CFC correction was conservatively set to 5% of the literature CFC mixing ratios. This value encompasses the 0.12% precision of the Medusa instrument used at Kennaook/Cape Grim (Miller et al., 2008), the approx. 2% variability of CFC mixing ratios observed over the two-month campaign periods across nine AGAGE stations, and an extra margin to account for additional variability within the tropospheric column.

For compounds for which the CFC-based correction could not be applied, an additional uncertainty must be considered. This extra uncertainty depends on the compound’s retention time and therefore has to be evaluated on a case-by-case basis. Isoprene (C_5H_8) elutes between CFC-11 and CFC-113 and is consequently subject to the same sudden sensitivity changes observed for

¹Personal communication with Dr. Frank Helleis, 13.05.2025.

Table 2.3.: Instrument precision, total relative uncertainty, and LOD for selected compounds, for CAFE-Brazil (CAFE-Pacific).

	Precision (%)	Uncertainty (%)	LOD (pptv)
CH ₃ Cl	1.2 (1.0)	9.8 (11)	6.19 (7.8)
DMS	4.2 (2.2)	42 (22)	1.4 (1.6)
CH ₃ I	1.4 (3.1)	48 (36)	0.3 (0.2)
C ₅ H ₈	6.0 (2.8)	34 (15)	3.7 (3.1)

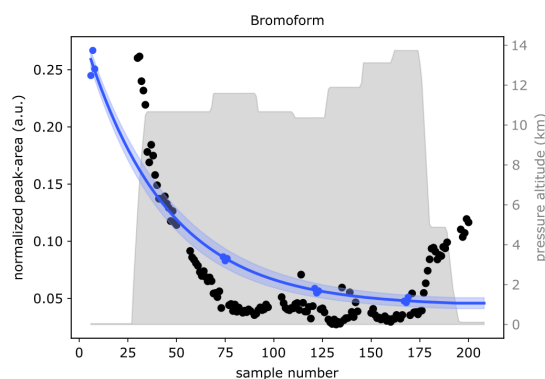


Figure 2.9.: Zero samples (blue) were higher than ambient samples (black) for bromoform for most of the flight. This representative example is from RF8 of CAFE-Brazil.

those CFCs in Figure 2.6: under the very dry conditions of the upper troposphere, the instrument sensitivity can increase by up to a factor of 2. This effect typically occurred at altitudes above ~5 km. Because the natural variability of isoprene mixing ratios in the upper troposphere (from below LOD to ~1 ppbv) far exceeds a factor of 2, the humidity artefacts don't affect the conclusions of this work, but they should be considered when working with this data in the future.

2.3.3. Instrument Limitations

A significant limitation of the instrumental setup was the characterisation of the background using the zero air generator, which produces blank samples by thermally decomposing VOCs from ambient air (see Section 2.1.1). While the generator was effective for most compounds, it proved inadequate for some heavier species.

One compound that clearly illustrates this problem is bromoform. As shown in Figure 2.9, the exponentially decaying background remains higher than the ambient mixing ratios for most of the flight. Although the ambient samples also decay, their decay rate is much faster, indicating two distinct processes.

The rapid decay in ambient samples reflects desorption of pollutants that had adsorbed onto the inlet lines during the initial ground phase, an effect analogous to that described for acetaldehyde above. In contrast, the slower background decay suggests a persistent source of bromoform within the sampling system itself. A plausible source is the surface of the ~1 m long stainless-steel

line immediately downstream of the zero air generator, which cools the air after it leaves the generator. If the generator does not completely remove bromoform from the polluted apron air sampled during pre-flight preparations on the ground, residual bromoform can adsorb onto this line and be released gradually during the flight, just as with the rest of the inlet system. Because this downstream section is flushed only during background measurements and calibrations (for 9 mins every hour), it receives far less flushing than the rest of the inlet lines, leading to a slower desorption rate. As a result, the background for bromoform, chlorobenzene and toluene is inadequately characterised and cannot be reliably corrected.

For future measurements, this issue could be mitigated by flushing the inlet with synthetic air while the aircraft is on the ground to prevent contamination. In addition, the inlet unit should be redesigned so that the zero air generator can be flushed continuously rather than only during the periods of background measurement.

Appendix

Table 2.4.: List of all VOCs included in the GC-MS method for CAFE-Brazil and Pacific. The given retention times are median values of different measurement days in the lab and the field. Actual retention times were subject to shifts, mainly influenced by the surrounding temperature, but the relative order of the peaks was always constant.

Name	Formula	Ret. time (s)	m/z
Dichlorodifluoromethane	CCl_2F_2	19.8	85
iso-Butane	C_4H_{10}	21.0	42
Chloromethane	CH_3Cl	22.0	52
n-Butane	C_4H_{10}	23.4	42
Vinylchloride	$\text{C}_2\text{H}_3\text{Cl}$	23.6	62
Acrolein	$\text{C}_3\text{H}_4\text{O}$	24.4	56
Acetaldehyde	CH_3CHO	25.9	29
Methanol	CH_3OH	28.1	31
Bromomethane	CH_3Br	28.8	94
iso-Pentane	C_5H_{12}	32.6	42
CFC-11	CCl_3F	36.3	101
n-Pentane	C_5H_{12}	37.6	42
Isoprene	C_5H_8	42.6	67
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	43.0	31
Propanal	$\text{CH}_3\text{CH}_2\text{CHO}$	46.2	58
CFC-113	$\text{CClF}_2\text{CCl}_2\text{F}$	47.7	101
Acetone	$\text{CH}_3\text{C}(\text{O})\text{CH}_3$	49.0	58
Dimethyl sulfide	CH_3SCH_3	49.0	62
Iodomethane	CH_3I	49.4	142

Table 2.4 continued from previous page

Name	Formula	Ret. time (s)	m/z
Carbon disulfide	CS ₂	50.8	76
Dichloromethane	CCl ₂ H ₂	57.5	49
Methyl nitrate	CH ₃ NO ₃	64.8	46
Hydroxyacetone	C ₃ H ₆ O ₂	64.9	43
Methyl tert-butyl ether	C ₅ H ₁₂ O	65.8	73
Methacrolein	C ₄ H ₆ O	70.0	70
1,1-Dichloroethane	C ₂ H ₄ Cl ₂	71.0	63
Butanal	C ₃ H ₇ CHO	75.8	72
3-Methylfuran	C ₅ H ₆ O	76.6	82
MVK	C ₄ H ₆ O	76.7	55
Butanone	CH ₃ C(O)C ₂ H ₅	78.3	72
Ethylacetate	C ₄ H ₈ O ₂	80.9	61
Chloroform	CHCl ₃	80.9	85
2-Methyl-3-buten-2-ol	C ₅ H ₁₀ O	82.5	71
1,1,1-Trichloroethane	C ₂ H ₃ Cl ₃	83.6	97
Ethyl nitrate	C ₂ H ₅ NO ₃	84.5	46
Carbon tetrachloride	CCl ₄	84.6	117
1,2-Dichloroethane	C ₂ H ₄ Cl ₂	86.3	62
Benzene	C ₆ H ₆	86.5	78
Trichloroethylene	C ₂ HCl ₃	91.8	130
iso-Propyl nitrate	C ₃ H ₇ NO ₃	92.4	46
Dibromomethane	CH ₂ Br ₂	94.4	93
Bromodichloromethane	CHCl ₂ Br	95.5	85
Toluene	C ₇ H ₈	101.9	91
1,1,2-Trichloroethane	C ₂ H ₃ Cl ₃	104.4	97
Tetrachloroethylene	C ₂ Cl ₄	106.4	166
Chlorobenzene	C ₆ H ₅ Cl	111.7	112
Bromoform	CHBr ₃	117.3	173
α -Pinene	C ₁₀ H ₁₆	119.0	93
β -Pinene	C ₁₀ H ₁₆	123.9	91
Limonene	C ₁₀ H ₁₆	127.7	68

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Chapter 3

Vertical and spatial distribution of Chloromethane and its natural sources in the tropics

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Contribution to this chapter by Bianca E. Krumm: *Designed the study, led the GC-MS measurements and data processing, curated other measurement data, conducted data analysis and interpretation, and wrote the chapter.*

Abstract. Chloromethane (CH_3Cl) is the most abundant biogenic source of chlorine to the atmosphere, and significantly contributes to stratospheric ozone depletion. Tropical vegetation, biomass burning, and the oceans have been identified as its main sources, while the reaction with hydroxyl radicals is the principal tropospheric sink. However, current source and sink estimates of CH_3Cl are not balanced, indicating that the origins of approximately 20% of global emissions remain unknown. Here, we present two extensive in-situ datasets of CH_3Cl obtained with a Fast GC-MS instrument aboard the HALO research aircraft above the Amazon rainforest (5°N – 11°S , 72°W – 34°W), and the Indo-Pacific Ocean including the rainforests of Papua New Guinea (PNG) (1°N – 41°S , 131°E – 162°E). Latent class analysis (LCA) was used to identify five clusters representing distinct source signatures with contributions from vegetation, biomass burning, and marine influences. We find substantial CH_3Cl enrichment relative to the tropical baseline above both, the Amazon and the PNG rainforests, while biomass burning and marine emissions had only minor influence on our observations. Interestingly, mixing ratios over PNG (846 ± 156 pptv) are notably higher than over the Amazon (614 ± 15 pptv), indicating a strong variability in CH_3Cl emissions across rainforest ecosystems. By combining our observations with ten previous airborne campaigns, we map the global CH_3Cl distribution, revealing substantial longitudinal heterogeneity throughout the tropical band, with marked enrichments over continents and islands. In the upper troposphere of the western Pacific sector, where most troposphere-to-stratosphere transport occurs, we observe roughly 10% higher CH_3Cl mixing ratios than inferred from ground-based remote monitoring networks.

3.1. Introduction

Chloromethane (CH_3Cl) is by far the most important natural source of atmospheric chlorine (WMO, 2022). As its reactivity towards tropospheric oxidants such as the hydroxyl radical (OH) is low compared to other organic trace gases, CH_3Cl has a relatively long tropospheric lifetime of about 0.9 yr (WMO, 2018). Consequently, a substantial fraction of the emitted CH_3Cl is transported into the stratosphere (e.g., Fabian et al., 1981; Santee et al., 2013; Umezawa; Baker; Brenninkmeijer, et al., 2015), where it undergoes photolysis and releases chlorine radicals that participate in stratospheric ozone depletion. At present, CH_3Cl accounts for roughly 17% of the total stratospheric chlorine budget, a proportion that is expected to increase substantially in the coming decades as the atmospheric chlorofluorocarbon (CFC) abundance from anthropogenic origin declines under the Montreal Protocol (WMO, 2022).

Surface CH_3Cl measurements from the late 1990s onward, e.g. by the global network of AGAGE stations R. G. Prinn et al., 2018, show a relatively stable global mean mixing ratio of ~ 550 pptv with a seasonal variability of ± 50 pptv. The corresponding annual global emission in 2020 was estimated as $4.7 \pm 0.9 \text{ Tg yr}^{-1}$ (WMO, 2022). The latitudinal pattern displays elevated mixing ratios in the tropics, while inter-hemispheric differences are negligible (Khalil and Rasmussen, 1999).

Early atmospheric measurements attributed the bulk of CH_3Cl emissions to oceans with contributions from smouldering biomass fires (Crutzen et al., 1979; Lovelock, 1975). However, in 1996, the work of Moore et al. demonstrated that the oceanic source can account for only a small fraction of the observed mixing ratios in the atmosphere (R. M. Moore et al., 1996). Since then, extensive research has aimed to identify and characterise CH_3Cl sources. Current consensus identifies tropical vegetation as the dominant source (Xiao et al., 2010; Yokouchi; Nojiri, et al., 2000), followed by biomass burning (BB) (Blake et al., 1996), oceans (R. M. Moore et al., 1996), salt marshes (Rhew; Miller, et al., 2000), and wood-rotting fungi (Saxena et al., 1998; Watling and Harper, 1998). In addition, recent studies have reported increasing anthropogenic emissions from industry and coal combustion over the past decades (X. Hu et al., 2022; Sun et al., 2021).

Biogenic CH_3Cl production proceeds via methylation of chloride ions (Cl^-) through biotic and abiotic pathways. Biotic production occurs in living plants and is enzymatically catalysed: halide methyl transferases methylate Cl^- with S-adenosyl-L-methionine (SAM) as methyl donor (Rhew; Østergaard, et al., 2003; Schmidberger et al., 2010). These enzymes are thought to be widespread among vascular plants and have also been reported in fungi (Saxena et al., 1998). Within the plant kingdom, members of the tree-fern order (Cyatheaales) are recognised for particularly high, predominantly biotic CH_3Cl emissions (Jaeger et al., 2018; Yokouchi; Ikeda, et al., 2002).

Abiotic formation occurs via non-enzymatic methylation of Cl^- . Cell wall constituents such as lignin and pectin can act as methyl donors (Hamilton et al., 2003), in addition to SAM and S-methylmethionine (SMM) (Keppler; Ninja Röhlings, et al., 2020). This pathway operates in both living and dead plant material and exhibits an exponential temperature dependence (Keppler; Ninja Röhlings, et al., 2020). It accounts for the majority of CH_3Cl released during BB events (Hamilton et al., 2003) and from halophyte ecosystems (Keppler; Ninja Röhlings, et al., 2020). A further

abiotic mechanism has been identified in soils, where Fe(III) acts as a redox catalyst for Cl⁻ methylation (Keppler; Eiden, et al., 2000).

The principal tropospheric sink for CH₃Cl is oxidation with OH, which accounts for a partial lifetime of 1.3 yr (Herndon et al., 2001). Although this pathway, via several intermediates, can ultimately produce inorganic chlorine, its contribution to the overall tropospheric chlorine budget is modest (Hossaini et al., 2016). Additional loss processes are uptake by soils (lifetime = 4.2 yr; WMO, 2014) and by the oceans (lifetime = 12 yr; L. Hu et al., 2013). The remaining CH₃Cl is advected upward into the stratosphere, where it is decomposed through photolysis (lifetime = 30.4 yr; WMO, 2014). Troposphere-to-stratosphere transport (TST) across the tropical tropopause layer (TTL) is most efficient above the tropical western Pacific (e.g., Fueglistaler et al., 2004; Newell and Gould-Stewart, 1981; Rex et al., 2014). Nevertheless, current source and sink estimates are unbalanced, and a recent study based on carbon isotope measurements suggests that a substantial, currently unidentified source is missing from the global CH₃Cl budget (Bahlmann et al., 2019).

To quantify the contribution of CH₃Cl to the stratospheric chlorine budget, it is essential to constrain its distribution in the upper troposphere, because TST originates there. The vertical and spatial variability of CH₃Cl has been investigated in numerous aircraft campaigns (e.g., Blake et al., 1996; Gebhardt et al., 2008; Smith et al., 2024; Umezawa; Baker; Brenninkmeijer, et al., 2015; Umezawa; Baker; Oram, et al., 2014) and by satellite observations (Santee et al., 2013). Most aircraft measurements have sampled oceanic regions, particularly the Pacific basin (e.g., PEM Tropics, HIPPO 1-5, ATom 1-4). In contrast, the GABRIEL campaign provided the first, and to date the only, vertical profile above the Amazon rainforest of Suriname and French Guiana, revealing a strong net ecosystem source from vegetation (Gebhardt et al., 2008). Umezawa; Baker; Oram, et al. (2014) reported consistently elevated CH₃Cl mixing ratios in the upper troposphere relative to surface background values at both mid-latitudes and the tropics, while comparison with CO data suggested tropical non-combustion emissions as primary source. Their findings raise concerns that extrapolating surface mixing ratios to the entire troposphere may underestimate upper-tropospheric CH₃Cl (WMO, 2022). However, vertical CH₃Cl measurements, especially over tropical rainforests, which are thought to be the dominant global source, remain scarce.

Here we present airborne, in-situ CH₃Cl measurements obtained over the Amazon rainforest and the Indo-Pacific Ocean during the Chemistry of the Atmosphere Field Experiment (CAFE) Brazil and Pacific campaigns. First, we describe the vertical distributions in both regions and compare them with previous observations. Using LCA of lower-tropospheric samples, we identify distinct clusters that capture the signatures of the main CH₃Cl sources—vegetation, BB, and marine emissions—and discuss the variability of CH₃Cl across these clusters. Finally, we combine our data with those from earlier campaigns to assess the variability of CH₃Cl globally and in the tropics, with particular emphasis on upper-tropospheric mixing ratios and their implications for TST.

3.2. Methods

3.2.1. Airborne Observations

We present airborne in-situ trace gas measurements covering altitudes from 0.2 to 14 km conducted aboard the High Altitude Long Range research aircraft (HALO) during the CAFE-Brazil and CAFE-Pacific field missions. Furthermore, we compare and combine the CAFE CH₃Cl data with a suite of previous tropical aircraft campaigns to obtain a more comprehensive view of tropical and global CH₃Cl distributions. Table 3.1 summarises these datasets, including the campaign periods, sampling techniques, and references, while Figure 3.1 shows their flight tracks. All campaigns will be briefly introduced below.

CAFE

The CAFE-Brazil campaign (December 2022–January 2023) comprises 16 research flights (RFs) over the Amazon Basin. Its primary objective was to investigate pristine biogenic emissions from the rainforest and their atmospheric processing under strong convection and minimal BB typical of the dry-to-wet transition season (Machado et al., 2004; Tripathi et al., 2025).

The CAFE-Pacific campaign (January–February 2024) operated from Cairns, Australia, covering 18 RFs that sampled marine air masses from the East Indo-Pacific Ocean and continental air masses from northern Australia and Papua New Guinea. The campaign period was dominated by the intense convective activity of the Australian summer monsoon (Pope et al., 2008).

The HALO payload for those missions comprised 14 scientific instruments designed to measure a wide range of atmospheric chemistry tracers (Voigt et al., 2022). The data used in this chapter comprises CH₃Cl, isoprene (C₅H₈), and dimethyl sulfide (DMS) from SOFIA, ozone from FAIRO, refractory black carbon (rBC) from SP2, and acetonitrile measured by PTR-ToF-MS. A detailed description of SOFIA is given in Chapter 2, the remaining instruments are introduced briefly below.

The Fast Airborne Ozone (FAIRO) instrument combines absolute quantification by absorption spectroscopy (UV photometer, Hartley band at $\lambda = 254$ nm) with relative measurement using a dry chemiluminescence sensor to achieve high-frequency (10 Hz) ozone measurements in the range from 3–5000 ppbv. The custom-built instrument has been described in detail elsewhere (Obersteiner, 2024; Zahn et al., 2012). In this chapter, data from the UV photometer were used, as it offers slightly lower uncertainty (2.1%) and its 0.25 Hz time resolution was sufficient. For both campaigns, the latest available data version in May 2025 (V02) was obtained from the HALO database (Re3data.Org, 2016).

Table 3.1.: Overview of time periods, sampling methods and references for all CH₃Cl datasets used from various flight campaigns.

Campaign	Time period	Sampling method	References
GABRIEL	Oct 2005	Electropolished canister samples & GC-MS	Gebhardt et al., 2008
HIPPO-1	Jan 2009	Advanced Whole Air Sampler (AWAS, U Miami), NOAA Whole Air Sampler (NWAS) & GC-MS; PANTHER (Fast GC-MS)	Atlas, 2013 Atlas and NSF NCAR EOL, 2009 Elkins; F. L. Moore, et al., 2001
HIPPO-2	Nov 2009		
HIPPO-3	Apr 2010		
HIPPO-4	Jun 2011		
HIPPO-5	Aug 2011		
ATom-1	Jul–Aug 2016	Whole Air Sampler (UC Irvine) & GC-(FID/ECD/MS)	Barletta et al., 2019
ATom-2	Jan–Feb 2017		
ATom-3	Sep–Oct 2017		
ATom-4	Apr–May 2018		
CAFE-Brazil	Dec 2022–Jan 2023	SOFIA (Fast GC-MS)	this work
CAFE-Pacific	Jan–Feb 2024		

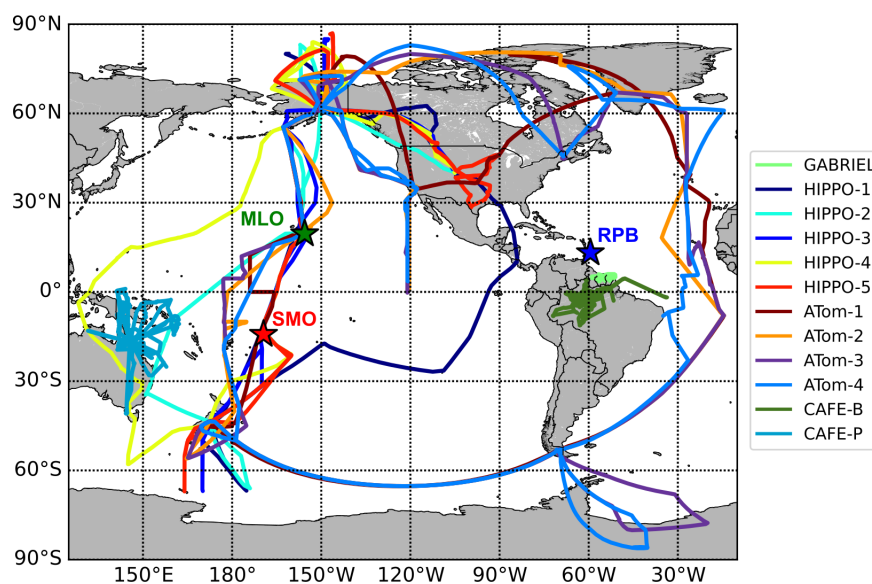


Figure 3.1.: Flight tracks from all campaigns included in this chapter. Stars mark the locations of the background-measurement stations Mauna Loa Observatory (MLO, Hawaii), Ragged Point (RPB, Barbados), and American Samoa Observatory (SMO, Tutuila).

A Proton Transfer Reaction-Time of Flight-Mass Spectrometer (PTR-ToF-MS, Ionicon 8000, Analytik GmbH, Austria) was used to measure acetonitrile among other VOCs at 1 Hz time resolution. VOCs with a proton affinity higher than that of water (691 kJ/mol) were ionised by proton transfer from hydronium primary ions (H_3O^+). More detailed information on the instrument configuration for the CAFE campaigns is provided elsewhere (Tripathi et al., 2025). In-flight background measurements were obtained by flushing the inlet with synthetic air, and calibrations against a gas standard (Apel Riemer Environmental, USA) were performed on the ground either the day before or after each RF. The raw data were processed using the Ionicon Data Analyser (IDA, version 2.2.0.4) software. Acetonitrile was quantified with a total uncertainty, including precision and calibration errors, of approximately 10–20% (Tripathi et al., 2025), and a limit of detection (LOD) of ~ 16 pptv.

Refractory black carbon was measured with a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, Longmont, USA) based on the laser-induced incandescence (LII) technique (Schwarz et al., 2006; Stephens et al., 2003), and a detailed description of the instrument is given elsewhere (Holanda et al., 2020; Krüger et al., 2022). Briefly, aerosol particles traverse a laser beam (Nd:YAG, $\lambda = 1064$ nm) while the instrument records both the scattered light and the incandescent signal generated when particles absorb sufficient laser energy to vaporise. The scattered-light intensity yields the particles' optical size, while the incandescent signal intensity is proportional to the rBC mass of the particle. The SP2 can detect rBC within particles in the nominal size range of 70 to 500 nm (Holanda et al., 2020).

GABRIEL

The Guyanas Atmosphere-Biosphere exchange and Radicals Intensive Experiment with the Learjet (GABRIEL) campaign took place in October 2005 (dry season) over Suriname, Guyana, and French Guiana. Ten RFs sampled air masses from 0.2 to 11 km altitude above the pristine Guianan moist forests, an ecoregion within the Amazon biome, and the adjacent Atlantic Ocean. A detailed campaign description is provided in the supplement of Lelieveld et al. (2008). Air was collected in electropolished stainless-steel canisters and later analyzed on the ground with a GC-MS system. CH₃Cl mixing ratios were obtained with a precision of 3.3%, a total uncertainty of 5.9%, and a LOD of 1.9 pptv (Gebhardt et al., 2008).

HIPPO

The HIPPER Pole-to-Pole Observations (HIPPO) comprised five airborne campaigns that sampled the entire Pacific basin (87°N–67°S, 128°W–84°E) across different seasons from 2009 to 2011. The High-performance Instrumented Airborne Platform for Environmental Research (HIPPER) aircraft performed consecutive vertical profiles from 0.3 to 8.5 km (occasionally up to 14 km), providing a latitudinal cross-section of the troposphere. Further information on HIPPO is given elsewhere (Wofsy et al., 2011).

In this study, we use the combined CH₃Cl dataset obtained with three sampling methods (Atlas, 2013). Whole-air samples were collected using (i) electropolished stainless-steel canisters (Advanced Whole Air Sampler, AWAS; Atlas and NSF NCAR EOL, 2009) from the University of Miami and (ii) glass vessels (NOAA Whole Air Sampler, NWAS) from the NOAA Global Monitoring Laboratory. After each flight the samples were analysed on the ground by GC-MS. In addition, CH₃Cl was measured with the PAN and other Trace Hydrohalocarbon Experiment (PANTHER), an airborne Fast GC-MS instrument (Elkins; F. L. Moore, et al., 2001).

ATom

The Atmospheric Tomography Mission (ATom) comprised four campaigns that circumnavigated the Americas (80°N–80°S, 180°W–180°E) while continuously profiling the atmosphere from 0.2 to 12 km using NASA's DC-8 aircraft. All flights followed similar tracks, yielding comparable measurements in the same regions across all four seasons between 2016 and 2018.

CH₃Cl mixing ratios were obtained from whole-air samples collected with the Whole Air Sampler (WAS) operated by UC Irvine. Air was drawn into electropolished stainless-steel canisters, transported to the laboratory, and subsequently analysed by GC-FID (Flame Ionisation Detector) and GC-MS. The CH₃Cl measurements have a precision of 1.5%, a total accuracy of 5% (Colman et al., 2001), and a LOD of 1 pptv (Barletta et al., 2019).

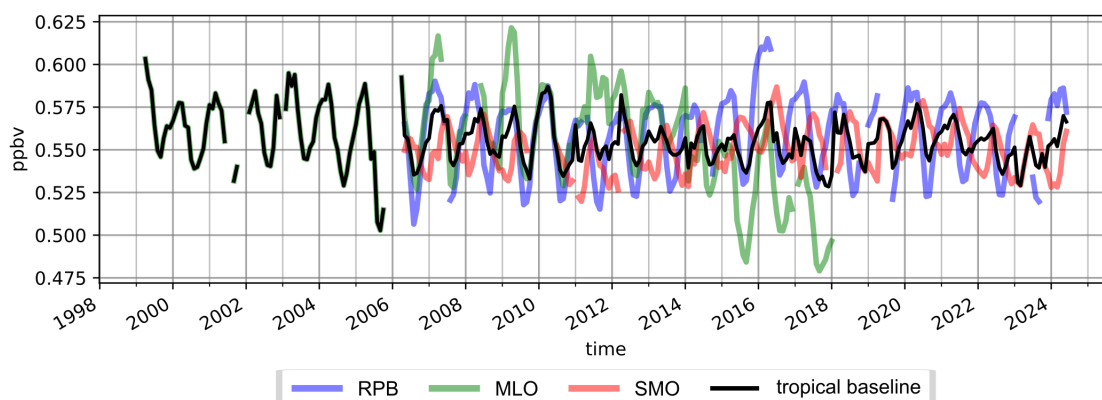


Figure 3.2.: Time series of CH_3Cl mixing ratios from three long-term monitoring stations: Ragged Point, Barbados (RPB, blue); Mauna Loa Observatory, Hawaii (MLO, green); and American Samoa Observatory, Tutuila (SMO, red). The black line shows the combined tropical baseline (see text for calculation details).

3.2.2. Enrichment relative to the tropical baseline ($\Delta\text{CH}_3\text{Cl}$)

The inter-comparability of atmospheric CH_3Cl mixing ratios measured in different seasons and across several decades is limited by its seasonal and inter-annual variability (~ 100 pptv), driven by changes in sources (e.g., vegetation growth periods, BB season) and sinks (e.g., atmospheric oxidative capacity). To minimise this effect, we subtracted a tropical baseline (conceptually similar to Santee et al. (2013) and Umezawa; Baker; Brenninkmeijer, et al. (2015)) defined as the mean of the northern and southern hemisphere monthly-mean mixing ratios reported by long-term monitoring stations (Figure 3.2). The northern hemisphere baseline is the average of the Mauna Loa Observatory (MLO, Hawaii) (Elkins; Nance, et al., 2017) and Ragged Point (RPB, Barbados) (R. Prinn et al., 2025), while the southern hemisphere baseline is represented by the American Samoa Observatory (SMO, Tutuila) (R. Prinn et al., 2025). This approach was chosen for two reasons: (i) the seasonal cycles are anti-correlated between the hemispheres, so using a single station would bias the other hemisphere's data, and (ii) each station record contains gaps that are largely filled by the combined average. The resulting parameter $\Delta\text{CH}_3\text{Cl}$ quantifies the enrichment or depletion of an air mass with CH_3Cl relative to the tropical baseline mixing ratio.

3.2.3. Latent Class Analysis (LCA)

To identify "hidden" (latent) groups of air masses with distinct source signatures in our CAFE datasets, we performed an LCA. In addition to CH_3Cl , the following variables were included: acetonitrile and rBC for BB, isoprene for vegetation emissions, DMS for marine influence, and ozone as an indicator of oxidised air masses and altitude. Unfortunately, due to issues with the SP2 instrument during CAFE-Pacific, black carbon data could only be included in the CAFE-Brazil analysis. All instrument data were merged onto the time base of SOFIA's samples. Rows with missing values (e.g., during background measurements or instrument failures) were removed, and values below the LOD were replaced by the LOD. Because the sources are confined to the surface,

only samples collected below 4 km altitude were retained. After these filters, 225 CAFE-Brazil and 248 CAFE-Pacific samples remained for the LCA.

Because the LCA model assumes that each variable follows a Gaussian distribution, we first examined and reduced the skewness of all tracers. Each variable was transformed using several functions (square-root, cube-root, fourth-root, decadic logarithm, or Yeo-Johnson) and the resulting skewness was evaluated. For each tracer, we selected the method that produced the most symmetric distribution, accepting skewness values between -2 and +2 as adequate for further analysis. The Yeo-Johnson transformation gave the best results for all tracers except DMS from the CAFE-Pacific campaign, for which the decadic logarithm was optimal. The transformed variables were then standardised by z-score normalisation.

Finally, the LCA was performed with the StepMix Python package (Morin et al., 2025), using the `gaussian_diag` model and a fixed random-seed (`random_state=42`). The choice of the number of classes was based on minima in Bayesian Information Criterion (BIC) and Consistent Akaike Information Criterion (CAIC), with a four-class (CAFE-Brazil) respective seven-class (CAFE-Pacific) model chosen for optimal fit.

3.2.4. FLEXPART back trajectories and PBL sensitivity

To gain insight into the individual measurements' flux footprint, we used the Flexible particle dispersion model (FLEXPART, version 10.2) (Pisso et al., 2019). FLEXPART, originally developed by Stohl et al. (1998), is a Lagrangian transport model used to solve the equation of motion for a large number of "particle parcels" over a predefined meteorological field. It also accounts for turbulent fluctuation using a detailed planetary boundary layer (PBL) turbulence scheme (Hanna, 1982) and a sub-grid convection parameterisation based on Emanuel and Živković-Rothman (1999). It has been widely used in studies on atmospheric transport over the past decades, including cases of pollutant plume transport (Halse et al., 2013), sahara dust transport (Williams et al., 2007), and nuclear accidents (Yasunari et al., 2011). Importantly, FLEXPART can also be used in a backwards-time mode to simulate the sensitivity (in sec) of a measurement to upwind regions (Eckhardt et al., 2017).

In this study, we performed 10-day back trajectory calculations for every GC-MS sample (3 min time resolution) using the mean altitude and position during the 1 min sampling interval. Each release included 10^5 particles to ensure statistical robustness of the resulting gridded sensitivity for the entire simulation period. Simulations were carried out using global European Centre for Medium-Range Weather Forecasts Re-Analysis 5 data (ECMWF ERA5; Hersbach et al., 2020; Setchell, 2020), while the output grid was set to approximately hemispheric. For both input and output, a 1° grid spacing was used to minimise computational load while maintaining an appropriate level of detail. The release species was set to an inert tracer with a molar mass of $\sim 93 \text{ g mol}^{-1}$ as a general proxy for all measured species and did not account for dry and wet deposition. Automation and post-processing of the simulations were carried out using the footprint version of the Dispersion Atlas (DispAtlas) FLEXPART wrapper (<https://gitlab.com/>

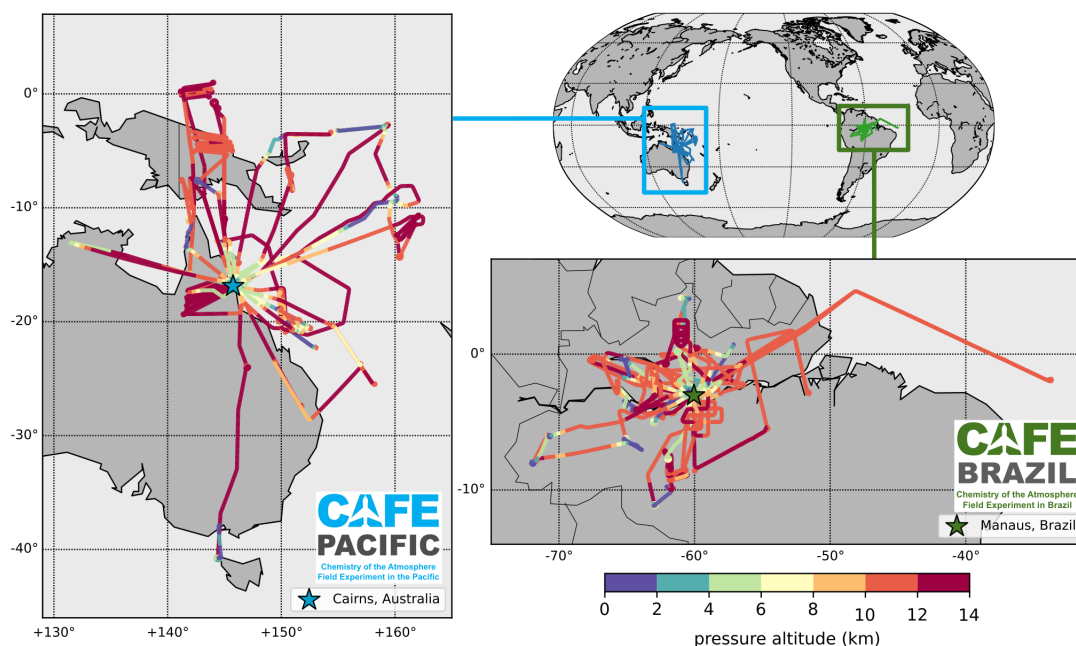


Figure 3.3.: Flight tracks and altitudes of HALO during the CAFE-Brazil and the CAFE-Pacific missions. Only flights during which the SOFIA instrument was operational are included. The campaign logos were provided by Tanja Pallien.

AlexPoulidis/dispatlas#).

To identify the source regions of the sampled air masses, we calculated the PBL sensitivity as the overlap between the total trajectory sensitivity and ERA5 PBL heights (based on the bulk Richardson number, following Seidel et al. (2012)). The uncertainty of ERA5 PBL heights is typically < 20% but can exceed 50% for shallow boundary layers (< 1 km), e.g. during nighttime or in cold regions.

3.3. Results and discussion

3.3.1. Chloromethane observations during the CAFE missions

Figure 3.3 shows the HALO aircraft's flight tracks for the CAFE-Brazil and CAFE-Pacific campaigns, covering the tropospheric column from 0.2 to 14 km. During CAFE-Brazil, the aircraft spent almost all flight hours over the Amazon basin, whereas CAFE-Pacific sampled a broader range of regions, including Papua New Guinea, New Ireland, eastern Australia, Tasmania, and the eastern Indo-Pacific Ocean.

Vertical distribution

To interpret the vertical distribution of a long-lived tracer such as CH_3Cl , which can be transported over long distances, the air mass footprints associated with different altitude ranges need

to be considered. We therefore combined the 10-day back trajectories of all samples within three representative layers—lower troposphere (0–4 km), mid-troposphere (4–9 km), and upper troposphere (9–14 km)—to obtain mean footprints (Figure 3.4 d-i).

In both campaigns, the lower-tropospheric footprints are dominated by local influences. During CAFE-Brazil, those air masses entered the Amazon basin from the Atlantic with north- and south-easterly trade winds, and spent at least two days within the Amazon PBL before sampling. Mid-tropospheric air masses also originated over the Atlantic but generally did not experience significant contact with the Amazon PBL. Upper-tropospheric air masses exhibited a broad footprint covering the entire South American continent and adjacent oceans, with the majority of their residence time over Brazil and the Amazon region.

During the CAFE-Pacific campaign, the lower-tropospheric airmasses had heterogeneous origins. Samples collected over the ocean were transported from the Pacific by trade winds, whereas the majority of those sampled over land originated from the Indo-Australian Archipelago in the northwest. Mid- and upper-tropospheric air masses had broader footprints, including Australia, the Indo-Australian Archipelago, and adjacent oceans.

The vertical distribution of CH_3Cl mixing ratios from both campaigns is shown in Figure 3.4 a. In the free and upper troposphere, the median values from CAFE-Brazil and CAFE-Pacific are very similar, whereas in the lower troposphere (< 4 km), they exhibit marked differences that reflect the pronounced influence of diverse surface sources. The profile above the Amazon rainforest (CAFE-Brazil) shows a clear increase toward the surface, whereas the CAFE-Pacific profile displays greater variability in the lower troposphere with a modest decreasing trend towards the surface, consistent with the influences of airmasses from heterogeneous source regions.

The CAFE-Brazil profile is compared with the sole previous CH_3Cl profile obtained above a tropical rainforest during the GABRIEL campaign (Figure 3.4 b). GABRIEL was conducted above the eastern Amazon close to the Atlantic coast of Suriname and French Guyana, and was largely confined to the lower troposphere with only a few samples above 5 km. Although GABRIEL was conducted during the dry season, low levels of CO (Stickler et al., 2007) and acetonitrile (Eerdekens et al., 2009) indicate only an insignificant influence of BB emissions (Gebhardt et al., 2008). The impact of BB on the CAFE-Brazil measurements is discussed in the following section, and was likewise low. Consequently, the observed variability in both datasets is attributed mainly to biogenic emissions.

In the lower troposphere (0–4 km), both the CAFE-Brazil and GABRIEL datasets exhibit an increase in CH_3Cl mixing ratios toward the surface, indicating a net positive flux from rainforest ecosystems. The increase is markedly stronger in the GABRIEL measurements over the coastal Amazon than in the CAFE-Brazil data from the central Amazon (Figure 3.4 d), indicating substantially larger emission fluxes from the coastal ecosystem. However, a part of this difference might also originate from seasonal effects, as CAFE-Brazil was conducted during the dry-to-wet transition while GABRIEL took place in the dry season.

In the mid-troposphere (4–9 km), CAFE-Brazil CH_3Cl measurements are at their lowest, reflecting the predominance of air masses that have been advected over the Atlantic Ocean (Figure 3.4 e). This agrees with earlier work showing that tropical oceans are far weaker CH_3Cl sources than

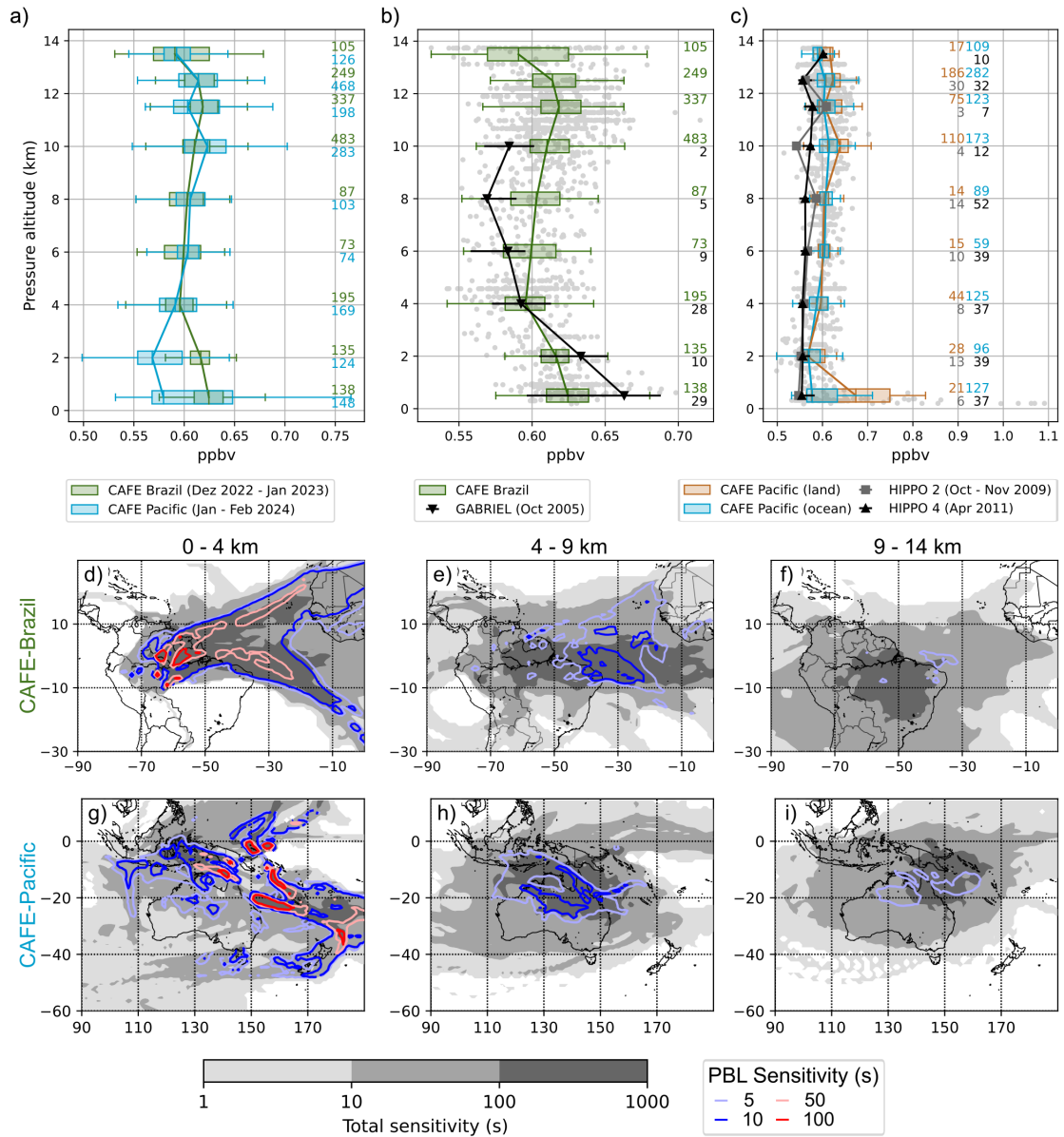


Figure 3.4.: Vertical profiles of CH_3Cl mixing ratios obtained during the CAFE campaigns. a) Comparison CAFE-Brazil and CAFE-Pacific. b) CAFE-Brazil profile alongside the GABRIEL rainforest profile. c) CAFE-Pacific data divided into over-land and over-ocean data points, compared to HIPPO-2 and HIPPO-4 over-ocean measurements in the same region (30°S–30°N; 130°E–170°E.) The CAFE distributions are shown as box and whisker plots grouped in 2-km bins, respectively 1 km bins above 11 km due to the higher sampling density in the upper troposphere. Error bars on GABRIEL and HIPPO data represent the 25-75percentile. The number of samples in each bin is given on the right-hand side of every panel. Individual measurements are shown as grey points in panels b) and c).

d)-i) 10-day back trajectory footprints of representative altitude ranges for both campaigns: lower troposphere (d, g), mid-troposphere (e, h), and upper troposphere (f, i). Grey shading denotes the mean total sensitivity, while the blue and red contours outline the regions where the trajectories intersect the PBL.

tropical vegetation (Xiao et al., 2010).

In the upper troposphere (9–14 km), mixing ratios rise again and peak at the main outflow level of deep convection during CAFE-Brazil (Tripathi et al., 2025). This pattern matches the upper tropospheric footprint, which indicates that the air parcels spent most of the preceding ten days over the Amazon (Figure 3.4 f), allowing for enrichment of CH_3Cl through deep-convective transport of surface emissions.

To illustrate the contrasting air-mass characteristics sampled during the CAFE-Pacific campaign, Figure 3.4 c separates the CH_3Cl profile into over-land and over-ocean observations.

The over-land profile exhibits a pronounced increase in the lowest altitude bin, with mixing ratios reaching 1.1 ppbv, indicative of strong surface emissions. A secondary enhancement appears in the upper troposphere, consistent with deep-convective uplift of those emissions.

In contrast, the over-ocean profile shows decreasing mixing ratios below 4 km. This decline likely reflects the influence of continental sources on the mid- and upper-tropospheric footprints (Figure 3.4 h,i), whereas the lower-tropospheric footprints are dominated by air that originates from the open Pacific Ocean (Figure 3.4 g). When compared with oceanic measurements from the HIPPO-2 and HIPPO-4 campaigns in the same region, the CAFE-Pacific oceanic profile matches best in the lower troposphere. At higher altitudes, however, the CAFE-Pacific mixing ratios are slightly elevated, reflecting residual terrestrial contributions.

During RF15 of CAFE-Pacific (02:37–02:52 UTC on 10 February 2024), HALO performed a fly-by of the Cape Grim/Kennaook Observatory on Tasmania. The ground-based station has measured CH_3Cl with high precision at 1–2 h intervals for decades as part of the AGAGE network (Miller et al., 2008; R. G. Prinn et al., 2018). SOFIA collected four PBL samples (identified by high absolute humidity) at altitudes between 180 to 900 m above the station, yielding a mean ($\pm\sigma$) mixing ratio of 561 (± 5) pptv. This value is in excellent agreement with the station’s contemporaneous measurements (545 pptv, mean value of 02:17 and 03:22 UTC; R. Prinn et al., 2025). The ~3% offset lies well within SOFIA’s total uncertainty (10%), thereby confirming the reliability of the airborne CH_3Cl data.

Identification of Chloromethane source regions

To isolate airmasses with distinct source signatures, we applied an LCA to the lower-tropospheric samples (0–4 km), which are closest to the surface sources and therefore minimally affected by dilution, oxidation, or long-range transport. The analysis incorporates tracers that characterise the main known CH_3Cl sources: isoprene for vegetation, black carbon and acetonitrile for BB, and DMS for marine emissions. Ozone was added as an indicator of oxidised air masses and of altitude. Because of SP2 instrument problems during CAFE-Pacific, black carbon data could be used only for the CAFE-Brazil analysis. The LCA yielded four clusters for CAFE-Brazil and seven for CAFE-Pacific. Out of those, five clusters (two for CAFE-Brazil and three for CAFE-Pacific) representing PBL conditions, with the majority of samples taken below 1 km, were selected for the present source-attribution study (see Figure 3.8). The distributions of the tracer mixing ratios

for the five clusters are shown in Figure 3.5. Below, we first describe the characteristics of each cluster, and then examine how CH_3Cl mixing ratios vary among them.

The two CAFE-Brazil clusters (blue and orange) both have mean isoprene mixing ratios of ~ 2.5 ppbv, which is typical for the Amazonian PBL (e.g., Pfannerstill et al., 2021; Yáñez-Serrano et al., 2015). Hence, both clusters are considered to be comparably influenced by vegetation emissions. BB markers, however, differ between the clusters. The orange cluster exhibits modestly elevated mean ($\pm\sigma$) values of $170 (\pm 48)$ pptv of acetonitrile and $0.124 (\pm 0.105) \mu\text{g m}^{-3}$ of black carbon. These concentrations are lower than those found in fresh BB plumes (e.g., Holanda et al., 2020), but indicate a diluted, somewhat aged BB influence that has been transported over longer distances. In contrast, the blue cluster shows no such enrichment. Accordingly, the blue cluster represents a pristine Amazon PBL (AMZ), whereas the orange cluster reflects an Amazon PBL with an aged, diluted BB background (AMZ+BB).

To investigate the origins of these BB emissions, we computed a mean PBL footprint for each cluster by averaging the PBL sensitivity fields of all samples belonging to that cluster. Figure 3.6 a and b display the resulting footprints together with the spatial distribution of active fires during the campaign. The AMZ+BB footprint overlaps with two regions of intense burning at Brazil's eastern coast and a part of West Africa, whereas the AMZ footprint exhibits only negligible overlap with these fire-affected areas. Although the presented data do not allow a further quantitative partitioning of the contributions from these two source regions, the combined evidence from BB tracer concentrations and the footprints indicates that the AMZ+BB airmasses are indeed influenced by BB emissions, whereas the AMZ airmasses are significantly less affected.

The three CAFE-Pacific clusters (green, red, and purple) capture the contrasting signatures of marine and terrestrial environments, as evident from their sampling locations (Fig. 3.5 b) and the associated back-trajectory footprints (Fig. 3.6 c–e).

The green cluster corresponds to the marine Pacific PBL (PAC). It is characterised by elevated DMS mixing ratios (100 ± 43 pptv) and isoprene concentrations that are consistently below the LOD. The footprint analysis (Fig. 3.6 e) confirms that the sampled air masses originated over the open Pacific Ocean.

The purple cluster comprises samples collected in the PBL over the coastal rainforest of Papua New Guinea (PNG). Their footprints show a strong influence from the local rainforest PBL and from nearby Indonesian islands, which are also forested. Air masses in this cluster are characterised by high isoprene mixing ratios (3.2 ± 2.8 ppbv), indicating intense vegetation emissions, while acetonitrile, ozone and DMS are low, reflecting minimal BB and marine influences.

The red cluster represents a variety of coastal regions (CST), including New Ireland, Tasmania and the north-Australian coast, and displays a mixed signature with high variability of both isoprene (0.5 ± 1.0 ppbv) and DMS (87 ± 27 pptv), while acetonitrile remains low, suggesting combined vegetation and marine influences with little contribution from BB sources.

The CH_3Cl mixing ratios for the five clusters are summarised in Table 3.2. Because background mixing ratios of CH_3Cl vary seasonally and inter-annually, we use the parameter $\Delta\text{CH}_3\text{Cl}$ (defined in Section 3.2.2) to assess CH_3Cl enrichment with respect to its tropical baseline across the five clusters (Figure 3.5 c).

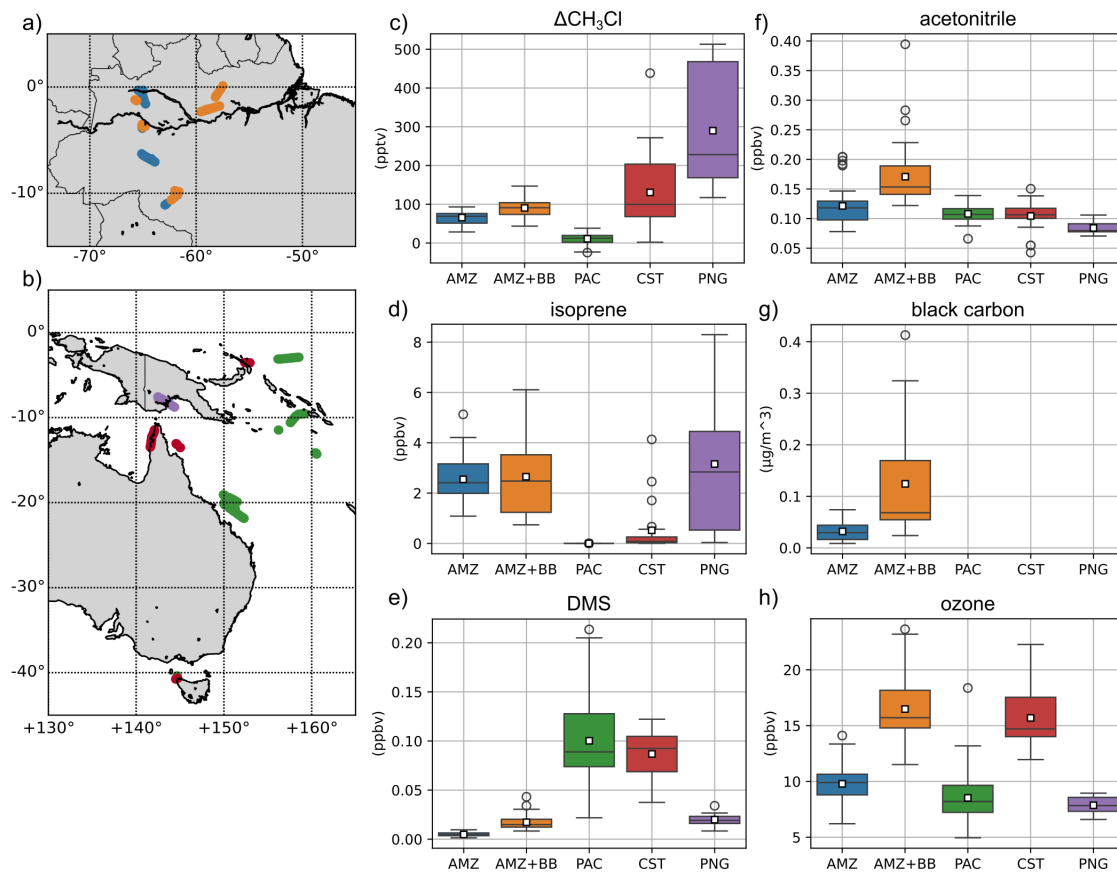


Figure 3.5.: Variability of six atmospheric tracers across the five LCA clusters, representing distinct air masses: AMZ – pristine Amazon; AMZ+BB – AMZ with biomass burning background; PAC – Pacific ocean; CST – coastal vegetation; PNG – rainforest of Papua New Guinea. Panels a)–b) show the geographic sampling locations of samples within the clusters. Panels c)–h) display the distributions of $\Delta\text{CH}_3\text{Cl}$, isoprene, DMS, acetonitrile, black carbon, and ozone, respectively, for each group.

Table 3.2.: Chloromethane mixing ratio statistics for the five LCA clusters. Columns give the enrichment relative to the tropical baseline ($\Delta\text{CH}_3\text{Cl}$), the absolute CH_3Cl mixing ratios, the mean, standard deviation (σ), 1st percentile (P1), and 99th percentile (P99) of each distribution, and the number of samples (n) in each cluster.

	$\Delta\text{CH}_3\text{Cl}$ (pptv)				CH_3Cl (pptv)				
cluster	mean	σ	P1	P99	mean	σ	P1	P99	n
PAC	11	13	-24	36	566	13	533	591	74
AMZ	66	15	31	92	617	15	583	644	48
AMZ+BB	90	22	48	142	639	22	596	693	49
CST	131	106	3	405	687	106	559	961	21
PNG	290	156	119	512	846	156	676	1069	12

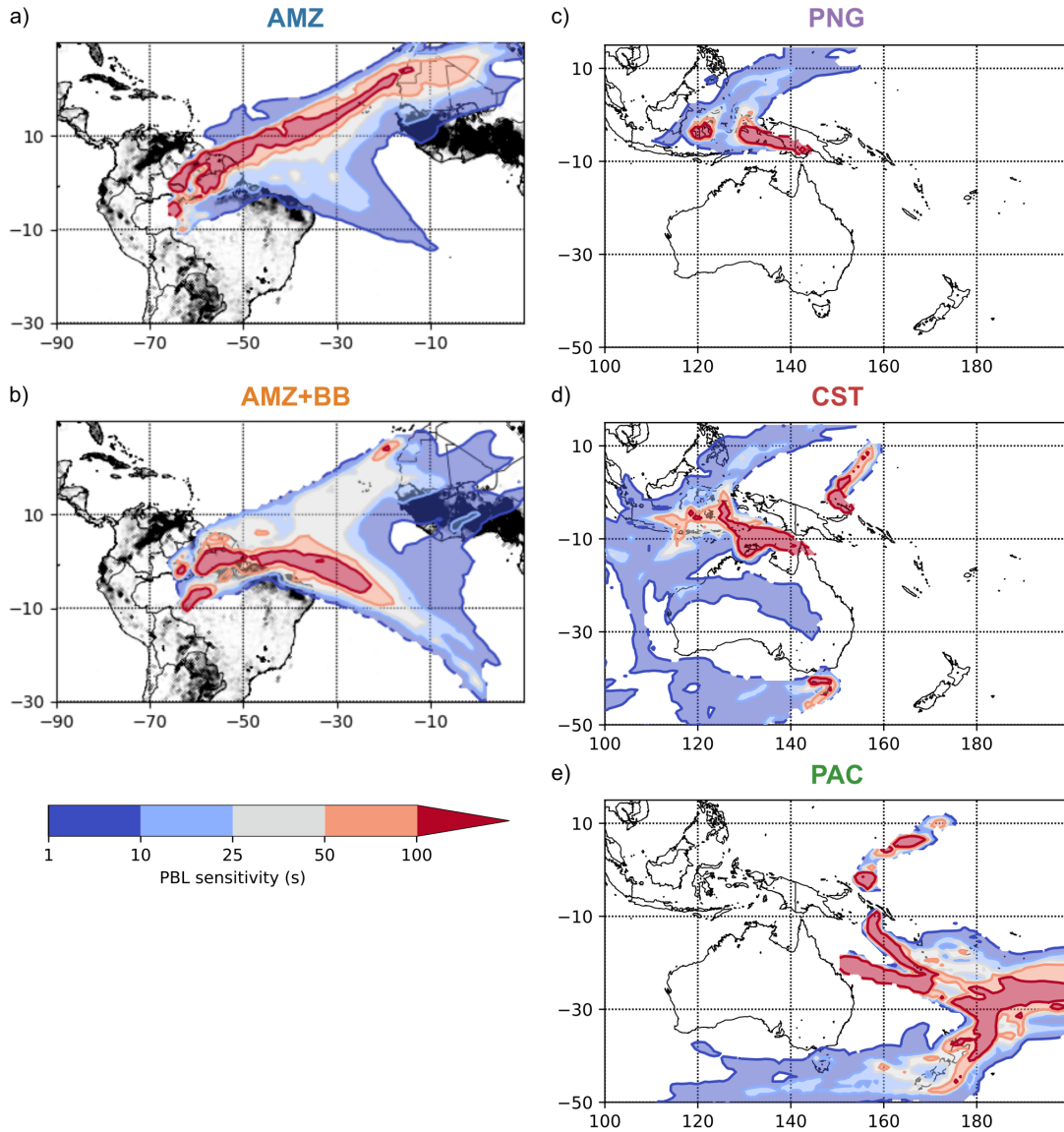


Figure 3.6.: Contour plots of 10-day PBL footprints for the five clusters, derived as the average PBL sensitivity of all samples in that cluster. Black areas on the maps in panel a) and b) denote locations of all fires detected by VIIRS (downloaded from FIRMS, Earth Science Data Systems, 2024, on 16 Dec 2025) throughout the CAFE-Brazil campaign period (Dec 2022–Jan 2023).

The smallest enrichment ($\Delta\text{CH}_3\text{Cl} = 11 \pm 13$ pptv) occurs in the PAC cluster, which represents the marine PBL. Since the tropical baseline reflects background mixing ratios in the marine PBL, the PAC cluster is expected to match the baseline closely. The observed modest increase may reflect recent contact of the sampled air masses with tropical islands such as New Caledonia, Vanuatu, and Fiji (see Figure 3.6 e). However, the elevation over the tropical baseline is not significant and lies well within our total measurement uncertainty of 10%.

The direct influence of BB on our data is generally small, but its effect on CH_3Cl levels can still be observed when comparing the AMZ cluster with AMZ+BB. We find slightly higher enrichment (33 pptv) in the air masses affected by BB than in the pristine AMZ cluster. This indicates that, although the BB emissions are already somewhat diluted, there is still a notable increase in CH_3Cl .

To evaluate the impact of tropical vegetation, we compare the pristine central Amazon rainforest cluster (AMZ, $\Delta\text{CH}_3\text{Cl} = 66 \pm 15$ pptv) with the Papua New Guinea rainforest cluster (PNG, $\Delta\text{CH}_3\text{Cl} = 290 \pm 156$ pptv). Both clusters exhibit an enrichment in CH_3Cl , confirming that each rainforest acts as a net source. However, the enrichment over PNG is roughly four times larger than over AMZ. Strong CH_3Cl emissions from other tropical islands of the Indo-Australian archipelago are well documented (Blei et al., 2010; Saito; Yokouchi; Kosugi, et al., 2008; Yokouchi; Noijiri, et al., 2000), whereas comparable measurements above the central Amazon have not previously been reported. The GABRIEL campaign measured a CH_3Cl enrichment of $\Delta\text{CH}_3\text{Cl} = 143 (\pm 42)$ pptv (average of 24 over-land samples below 1 km) above the coastal Amazon in Suriname and French Guiana, an intermediate value between the AMZ and PNG clusters. Direct comparison is, however, limited because GABRIEL was conducted in a different season than the CAFE campaigns.

Together, these results reveal substantial variability in CH_3Cl emissions among different rainforest ecosystems. This finding is qualitatively consistent with a previous inversion-modelling study, which predicted emission fluxes from the Indo-Australian archipelago to be about twice those from African or South American rainforests (Xiao et al., 2010). Two main factors can explain this variability. First, South East Asian rainforests contain a higher abundance of CH_3Cl -emitting taxa, notably tree ferns (Cyatheales) (Jaeger et al., 2018; Saito and Yokouchi, 2006; Yokouchi; Ikeda, et al., 2002; Yokouchi; Saito, et al., 2007; Yokouchi; Takenaka, et al., 2015) and Dipterocarp trees (Blei et al., 2010; Saito; Yokouchi; Phillip, et al., 2013; Yokouchi; Ikeda, et al., 2002). Dipterocarps in particular are largely confined to South East Asian lowland rainforests, where they account for approximately 30% of the basal area (Aiba and Kitayama, 1999). Second, the islands of the Indo-Australian archipelago possess extensive coastal zones with hypersaline soils and halophytic vegetation, both known to release large amounts of CH_3Cl (Keppler; Ninja Röhlings, et al., 2020; Rhew; Miller, et al., 2000; Yokouchi; Saito, et al., 2007). Additional contributions from other sources, such as wood-rotting fungi (Watling and Harper, 1998) and soils, may also play a role.

In the coastal cluster (CST), CH_3Cl is also markedly enriched ($\Delta\text{CH}_3\text{Cl} = 131 \pm 106$ pptv) and displays pronounced variability. This variability follows a spatial pattern: samples collected over Tasmania show negligible enrichment, whereas those obtained at lower latitudes, over the north Queensland coast and New Ireland, exhibit substantially higher values. The highest mixing ratios

of up to 995 pptv were observed during RF22 (23:00–23:37 UTC 24 February 2024) while flying ~200 m above a coastal mangrove forest on the north-west Queensland coast between Aurukun and Mapoon. These observations underscore the importance of halophyte ecosystems, particularly at low latitudes, as significant CH_3Cl sources, as previously reported by Rhew; Whelan, et al. (2014).

3.3.2. Chloromethane distribution in the tropics and globally

To place our observations in the wider context of previous tropical CH_3Cl measurements, we merged the CAFE data with those from ten earlier aircraft campaigns (GABRIEL, HIPPO 1–5, ATom 1–4). The limitations of this comparison are: (i) the CAFE datasets represent only the austral summer (DJF) season, whereas HIPPO and ATom span all seasons, and (ii) data points over tropical continents are mainly concentrated in the southern hemisphere, while the northern hemisphere tropical landmasses are underrepresented.

Figure 3.7 a displays the longitude-altitude cross section of $\Delta\text{CH}_3\text{Cl}$ in the tropical band (30°N – 30°S). It illustrates that, although the overall atmospheric lifetime of CH_3Cl of 0.9 yr (WMO, 2018) is about equal to the number often given for the total inter-hemispheric mixing time of the atmosphere (~1 yr; Seinfeld and Pandis, 2016), it is not long enough for CH_3Cl to be equally distributed throughout the tropical troposphere. CH_3Cl enrichments are observed over the terrestrial source regions Australia/New Guinea, South America, in the outflow from West Africa, and over islands such as Hawaii (~ 200 – 205°) and Fiji (~ 177 – 178°), extending through the entire tropospheric column. Figure 3.7 c displays the lower-tropospheric (0–4 km) mixing ratios, confirming that the strongest enrichments are observed over tropical landmasses. These patterns demonstrate that CH_3Cl is a robust tracer of air masses of tropical terrestrial origin.

The vertical cross-section along latitude in Figure 3.7 b illustrates the global tropospheric distribution of CH_3Cl . As previously reported for surface and upper-tropospheric measurements (e.g., Khalil and Rasmussen, 1999; Umezawa; Baker; Brenninkmeijer, et al., 2015; Yokouchi; Noijiri, et al., 2000), mixing ratios are highest in the tropics and decrease poleward, confirming the tropics as the dominant source region. In the mid-latitudes, however, CH_3Cl exhibits a pronounced maximum in the mid-to-upper troposphere (7–11 km) while surface concentrations remain low, producing a positive vertical gradient. This feature, unique to CH_3Cl , has been documented in the Northern Hemisphere mid-latitudes (Umezawa; Baker; Brenninkmeijer, et al., 2015; Umezawa; Baker; Oram, et al., 2014) and is attributed to convective uplift of tropical-influenced air followed by meridional long-range transport in the upper troposphere. Because the rate of reaction of CH_3Cl with OH is strongly dependent on temperature, its lifetime aloft (~1 yr) is roughly an order of magnitude longer than in the lower troposphere (~1 month) (Herndon et al., 2001), making transport far more efficient at higher altitudes.

Our upper-tropospheric results (10–15 km; Figure 3.7 d) reveal extensive regions of CH_3Cl enrichment, often > 50 pptv and occasionally > 70 pptv, above tropical continents. This has important implications for the flux of CH_3Cl into the stratosphere. Numerous studies have shown that the

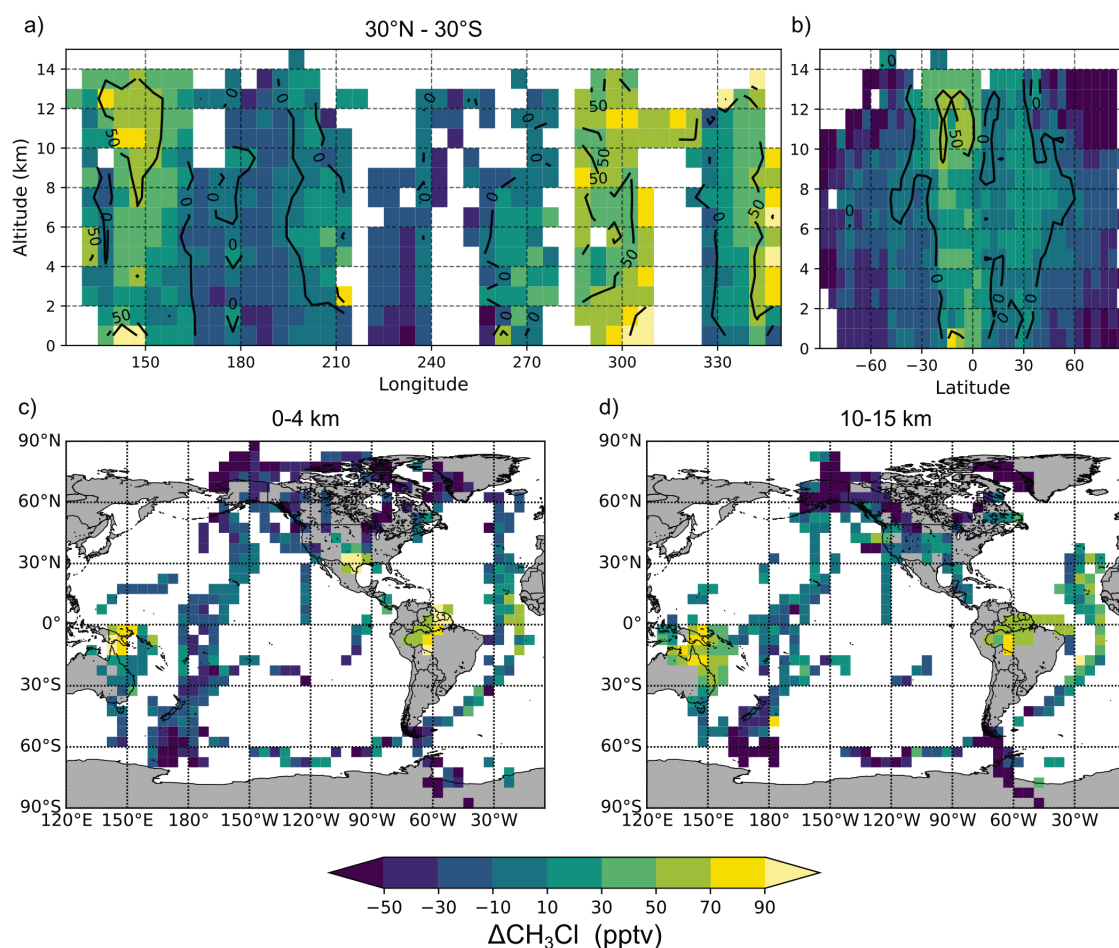


Figure 3.7.: Gridded mean chloromethane enrichment ($\Delta\text{CH}_3\text{Cl}$) relative to the tropical baseline derived from combined datasets of GABRIEL, HIPPO 1–5, ATom 1–4, and CAFE B/P. a) Longitudinal cross-section of the tropical band (30°N–30°S, 125°W–10°E) binned in 5° longitude x 1 km altitude intervals bins. b) Latitudinal cross-section binned in 5° latitude x 1 km altitude intervals. c) 5° x 5° grid-plot lower troposphere (0–4 km). d) 5° x 5° grid-plot upper troposphere (10–15 km).

TST mainly occurs via the TTL above the tropical western Pacific (e.g., Fueglistaler et al., 2004; Newell and Gould-Stewart, 1981), and a substantial portion of those air masses originates from the northern Australia/New Guinea region (Rex et al., 2014), where we observe strong upper tropospheric CH₃Cl enhancements. Consequently, surface mixing ratios measured at remote sites (e.g., MLO, RPB, SMO) likely underestimate the CH₃Cl entering the stratosphere in this region by roughly 10% during the Australian summer-monsoon season (Jan–Feb 2024).

3.4. Summary and conclusions

We present two comprehensive in-situ CH₃Cl datasets spanning 0.2–14 km, obtained during the CAFE-Brazil and CAFE-Pacific campaigns over the Amazon rainforest and the Indo Pacific Ocean. Over the Amazon, mixing ratios increase toward the surface, indicating a net ecosystem source, and exhibit a pronounced elevation in the upper troposphere at the main convective outflow level. In the CAFE-Pacific data, over-land samples show a strong lower tropospheric enrichment, whereas over-ocean measurements display decreasing mixing ratios with decreasing altitude, reflecting the greater influence of terrestrial CH₃Cl-rich air at higher levels. A fly-by of the Cape Grim/Kennaook station in Tasmania demonstrates excellent agreement between our airborne measurements and the ground-based observations.

Based on LCA of the lower-tropospheric data, five low-altitude clusters were selected and attributed to distinct source signatures within the PBL. To reduce the impact of seasonal and inter-annual variability, we expressed CH₃Cl levels as the enrichment $\Delta\text{CH}_3\text{Cl}$ relative to a tropical baseline derived from the northern hemisphere stations MLO and RPB and the southern hemisphere station SMO. The variability of $\Delta\text{CH}_3\text{Cl}$ across the five clusters associated with vegetation, BB, and marine sources is examined. A direct comparison between the pristine central Amazon cluster and the Papua New Guinea rainforest cluster reveals a fourfold higher CH₃Cl enrichment in the latter, revealing substantial spatial variability in CH₃Cl emissions across different rainforest ecosystems. Significant enrichments are also observed over coastal ecosystems, especially at low latitudes. Although BB influence is generally low in the CAFE datasets, one cluster above the Amazon exhibits moderately elevated BB tracers that coincide with increased CH₃Cl, whereas the marine-dominated cluster shows no significant enrichment.

Future work should aim at pinpointing the drivers of the observed CH₃Cl variability among rainforest ecosystems. Long-term, ground-based CH₃Cl flux measurements in the three major tropical rainforests (Amazon, Congo, South East Asia), combined with targeted experiments, are needed.

Finally, we combined the CAFE datasets with the results of ten previous airborne campaigns (GABRIEL, HIPPO 1-5, ATom 1-4) to examine the CH₃Cl distribution in the tropics and globally. The combined data confirm that the tropics are the dominant source region, but the longitudinal pattern across the tropical band is far from homogeneous: marked enrichments occur over continents and islands, consistent with the predominance of terrestrial emissions.

Our observations cover parts of the West Pacific sector, the source region of most troposphere-to-stratosphere transport (Fueglistaler et al., 2004; Rex et al., 2014). In the upper troposphere over this area, we find enrichments of 50–90 pptv with respect to the tropical baseline, suggesting that CH_3Cl mixing ratios entering the stratosphere may be $\sim 10\%$ higher than indicated by the measurements at remote sites from global monitoring networks. This finding is in line with earlier studies from the northern hemisphere upper troposphere (Umezawa; Baker; Brenninkmeijer, et al., 2015; Umezawa; Baker; Oram, et al., 2014) and has been highlighted in the most recent assessment of ozone depletion (WMO, 2022). Based on these results, we recommend expanding the existing monitoring network with additional stations in the outflow regions of all tropical continents to gain a more realistic representation of CH_3Cl .

Current global troposphere- and stratosphere-resolving chemistry-climate models such as EMAC prescribe a nearly uniform surface CH_3Cl mixing ratio, e.g., based on WMO (2007) observations (Meul et al., 2014) or future emission scenarios such as Hegglin et al. (2015)¹, thereby missing much of the longitudinal emission variability documented in this study. Since TST is strongly longitude-dependent (Fueglistaler et al., 2004; Rex et al., 2014), such homogeneous emissions are likely to underestimate the amount of CH_3Cl reaching the stratosphere. Consequently, the emission parametrisation should be refined to account for the spatial heterogeneity. We propose that future studies use the inventory of Xiao et al. (2010) as a starting point for developing a more realistic global CH_3Cl emission scheme.

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Author contributions. BEK, AG, JL, and JW designed the study. BEK, NT, FO, JB, AE, NW, AR, and MP conducted the measurements, while BEK, NT, AG, YY, and FO processed the data. AP prepared the FLEXPART simulations, with supervision from MV. BEK curated, analysed, and interpreted the data and wrote the manuscript with contributions from all co-authors.

¹Personal communication with Dr. Anna Martin, 17.03.2026.

Appendix

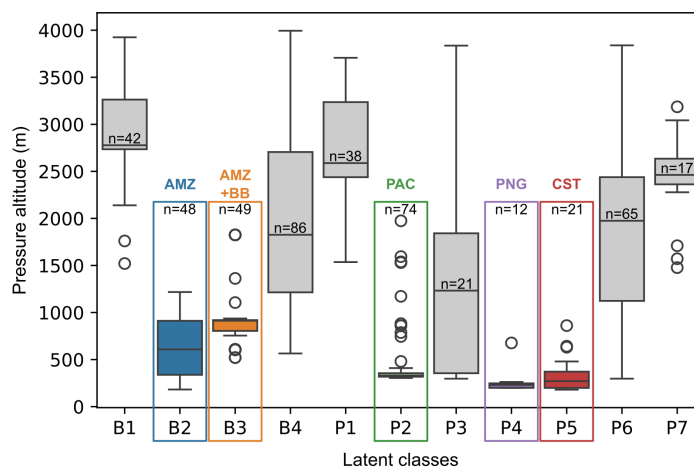


Figure 3.8.: Box-Whisker plot of the altitude distributions across all latent classes for CAFE-Brazil (B1–4) and CAFE-Pacific (P1–7). For each class the number of samples (n) is given. The classes that were selected for the source-attribution analysis in Section 3.3.1 are indicated with coloured boxes and labels.

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Chapter 4

Airborne measurements and model evaluation of dimethyl sulfide over the Amazon rainforest and Pacific Ocean

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Contribution to this chapter by Bianca E. Krumm: *Designed the study, led the GC-MS measurements and data processing, conducted data analysis and interpretation, and wrote the chapter.*

Abstract. Dimethyl sulfide (DMS) is the primary natural source of reduced sulfur to the atmosphere and, as a precursor to sulfate aerosols, indirectly influences Earth's climate. Despite its global significance, upper tropospheric DMS measurements, particularly in deep-convective outflows, remain limited. Here we present two airborne datasets of in-situ DMS observations spanning 0.3–14 km over the Amazon rainforest and eastern Indo-Pacific Ocean, obtained during the CAFE-Brazil and CAFE-Pacific campaigns. These measurements confirm an east-west decreasing concentration gradient in the Amazonian boundary layer and reveal frequent elevated DMS (up to 56 pptv) in marine upper tropospheric convective outflows. Model-observation comparisons were performed with the EMAC (ECHAM5/MESSy2 Atmospheric Chemistry) model using several marine and terrestrial emission inventories and three different convection parametrisations. The sole available global terrestrial inventory (Spiro et al., 1992) overestimates Amazonian DMS by approximately a factor of three. Among the marine DMS climatologies, the Hulswar et al. (2022) inventory provides the closest agreement with the measurements, although further refinements remain necessary. Of the convection schemes tested, the Tiedtke-Nordeng scheme best reproduces the observed vertical DMS profile. These results highlight the need for improved DMS emission parametrisations and more realistic convection schemes in global models to accurately represent the atmospheric sulfur cycle and its climatic impacts. The frequent occurrence of DMS in deep convective outflow underscores the importance of further investigations into its transport, oxidation at cold temperatures, and role in new particle formation in the upper troposphere and stratosphere.

4.1. Introduction

Dimethyl sulfide (DMS) is the dominant natural source of reduced sulfur to the Earth's atmosphere, emitted mainly from the oceans with smaller contributions from terrestrial vegetation and soils (M. O. Andreae, 1990). In the atmosphere, DMS is oxidised to secondary sulfate aerosol, which influences climate both directly—by scattering and absorbing radiation (R. Charlson et al., 1991; Myhre et al., 2013)—and indirectly, by acting as a precursor for cloud condensation nuclei (CCN) that modify cloud albedo (Ayers and Gras, 1991; R. J. Charlson et al., 1987; Fiddes et al., 2018; Korhonen et al., 2008). It has been proposed that this mechanism could provide a negative feedback to global warming: as oceans warm, DMS emissions would increase, leading to more reflective aerosol and clouds that cool the planet (R. J. Charlson et al., 1987; G. E. Shaw, 1983). Although anthropogenic fossil fuel combustion now dominates global sulfur emissions, natural sources still account for the bulk of atmospheric sulfate aerosol (Chin and Jacob, 1996). Therefore, a better understanding of the emission mechanisms and tropospheric distribution of natural sulfur sources, particularly DMS, and their representation in global climate models is essential for reducing uncertainties in indirect aerosol forcing (Carslaw et al., 2013).

DMS in surface waters is produced mainly by bacterial and algal degradation of dimethylsulfoniopropionate (DMSP), a phytoplankton metabolic product (Hopkins et al., 2023). Once dissolved, DMS can be (i) consumed by bacteria (Simó et al., 1998), (ii) photo-oxidised by UV radiation (Brimblecombe and Shooter, 1986; Galí; Devred, et al., 2023), or (iii) emitted to the atmosphere. Sea-air exchange of DMS (and other trace gases) is controlled by the concentration gradient across the air-sea interface and by the surface wind speed (Liss and Slater, 1974; Mesarchaki et al., 2015). In the marine boundary layer, DMS shows a characteristic diurnal pattern: photochemical loss by OH radicals and boundary layer dynamics produce a midday minimum, while night-time accumulation leads to an early morning maximum (M. O. Andreae and Raemdonck, 1983; Jackson et al., 2020; Nowak et al., 2001). Numerous shipborne campaigns have measured DMS over the world's oceans in the tropics (Williams; Holzinger, et al., 2004), mid-latitudes (Colomb et al., 2009), and the poles (Leck and Persson, 1996). In addition, aircraft campaigns have characterised the vertical distribution of DMS in the marine atmosphere (Conley et al., 2009; Marandino et al., 2013; Novak et al., 2021; Nowak et al., 2001; Thornton et al., 1997), yet observations of DMS that have been lofted to the upper troposphere (10–14 km) by deep convection remain scarce, because few research aircraft are capable of reaching those altitudes.

Terrestrial DMS emissions are dominated by biogenic sources, mainly from vegetation and soils with minor contributions from wetlands and salt marshes, and represent ~ 15% of the global DMS budget (Watts, 2000). Plant-derived DMS fluxes are controlled by photosynthetically active radiation (PAR) and temperature, and exhibit strong inter-species variability (Geng and Mu, 2006; Jardine et al., 2015; Vettikkat et al., 2020; Yonemura et al., 2005). Sulfur is an essential nutrient for plants, primarily taken up as sulfate through the roots (Droux, 2004), but it can also be absorbed from the atmosphere as gaseous sulfur compounds such as carbonyl sulfide (Li et al., 2024). It has been proposed that the emission of reduced sulfur gases serves as a mechanism for plants to dispose of excess sulfur (Rennenberg, 1984). However, the biochemical pathway responsible

for primary DMS production in higher plants remains unresolved. Soil- and leaf litter-derived emissions have also been reported and are linked to microbial respiration, with temperature and soil moisture as the main drivers (Jardine et al., 2015; Kesselmeier and Hubert, 2002; Pugliese et al., 2023; Staubes et al., 1989). Anthropogenic activities have also been identified as DMS sources: agricultural cultivation of crops (Fall et al., 1988; Kanda et al., 1992; Kanda et al., 1995; Loubet et al., 2022), and livestock farming (Filipy et al., 2006; Kammer et al., 2020; S. L. Shaw et al., 2007; Williams; N.-Y. Wang, et al., 1999). The contribution of these anthropogenic emissions to the terrestrial DMS budget is small, but they can be of importance locally (Williams; N.-Y. Wang, et al., 1999).

Ecosystem scale measurements in the Amazon rainforest reveal DMS mixing ratios reaching up to 80 pptv at canopy level, where a modest midday peak in the diurnal cycle above the canopy was reported (Jardine et al., 2015). Elevated mixing ratios ($\sim 5\text{--}10$ pptv) at canopy level have also been reported from temperate forests (Berresheim and Vulcan, 1992; Vermeuel et al., 2023). The lower-tropospheric DMS vertical distribution over the Amazon Basin was previously characterised by two aircraft campaigns in the 1980s (M. O. Andreae and T. W. Andreae, 1988; M. O. Andreae; Berresheim, et al., 1990), yet no observations exist for the upper troposphere.

Once emitted into the atmosphere, DMS undergoes complex oxidation pathways involving gas- and liquid-phase reactions with radicals such as hydroxyl (OH), bromine oxide (BrO), bromine (Br), chlorine (Cl), and nitrate (NO_3) (Barnes et al., 2006; Hoffmann et al., 2016), resulting in a global mean atmospheric lifetime of 1-2 days (Chen et al., 2018). These reactions generate, among other products, methanesulfonic acid (MSA) and sulfuric acid (H_2SO_4), both of which are low-volatility species that are involved in new particle formation and growth of sulfate aerosol (Rasmussen et al., 2022; Sipilä et al., 2010). DMS-derived sulfate aerosol particles constitute an important source of CCN in the marine atmosphere (Korhonen et al., 2008).

Accurate global modelling of DMS is essential for quantifying the Earth's radiative budget (Fiddes et al., 2018), yet it remains challenging for several reasons. First, the emission mechanisms are complex and highly variable in space and time. Although multiple global sea water DMS inventories have been produced using different approaches (Galí; Levasseur, et al., 2018; Hulswar et al., 2022; Kettle et al., 1999; Lana et al., 2011; W.-L. Wang et al., 2020; Zhou et al., 2024), capturing mesoscale variability is still difficult (Bell et al., 2021; Salignat et al., 2025). In contrast, for terrestrial emissions, only a single inventory (Spiro et al., 1992) exists, and it has scarcely been evaluated against measurements. Second, sea air exchange velocities differ among parametrisations, and this can dominate the emission uncertainty in some regions (Joge et al., 2024). Third, the atmospheric chemistry of DMS is still uncertain because oxidant concentrations, particularly BrO and dissolved OH in cloud droplets, are poorly constrained (Chen et al., 2018). Finally, shortcomings in convection parametrisations further affect model performance (Rybka and Tost, 2014), underscoring the need for systematic validation against observational datasets.

Here we present airborne, in-situ DMS measurements covering most of the tropospheric column (0.3–14 km) over the Amazon rainforest and the east Indo-Pacific Ocean during the Chemistry of the Air Field Experiment (CAFE) Brazil and CAFE-Pacific campaigns, respectively, aboard the High Altitude Long Range (HALO) research aircraft. As the majority of flight time was dedicated

to the upper troposphere and to sampling deep convective events, this dataset provides new insight into the vertical distribution of DMS, especially within rarely explored deep convective outflows. We also examine the spatial DMS patterns in both regions and compare them with the state-of-the-art global atmospheric chemistry model EMAC, focusing on how current marine and terrestrial emission climatologies represent DMS sources. Finally, we evaluate EMAC's ability to reproduce the observed vertical DMS distribution above the Pacific by testing three different global model convection parametrisations.

4.2. Methods

4.2.1. Instrumentation

Airborne in-situ measurements of dimethyl sulfide (DMS) were conducted with a custom-made Fast Gas Chromatography-Mass Spectrometer (Fast GC-MS) instrument called System for Organic Fast Identification Analysis (SOFIA) aboard the German research aircraft High Altitude Long Range (HALO). The custom-made system has been described in detail elsewhere (Bourtsoukidis et al., 2017), as well as its configuration within the CAFE payload aboard the High Altitude Long Range (HALO) aircraft (Voigt et al., 2022).

Briefly, ambient air was drawn through the Trace Gas Inlet (TGI, Enviroscope GmbH) and conveyed to the instrument via a heated PFA line (2 m, 0.6 cm o.d., 40°C) equipped with an ozone scrubber (Ernle et al., 2023). Within the inlet assembly, the air was compressed to standard pressure (1 atm) at a flow rate of 200 sccm. Blank samples were generated by thermal decomposition of VOCs over a platinum catalyst (Pt/Al₂O₃, 3.2 mm pellets, Sigma-Aldrich) at 350°C in the Zero-Air-Generator. A gravimetrically prepared Calibration Standard (~ 50 ppbv VOCs in N₂, 5% stated uncertainty, Apel Riemer Environmental Inc.) was diluted with zero air to prepare calibration samples. The inlet system was constructed entirely from uncoated stainless steel tubing (0.6 cm o.d.). The total residence time of air between the TGI and the sampling point was approximately 15 s.

The sample stream was drawn from the inlet system at 40 sccm and passed through a series of cold traps, where it was dried at -10°C, cryogenically pre-concentrated for 1 min at -160°C, and finally re-focused at -160°C before injection into the GC. VOCs were separated on a mid-polarity capillary column (10 m x 0.25 mm i.d., 1.40 µm film thickness, DB-624 UI, Agilent Technologies). The custom-made GC oven was programmed as follows: hold at 30°C during the first 50 s, ramp at 1.8°Cs⁻¹ to 200°C, then maintain 200°C until the end of the run after 144 s. After chromatographic separation, the VOCs were ionised by electron impact at -70 eV and detected with a quadrupole mass spectrometer (Agilent Technologies 5973 MSD) operating in selected ion monitoring (SIM) mode. The SIM method employed during the CAFE campaigns enabled the separation and quantification of >35 VOCs, including DMS, which eluted at 49.0 s (detected at $m/z = 62$). In this configuration, the instrument provided one data point every 3 minutes. 1860 airborne, ambient samples (equivalent to approx. 93 flight hours) were collected during CAFE-Brazil, and 1772 samples (approx. 89 flight hours) during CAFE-Pacific.

Full five-point calibrations were typically carried out on the ground before and after each research flight (RF). During flight, blank and calibration samples were measured at roughly hourly intervals to monitor the background signal and sensitivity.

Peak integration was carried out with the in-house MPIC-Chrom software (version 7) written in IGOR (Wavemetrics). During the data processing, we identified an interference caused by the water content of the samples, which affected the instrument's sensitivity. Consequently, this effect on the DMS signal was corrected by normalising to the area of the nearby CFC-113 peak (see Section 2.3.2 for details on the correction).

SOFIAs limit of detection (LOD) for DMS, defined as three times the standard deviation of the blank measurements, was 1.42 pptv during CAFE-Brazil and 1.63 pptv during CAFE-Pacific. The relative total uncertainty of DMS mixing ratios was $\sim 40\%$ for values between $3 \times \text{LOD}$ and $10 \times \text{LOD}$, and $\sim 20\%$ for values higher than $10 \times \text{LOD}$, while the precision was better than 5%. The aircraft's altitude and position, along with basic meteorological parameters were provided by the Basis HALO Measurement and Sensor System (BAHAMAS) (Giez et al., 2022).

4.2.2. EMAC model setup

Numeric simulations were performed with the ECHAM/MESSy Atmospheric Chemistry (EMAC) model, a numerical chemistry and climate simulation system that includes sub-models describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel; Kerkweg, et al., 2010). It uses the second version of the Modular Earth Submodel System (MESSy2) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5) (Roeckner et al., 2006)). The physics subroutines of the original ECHAM code have been modularised and reimplemented as MESSy submodels and have continuously been further developed. Only the spectral transform core, the flux-form semi-Lagrangian large-scale advection scheme, and the nudging routines for Newtonian relaxation remain from ECHAM. For the present study, we applied EMAC (MESSy version 2.55.0) in the T63L90MA-resolution, i.e., with a spherical truncation of T63 (corresponding to a quadratic Gaussian grid of approx. $1.8^\circ \times 1.8^\circ$ in latitude and longitude) with 90 vertical hybrid pressure levels up to 0.01 hPa. Gas phase and heterogeneous chemistry were represented by the Mainz Isoprene Mechanism (MIM1) within the MECCA submodel (Jöckel; Tost, et al., 2006; Pöschl et al., 2000; Sander et al., 2019). All reactions involving DMS are listed in Table 4.1. The configuration of the submodels follows the setup described in Kohl et al. (2023).

Following Jeuken et al. (1996), the tropospheric dynamics in the EMAC simulations are nudged toward the ERA5 meteorological reanalysis (Hersbach et al., 2020) from the European Centre for Medium-Range Weather Forecasts (ECMWF) to reproduce the observed day-to-day variability of tropospheric meteorology.

The simulations covered the period from January 01 2022 to January 31 2023 for CAFE-Brazil and from January 01 2023 through April 01 2024 for CAFE-Pacific, providing a full year for model

Table 4.1.: Second order rate coefficients of reactions involving DMS in the MIM1 atmospheric chemistry mechanism. T refers to the temperature in K, while $[O_2]$ stands for the oxygen concentration in cm^{-3} .

Reaction	Rate coeff. ($\text{cm}^3 \text{s}^{-1}$)	Reference
$\text{DMS} + \text{OH} \rightarrow \text{CH}_3\text{SO}_2 + \text{HCHO}$	$1.13 * 10^{-11} * e^{-253/T}$	Atkinson et al. (2004)
$\text{DMS} + \text{OH} \rightarrow \text{DMSO} + \text{HO}_2$	$\frac{1.0 * 10^{-39} * e^{5820/T} * [O_2]}{(1 + 5.0 * 10^{30} * e^{6280/T} * [O_2])}$	Atkinson et al. (2004)
$\text{DMS} + \text{NO}_3 \rightarrow \text{CH}_3\text{SO}_2 + \text{HNO}_3 + \text{HCHO} - \text{O}_3$	$1.9 * 10^{-13} * e^{520/T}$	Atkinson et al. (2004)
$\text{DMS} + \text{Cl} \rightarrow \text{CH}_3\text{SO}_2 + \text{HCl} + \text{HCHO}$	$3.3 * 10^{-10}$	Atkinson et al. (2004)
$\text{DMS} + \text{Br} \rightarrow \text{CH}_3\text{SO}_2 + \text{HBr} + \text{HCHO}$	$9.0 * 10^{-11} * e^{-2386/T}$	Jefferson et al. (1994)
$\text{DMS} + \text{BrO} \rightarrow \text{DMSO} + \text{Br}$	$4.4 * 10^{-13}$	Ingham et al. (1999)

Table 4.2.: List of performed Simulations for CAFE-Pacific.

Short Name	Marine Climatology	Terrestrial Climatology	Convection Scheme
H22 / T1	Hulswar et al. (2022)	Spiro et al. (1992)	Nordeng (1994) and Tiedtke (1989)
L11	Lana et al. (2011)	Spiro et al. (1992)	Nordeng (1994) and Tiedtke (1989)
W20	W.-L. Wang et al. (2020)	Spiro et al. (1992)	Nordeng (1994) and Tiedtke (1989)
EC	Hulswar et al. (2022)	Spiro et al. (1992)	ECMWF (Bechtold et al., 2004)
EM	Hulswar et al. (2022)	Spiro et al. (1992)	Emanuel and Živković-Rothman (1999)

spin-up in both model runs. For comparison with aircraft observations, model results sampled along the flight trajectories were extracted at 7.5-minute intervals (respective 10 minutes for CAFE-Pacific) using the S4D submodel (Jöckel; Kerkweg, et al., 2010). In addition, complete three-dimensional output fields were stored at hourly resolution.

Marine DMS emissions in the model are parametrised as a function of surface wind speed, temperature and sea-water DMS concentration, derived from a climatology, following Liss and Merlivat (1986). Three different sea-water DMS climatologies were evaluated in this study (Table 4.2). Terrestrial DMS emissions are derived directly from the Spiro et al. (1992) land-surface climatology, and sensitivity runs were performed with, without and with reduced terrestrial DMS emissions to assess their impact (Table 4.3).

Additional sensitivity experiments were performed to assess how the choice of convection parametrisation influences the simulated vertical distribution of DMS. Three convection schemes were employed: the EMAC default Tiedke-Nordeng formulation (Nordeng, 1994; Tiedtke, 1989), the ECMWF scheme (Bechtold et al., 2004), and the Emanuel and Živković-Rothman scheme (Emanuel and Živković-Rothman, 1999). Detailed descriptions of these convection schemes and their implementation in EMAC are provided by Tost et al. (2006) and references therein.

Table 4.3.: List of performed Simulations for CAFE-Brazil.

Short Name	Marine Climatology	Terrestrial Climatology	Convection Scheme
S92	Hulswar et al. (2022)	Spiro et al. (1992)	Nordeng (1994) and Tiedtke (1989)
noTER	Hulswar et al. (2022)	none	Nordeng (1994) and Tiedtke (1989)
rdS92	Hulswar et al. (2022)	0.39*Spiro et al. (1992)	Nordeng (1994) and Tiedtke (1989)

4.2.3. Satellite imagery

Aqua-MODIS ocean chlorophyll-a concentration data (OCI-Algorithm) was obtained via NASA's Ocean Color Earthdata (OB.DAAC) on November 11 2025. To obtain the campaign average of chlorophyll-a concentrations, five 8-day, 4-km spatial resolution rasters were averaged into a single map with an ESRI ArcGIS Pro raster cell average function, altogether spanning a period from January 17 to February 25 2024. Cloud top temperature (CTT) (Bureau Of Meteorology, 2024a) and cloud type (CT) (Bureau Of Meteorology, 2024b) data, at hourly temporal and $0.02^\circ \times 0.02^\circ$ spatial resolution, were obtained from the Himawari Geostationary Meteorological Satellite 8/9 and processed by the Australian Government Bureau Of Meteorology (2021).

4.3. Results and Discussion

4.3.1. DMS observations during the CAFE missions

The DMS measurements reported here were obtained aboard the HALO research aircraft during the Chemistry of the Atmosphere (CAFE) campaigns CAFE-Brazil (2022–2023), and CAFE-Pacific (2024).

The CAFE-Brazil campaign (Dec 2022–Jan 2023) operated from Manaus during the dry-to-wet transition. DMS was measured on 13 of the 16 research flights (RFs) over the Amazon Basin, providing the high vertical and spatial coverage shown in Figure 4.1. This mission aimed to investigate the atmospheric processing of biogenic rainforest emissions under conditions of strong convection and low biomass-burning activity (Machado et al., 2004; Tripathi et al., 2025). The CAFE-Pacific campaign (January–February 2024) took place during the Australian summer monsoon, a period characterised by high convective activity in the studied region (Pope et al., 2008). DMS was measured on 14 of the 18 RFs, sampling different regions of the east Indo-Pacific Ocean, including the Coral Sea, Bismarck Sea, Solomon Sea, and the Indo-Pacific Warm Pool, as well as continental air masses above Papua New Guinea and Australia (Figure 4.1).

Vertical and spatial distribution

Vertical profiles of DMS mixing ratios for the two campaigns are presented in Figure 4.2 a. In the lower troposphere (<1 km), the marine measurements are roughly an order of magnitude higher than those obtained over the Amazon rainforest, consistent with the predominance of marine sources in the global DMS budget (M. O. Andreae, 1990; Watts, 2000). In both environments, the mixing ratios decline approximately exponentially with altitude up to approx. 4 km, reflecting dilution by turbulent entrainment of cleaner air aloft and chemical loss (e.g., via reaction with OH). In the mid-troposphere (4–9 km), the median mixing ratios fall below the limit of detection (LOD), with only occasional elevated values that may result from mid-level detrainment. In the upper troposphere (9–14 km), the CAFE-Pacific data frequently exhibit enhanced DMS mixing

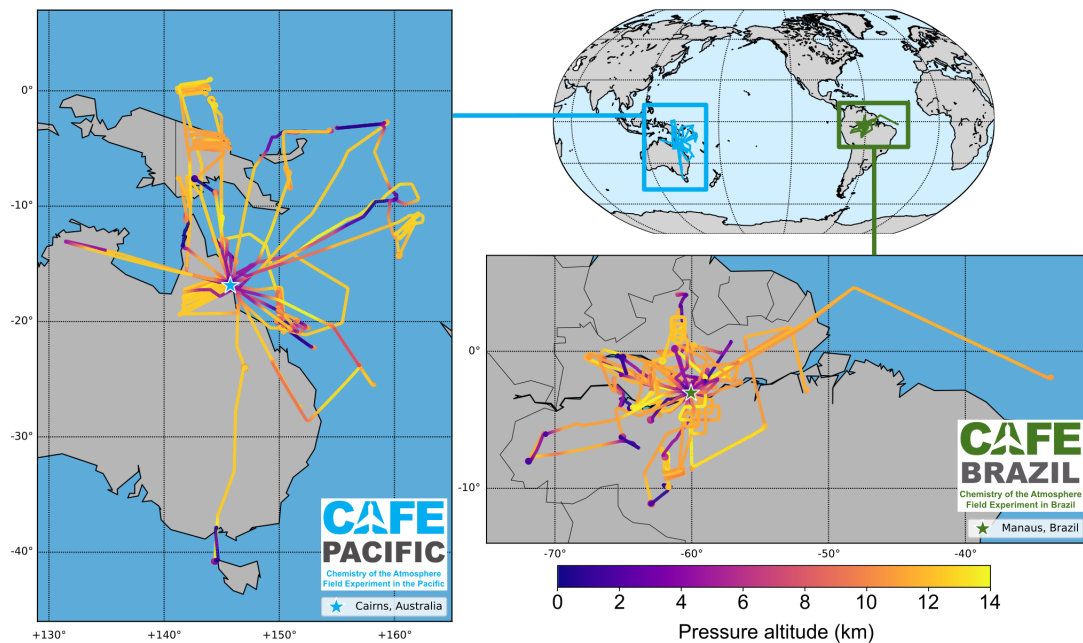


Figure 4.1.: Flight tracks of the HALO aircraft for the CAFE-Brazil (Dez 22–Jan 23) and CAFE-Pacific (Jan–Feb 2024) campaigns, colour coded by altitude. Only those flights for which DMS measurements from the SOFIA instrument are available are shown. Campaign logos were designed by Tanja Pallien.

ratios associated with deep-convective transport, whereas only a few points above the Amazon exceed the LOD despite the occurrence of multiple deep-convective events (Curtius et al., 2024; Tripathi et al., 2025).

Figure 4.2 b compares the CAFE-Brazil vertical profile with the only two previous investigations of DMS vertical distribution above the Amazon Basin to the best of the authors' knowledge. Both studies were part of the Atmospheric Boundary Layer Experiment (ABLE) missions conducted with NASA's Electra aircraft in the 1980s and were limited to the lower troposphere (<6 km). The first campaign (ABLE-2A) was carried out at the onset of the dry season (July–August 1985; M. O. Andreae and T. W. Andreae, 1988), and the second (ABLE-2B) during the wet season (April–May 1987; M. O. Andreae; Berresheim, et al., 1990). In each season, the reported DMS mixing ratios were very similar, with slightly lower values in the wet season. Their boundary layer measurements agree remarkably well with our median value of 8.2 pptv below 1 km. In the free troposphere, the ABLE values lie just below our LOD, consistent with the fact that most of our observations in this altitude range are also below the LOD. Canopy level measurements near Manaus reported diurnal mean mixing ratios of 14–22 pptv at 40 m altitude during December–January (Jardine et al., 2015), which likewise match the lower tropospheric values obtained in the present work. A comparable vertical distribution was observed above the Congolian rainforest during the DECAFE-88 campaign (Bingemer et al., 1992). Together, these independent datasets suggest that the DMS vertical profile reported here is consistent with previous observations in tropical rainforest environments over the past decades.

The spatial distribution of DMS mixing ratios below 1 km (Figure 4.3 a,b) shows a clear east-west

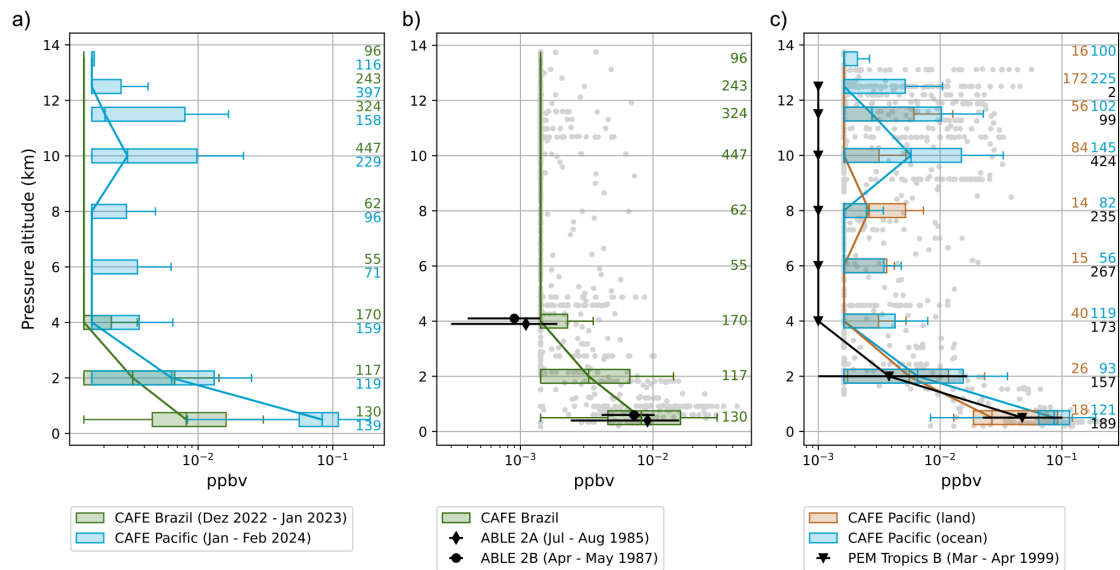


Figure 4.2.: Vertical distribution of DMS volume mixing ratios. Values that fell below the LOD were set to the LOD. Data above 11 km were grouped into 1 km altitude bins because of the higher sampling density, whereas all remaining data were placed in 2 km bins; the number of observations in each bin is indicated on the right-hand side of the panels. The distributions are shown as box and whisker plots (25th–75th percentile boxes, median line), and in panels b) and c), the individual measurements are plotted in light grey. a) comparison of the CAFE-Brazil and CAFE-Pacific campaigns. b) CAFE-Brazil data together with measurements from the ABL-2 campaign for two contrasting seasons (M. O. Andreae; Berresheim, et al., 1990). c) CAFE-Pacific data separated into over ocean and over-land points, the over ocean subset from the PEM-Tropics B campaign DC-8 measurements is overlaid for comparison (Colman et al., 2001; Simpson et al., 2001).

gradient, with the highest values east of Manaus, nearer to the Atlantic coast and a systematic decrease toward the western Amazon. A comparable gradient was reported from the ABLE campaigns (M. O. Andreae and T. W. Andreae, 1988). In the lower troposphere over the Amazon basin east of Manaus, the prevailing wind was easterly, and west of Manaus, north-easterly (Figure 4.3 b). The sampled air masses were transported from the Atlantic coast toward the interior, typically within at least 2–3 days (Pöhlker et al., 2019). DMS from marine or coastal salt marsh origin could therefore contribute to the elevated eastern concentrations, although the transport time from the coast to the study region slightly exceeds the lower tropospheric atmospheric lifetime of DMS with respect to OH of approx. 1–1.5 days (Albu et al., 2006). To quantify the potential contribution of long-range transported marine DMS, we performed an EMAC simulation with marine emissions only (noTER; see Table 4.3). The model predicts mixing ratios up to 7 pptv and a north-south gradient, which is far smaller than the observed east-west gradient of ~ 20 pptv (Figure 4.3 c). Consequently, the gradient is likely mainly driven by spatial variations in terrestrial DMS emissions, with contributions from marine sources. The pronounced east-west gradient across Manaus aligns with the gradient across recently identified Amazonian geoeological classes derived from floristic field data, satellite imagery, and climatic data, in which soil properties were found to be the primary driver (Tuomisto et al., 2019). This suggests that the Amazon rainforest may not be a uniform DMS source and that spatial variations in soil-related geoeological zones might influence DMS emissions.

The vertical profile for the CAFE-Pacific campaign, separated into over-land and over-ocean observations, is shown in Figure 4.2 c. Over-land, most measurements were obtained in the upper troposphere, with relatively few data points below 9 km. Furthermore, the lower tropospheric measurements over-land were primarily collected near the ocean and are likely influenced by marine emissions, making them unrepresentative of purely terrestrial conditions in the study region. In the upper troposphere over-land, DMS mixing ratios were generally below the LOD, consistent with the observations from CAFE-Brazil.

The over-ocean profile is compared in Figure 4.2 c with measurements from the Pacific Exploratory Mission (PEM) Tropics-B campaign aboard NASA's DC-8, which sampled the tropical Pacific during the wet season (March–April 1999) (Colman et al., 2001; Simpson et al., 2001). This dataset was selected because, among the available aircraft DMS measurements in marine regions, it provides the greatest overlap in region, season, and altitude range with our observations. Both profiles exhibit a comparable exponential decline of DMS mixing ratios with altitude in the lower troposphere. Our median values are slightly higher, likely reflecting the predominance of coastal sampling (e.g., above the biologically productive waters of the Great Barrier Reef), while PEM Tropics-B sampled more over open oligotrophic ocean waters. A pronounced discrepancy between the two datasets appears in the upper troposphere. During CAFE-Pacific, we repeatedly observed deep convectively transported DMS with mixing ratios up to 56 pptv between 9 and 14 km. In contrast, the PEM Tropics-B data at those altitudes, despite extensive sampling, never exceeded 5 pptv. The reasons for this discrepancy are not clear. One possible explanation is differences in flight planning, as our campaign specifically targeted regions where deep convection was expected. To date, only a limited number of in-situ measurements of similarly elevated

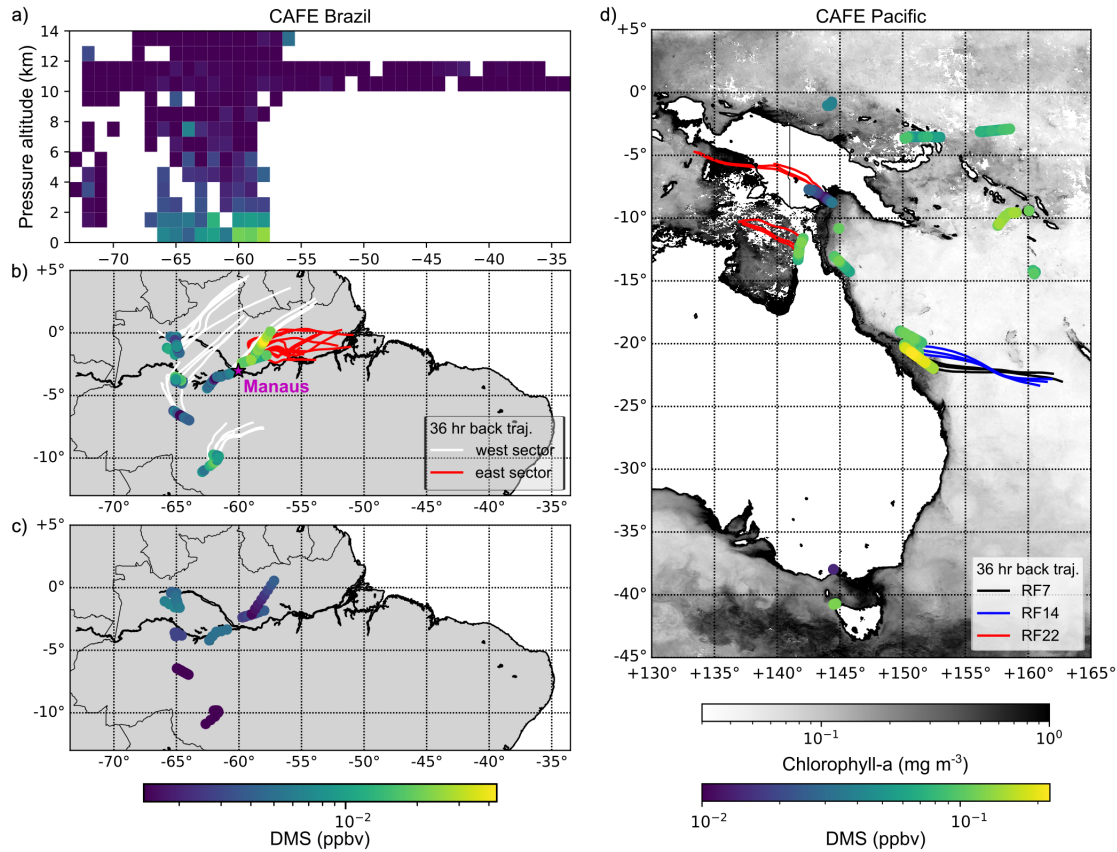


Figure 4.3.: Spatial distribution of observed and modelled DMS volume mixing ratios during both campaigns. a) Longitudinal cross section of the CAFE-Brazil observations, mean values in a $1^\circ \times 1$ km latitude-altitude grid. b) CAFE-Brazil observed DMS mixing ratios at altitudes <1 km. c) CAFE-Brazil modelled DMS mixing ratios (<1 km) with marine emissions only (noTER). The colour scale for panels a)–c) is shown on the left. d) CAFE-Pacific measurements at altitudes <0.5 km, with its colour scale indicated on the right. The data is overlaid on an Aqua MODIS chlorophyll-a concentration map (average for the campaign period). 36 Hours back trajectories of selected points along the flight tracks were generated with the HYSPLIT transport and dispersion modelling system (Stein et al., 2015). Values below the LOD were replaced with the LOD.

upper tropospheric DMS concentrations associated with convective uplift are available in the literature. Thornton et al. (1997) reported mixing ratios of up to 20 pptv (respectively 80 pptv during a typhoon) above 8.5 km altitude during the PEM West-A (September–October 1991) and B (February–March 1994) campaigns, which matches our observations. During the HIAPER Pole to Pole Observations (HIPPO) 2 campaign, elevated DMS levels around 100 pptv were found between 8–10 km (Marandino et al., 2013).

Figure 4.3 d displays the spatial distribution of DMS mixing ratios below 0.5 km during the CAFE-Pacific campaign. In the marine boundary layer (<1 km), the inter-quartile range (25–75 percentile) spans 65–115 pptv, with a median of 86 pptv. The highest value (223 ppt) was recorded during RF7 (January 21 2024, 12 h local time) at 0.35 km altitude above the Great Barrier Reef. By contrast, RF14 (February 15 2024, 12 h local) sampled the same altitude, location and time of day but observed markedly lower mixing ratios (~100 ppt). Our HYSPLIT back-trajectory analysis shows that the air masses sampled on both flights originated from similar regions of the Coral Sea. Although the tropical cyclone Kirrily was present in the Coral Sea during RF7 (see next section), its closest approach to the trajectory was more than 700 km away, making a direct impact on the measured DMS concentrations, e.g., via enhanced surface windspeeds, unlikely. The measured wind speed was slightly higher on RF7 (8–9 m s⁻¹) than on RF14 (6–7 m s⁻¹), which may account for part of the difference. Overall, DMS mixing ratios in the marine boundary layer (<0.5 km) show modest positive correlations with wind speed (Pearson $r = 0.43$) and the decadic logarithm of ocean chlorophyll-a concentrations (Pearson $r = 0.40$) at the sampling location.

During RF22, we sampled boundary layer air (~0.2 km) over mangrove and salt marsh habitats between Aurukun and Mapoon on the north west coast of Queensland. The airmasses were a mixture of local vegetation emissions (evidenced, e.g., by elevated isoprene levels) and a marine background, as they originated from the adjacent Gulf of Carpentaria. The mean DMS mixing ratio on this leg was 96 pptv, which falls well within the typical marine range and indicates that any contribution from the coastal wetlands was at most on the order of a few tens of pptv. This finding contrasts with the unusually large m/z 63 signal reported from a 1998 PTR-MS aircraft campaign over Surinam, which was interpreted as a DMS mixing ratio of 395 pptv in the forest boundary layer and attributed to strong emissions from coastal wetlands (Crutzen et al., 2000). The quadrupole mass spectrometer used in that study likely suffered from an interference at the DMS mass. In our extensive dataset, encompassing the Amazon rainforest with its numerous riverine wetlands, and the coastal wetlands of northern Australia, such elevated DMS concentrations are absent, indicating that intense DMS emissions from wetlands are either highly localised, episodic, or both.

In-situ observations of convective uplift into the upper troposphere

Although deep-convective transport of air masses was frequently observed over the Amazon rainforest (Curtius et al., 2024; Tripathi et al., 2025), the DMS measurements in those events were generally at or below the LOD, with only a few outliers. In contrast, elevated DMS mixing ratios

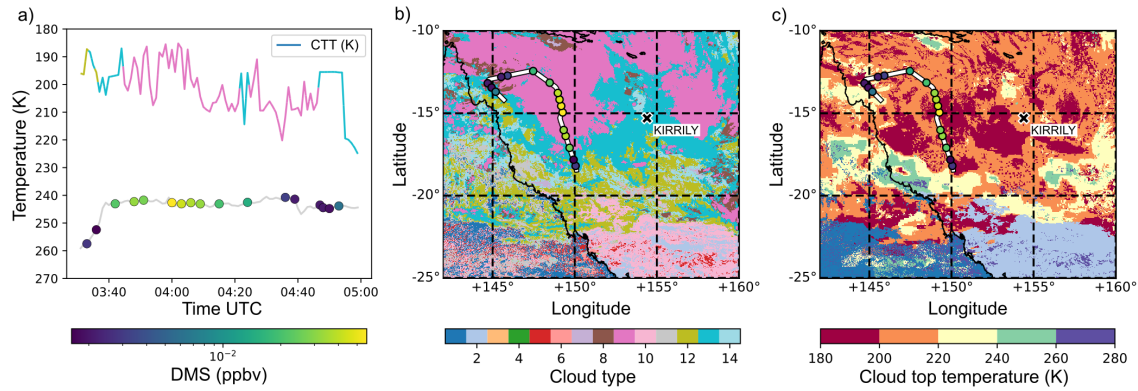


Figure 4.4.: Convective outflow observed during RF7 on January 21 2024. a) Time series of cloud-top temperature (CTT) colour-coded with the cloud type (CT) together with the DMS mixing ratios measured along the flight track. b) Flight track and DMS mixing ratios overlaid on the CT map. c) Flight track and DMS mixing ratios overlaid on the CTT map. CT and CTT data correspond to 05 UTC on January 21 2024. Cloud type legend: 1 = cloud free land; 2 = cloud free sea; 3 = snow over-land; 4 = sea ice; 5 = very low clouds; 6 = low clouds; 7 = mid level clouds; 8 = high opaque clouds; 9 = very high opaque clouds; 10 = fractional clouds; 11 = high semitransparent thin clouds; 12 = high semitransparent moderately thick clouds; 13 = high semitransparent thick clouds; 14 = high semitransparent clouds above low or medium clouds. Colours 1 and 2 of the CT map have been adopted to represent cloud-free land and sea of the CTT map. The position of tropical cyclone Kirrily, denoted by the black cross, was reproduced with permission from the Bureau of Meteorology, ©Commonwealth of Australia.

associated with deep convection were encountered repeatedly in the marine upper troposphere above the Pacific Ocean. Below, we describe two of those convective events in detail.

The first event was recorded during RF7 on January 21 2024 (Figure 4.4). While flying northward, HALO penetrated the upper-level (13–16 km) anvil that constituted the outflow cloud shield of a tropical depression, which intensified into Tropical Cyclone Kirrily over the following days. During the outflow passage, we measured elevated DMS mixing ratios, with a maximum of 56 pptv and decreasing quasi-exponentially across a swath of roughly 500 km until reaching the LOD. The highest DMS values were encountered within a very high, optically thick cloud deck, indicating that the aircraft was in close proximity to the convective core. Because the inflow region of the system was not sampled, we estimated the fraction of boundary layer DMS that reached the outflow by using the interquartile range of DMS mixing ratios observed below 1 km throughout the campaign (65–115 pptv) as bounding source values. This approach yields a transport efficiency of 49%–86% for the proportion of boundary layer DMS lofted to the upper tropospheric outflow of a tropical depression.

The second event occurred during RF10 on January 27–28 2024 as HALO flew from the Coral Sea towards the Indo-Pacific Warm Pool region (Figure 4.5). This area is characterised by extraordinarily low ozone concentrations in the upper troposphere, a consequence of non-electrified convection (Nussbaumer et al., 2025). The resulting scarcity of hydroxyl radicals prolongs the atmospheric lifetime of reactive trace gases such as DMS in this region (Kley et al., 1996; Rex et al., 2014). Between 22:00 and 22:30 UTC the aircraft traversed a small convective system and

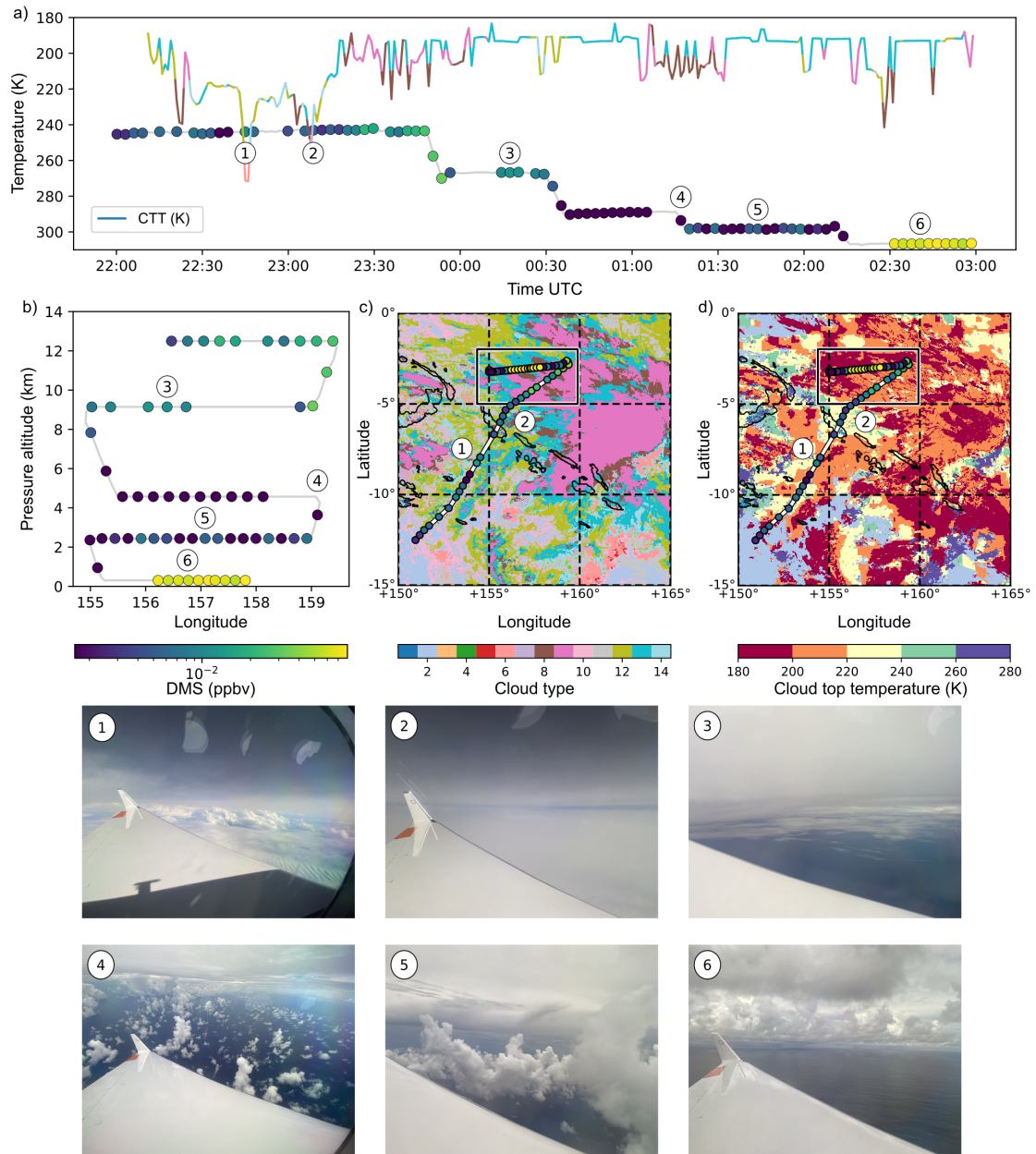


Figure 4.5.: Convective outflow observed during RF10 on January 27–28 2024. a), c), d) analogue to Figure 4.4; CT and CTT data correspond to 01 UTC on January 28 2024. b) Longitude-altitude cross section of DMS mixing ratios through the convective system; the area shown corresponds to the box indicated in panels c)–d). Photographs 1–6 illustrate the observed cloud layers along the profile.

measured elevated DMS, reaching a maximum of 7.5 pptv. After remaining above a cloud deck, HALO entered the cloud field of a mesoscale convective system at 23:15 UTC. Within this system DMS mixing ratios rose to as high as 33 pptv at altitudes of 9.5–12.5 km and persisted over a horizontal distance of roughly 300 km. The vertical structure of the system was sampled with five stacked flight legs at different altitudes (Figure 4.5 b). Below the anvil, several small cumulus “towers” were observed near 2.4 km altitude (pictures 4–6 in Figure 4.5), which exhibited slightly elevated DMS mixing ratios of around 7 pptv. DMS mixing ratios during the lowest flight level (0.3 km), which we consider representative of the boundary layer inflow, ranged from 54 to 92 pptv, implying a transport efficiency of 36–61% for the lofting of DMS into the upper tropospheric outflow.

These transport efficiencies are approximate estimates of the DMS that can be advected into the upper-tropospheric outflow of deep convective systems. Because the age of the studied outflows is uncertain and they may already have undergone some loss prior to being sampled, the values reported here should be interpreted as lower bounds on the true efficiencies.

The efficient transport of DMS from the marine boundary layer to the upper troposphere may have ramifications for sulfur chemistry both aloft in the troposphere and even in the stratosphere. In the upper troposphere, DMS serves as a precursor for H_2SO_4 and sulfate aerosol formation via oxidation to SO_2 and MSA. To date, only a limited number of studies have examined DMS chemistry at these altitudes and associated temperatures and pressures, the majority of investigations having focused on the marine boundary layer (e.g., Barnes et al., 2006; Hoffmann et al., 2016; Korhonen et al., 2008; Quinn and Bates, 2011; Sanchez et al., 2018). The present results therefore motivate dedicated chamber experiments and modelling efforts that address DMS chemistry under cold and dry upper tropospheric conditions. Moreover, because troposphere-stratosphere exchange is exceptionally efficient in the tropical western Pacific (Bonazzola and Haynes, 2004; Fueglistaler et al., 2004), deep convective transport of DMS in this region could provide a pathway for its injection into the stratosphere, where the gas can persist for long periods and contribute to the Junge layer of stratospheric aerosol, as previously proposed by Marandino et al. (2013).

Diurnal variations

Diurnal cycles of DMS mixing ratios in the planetary boundary layer have been documented for both environments. Over the Amazon rainforest, DMS exhibits a modest midday maximum that coincides with a peak in photosynthetic available light (PAR) and temperature (Jardine et al., 2015). In contrast, marine boundary layer DMS concentrations increase overnight and display a midday minimum, reflecting the strongest photochemical loss during daylight hours (M. O. Andreae and Raemdonck, 1983; Jackson et al., 2020; Nowak et al., 2001).

Here we present, for the first time, the diurnal distribution of DMS mixing ratios throughout the entire tropospheric column for the CAFE-Brazil and CAFE-Pacific campaigns (Figure 4.6). In both regions, the DMS vertical distribution follows the diurnal pattern of convective activity (Yang and Slingo, 2001). Over the rainforest, larger DMS fluxes are lofted into the free, and occasionally

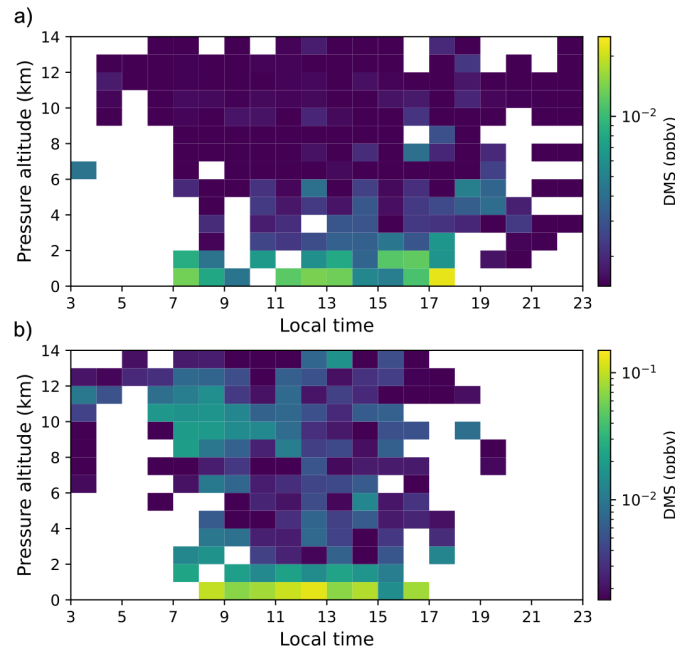


Figure 4.6.: Diurnal variation of DMS volume mixing ratios. a) CAFE-Brazil data, local time corresponds to AMT (UTC-0400). b) CAFE-Pacific over-ocean data, local time corresponds to AEST (UTC+1000). Both data sets are displayed as gridded mean values within 1 hr×1 km grid cells.

upper, troposphere in the afternoon, consistent with the afternoon peak in convection (Machado et al., 2004). Over the Pacific Ocean, upper tropospheric DMS concentrations peak in the morning, matching the typical late morning maximum in marine convection (Pope et al., 2008).

However, these diurnal profiles must be interpreted with caution. The dataset, especially in the upper troposphere, does not represent background conditions because the flights were deliberately targeted toward areas of intense convective activity.

4.3.2. Global model simulations

In this section, we compare the observational data with simulations of the state-of-the-art atmospheric chemistry model EMAC, with special emphasis on the representation of DMS sources and vertical transport.

Marine DMS emissions

For the CAFE-Pacific campaign, we performed EMAC simulations with three marine seawater DMS climatologies. Lana et al. (2011) (L11) provides an observation-based interpolation of seawater DMS concentrations within biogeographic provinces and has been the standard inventory in global models for the past decade. Hulswar et al. (2022) (H22) is an updated version of L11 that incorporates newer observations and refined interpolation methods. W.-L. Wang et al. (2020) (W20) employs a parameterisation derived from an artificial neural network analysis that links seawater

DMS to environmental proxies such as chlorophyll a, nutrients, sea-surface temperature, and other factors. These three climatologies were used to evaluate how well the simulated boundary layer (<0.5 km) DMS fields agree with our observations.

The corresponding correlations and the spatial distribution of the model-to-observation ratios are shown in Figure 4.7, and for each correlation we report the coefficient of determination (R^2), the median model-to-observation ratio (M/O), and the percentage of points that lie within a factor of 2 of the observations (PF2). In the boundary layer, the L11 simulation overestimates DMS by an average of 43% relative to our measurements and shows essentially no correlation with the observations (Figure 4.7 a). The bias is especially large over the Bismarck Sea and north of Papua New Guinea (Figure 4.7 d). The H22 simulation on average gives a close match with the measured values ($M/O \approx 1$) and reproduces the observed variability best among the tested climatologies ($R^2 = 0.228$). In contrast, the W20 simulation underestimates DMS by about 34% on average and explains less of the observed variability ($R^2 = 0.141$). These results demonstrate that the updates from L11 to H22 substantially improve the representation of seawater DMS, making H22 the most suitable choice for the season and region examined. Consequently, we adopt the H22 climatology for marine DMS emissions in our CAFE-Brazil simulations.

Terrestrial DMS emissions

For the CAFE-Brazil campaign, we ran a simulation using the sole terrestrial DMS inventory available in the literature (Spiro et al., 1992) (S92). The monthly fixed climatological emissions do not reproduce any of the observed variability (Figure 4.8 b) and overestimate boundary layer DMS (<1 km) by roughly a factor of 2.7, which propagates into an excess throughout the entire tropospheric column (Figure 4.8 a). To quantify the contribution of terrestrial emissions to the total DMS, we performed an additional simulation in which terrestrial DMS emissions were switched off (noTER), allowing only long-range-transported marine DMS to enter the domain. In this “marine-only” simulation, the mixing ratios below 2 km are substantially lower than our observations, indicating that the bulk of DMS measured above the central Amazon originates from terrestrial sources. Scaling the S92 emissions by a factor of 0.39 (rdS92, Figure 4.8 c) brings the model-to-observation median ratio (M/O) close to unity but does not improve the coefficient of determination, indicating that a simple linear scaling cannot rectify the structural deficiencies of the inventory. These results demonstrate the need for a refined terrestrial DMS emission parameterisation, and the present observations can provide a benchmark for developing such a scheme.

Vertical profile

To evaluate how well EMAC reproduces the observed convection during the CAFE-Pacific campaign, we compare the measured and simulated vertical distributions of DMS mixing ratios (Figure 4.9 a–c). Three convection parameterisations were tested: the default Tiedtke-Nordeng

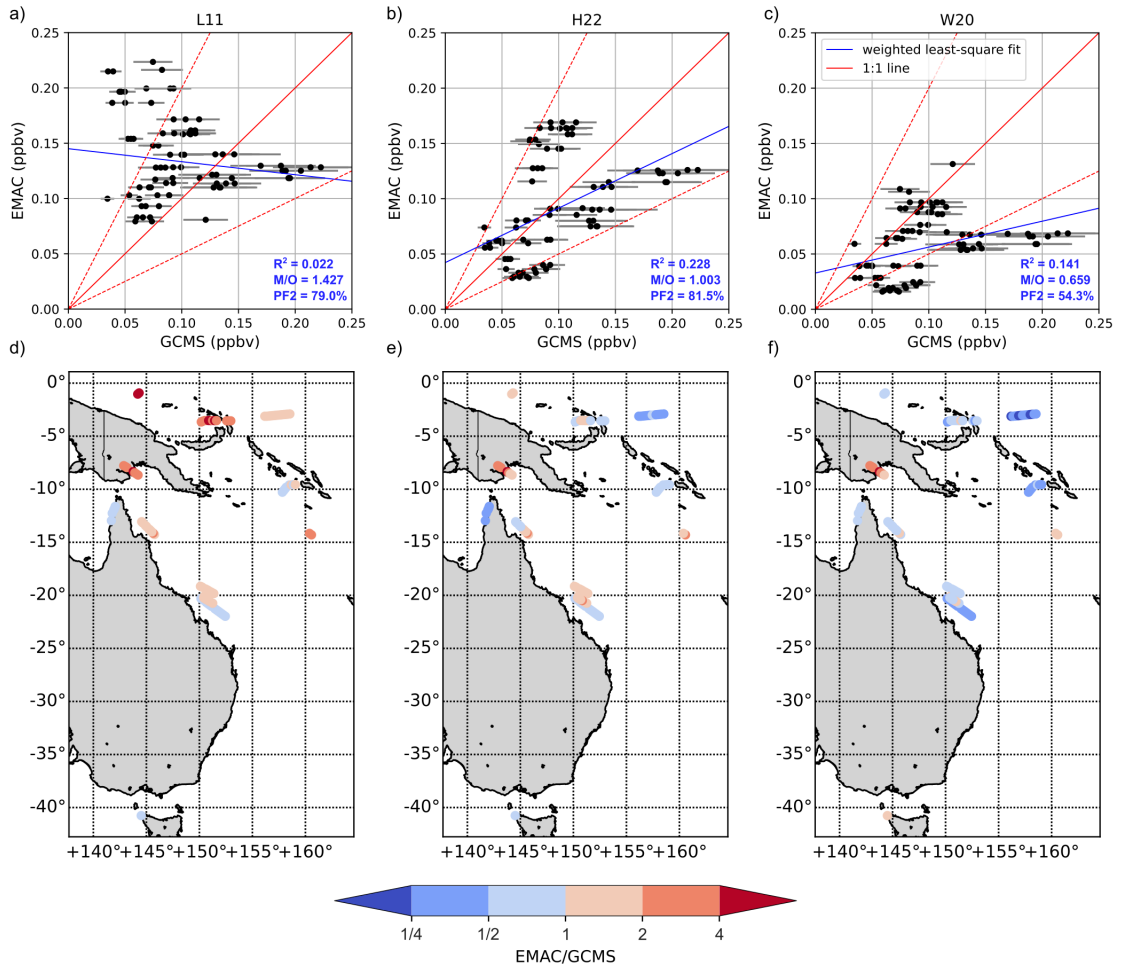


Figure 4.7.: Comparison of GC-MS DMS measurements with EMAC simulations for the marine boundary layer (<0.5 km). a)–c) Scatter plots of observed mixing ratios versus simulated mixing ratios for three emission climatologies: a) L11, b) H22, and c) W20. Data from RF22 was excluded because the sampled airmasses were strongly influenced by terrestrial emissions. The blue line in each panel is a weighted least squares fit, with weights equal to the inverse of the squared relative measurement uncertainties (error bars in grey). The coefficient of determination (R^2), the median model-to-observation ratio (M/O), and the percentage of points within a factor of 2 of the observation (PF2) are indicated. d)–f) Spatial maps of the model-to-observation ratio for the same climatologies.

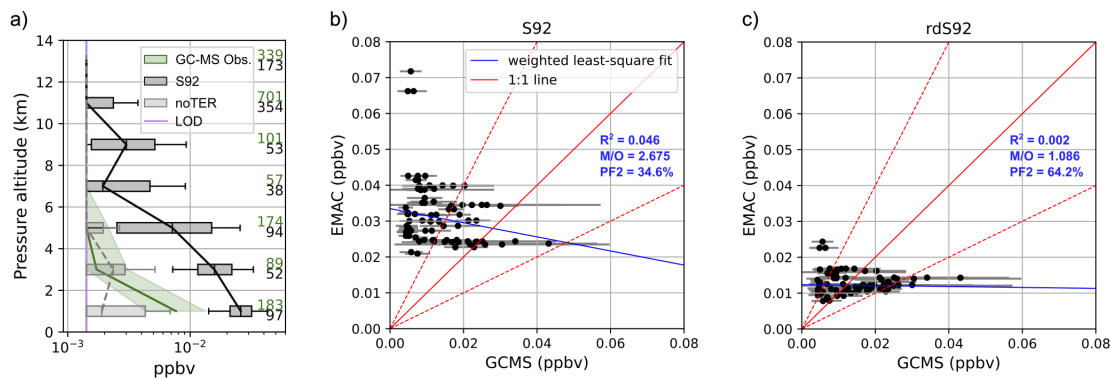


Figure 4.8.: Comparison of observed and simulated DMS mixing ratios for CAFE-Brazil. a) Vertical distribution, GC-MS observation in green, the simulation using the S92 climatology in black, and the noTER simulation with marine emissions only in grey. Values below the GC-MS LOD (illustrated as a purple line) have been replaced with the LOD in both observed and simulated DMS data. b)–c) Scatter plots of observed versus simulated (b) S92, c) rdS92) mixing ratios below 1 km. Same as Figure 7 a)–c).

scheme (T1), the ECMWF convection scheme (EC), and the Emanuel and Živković-Rothman scheme (EM) (see Table 4.2).

Both the T1 and EM simulations exhibit a discrepancy in the mid troposphere (2–6 km), with modelled mixing ratios more than one magnitude higher than the observations. This could be caused by an overestimation of mid-level detrainment in these schemes. In contrast, the EM scheme does not generate such a feature; however, it places the main convective outflow between 6 and 10 km, which is roughly 2 km lower than observed. Figure 4.9 d illustrates how the choice of convection scheme affects H_2SO_4 , a secondary oxidation product of DMS and other reduced sulfur species. In the mid-troposphere, the simulated H_2SO_4 concentrations differ by up to an order of magnitude among the three schemes, demonstrating that convection parametrisation also strongly influences secondary sulfur chemistry.

In the upper troposphere (9–14 km), the median DMS mixing ratios from all three simulations are lower than the measurements. This shortfall can partly be attributed to the $1.8^\circ \times 1.8^\circ$ resolution of EMAC, which smooths small-scale convective features. When the model data are interpolated to the flight track coordinates, the simulated convective outflow does not always intersect the aircraft trajectory, potentially shifting the apparent location of transported DMS relative to the aircraft observations. Figure 4.10 illustrates this offset for the T1 simulation, showing the modelled upper-tropospheric DMS fields over the entire region for the two case studies shown in Figures 4.4 and 4.5. The T1 and EM simulations reproduce the observed mixing ratio magnitudes but at slightly different locations, whereas the EC simulation predicts that considerably less DMS transport to the upper troposphere occurs and therefore it fails to match the observations.

Overall, the EMAC default Tiedtke-Nordeng scheme provides the closest agreement with our observations, although notable discrepancies remain in the mid-troposphere. This sensitivity analysis demonstrates that the choice of convection parametrisation influences the simulated DMS vertical profile, and also affects downstream sulfur chemistry in the model. Consequently,

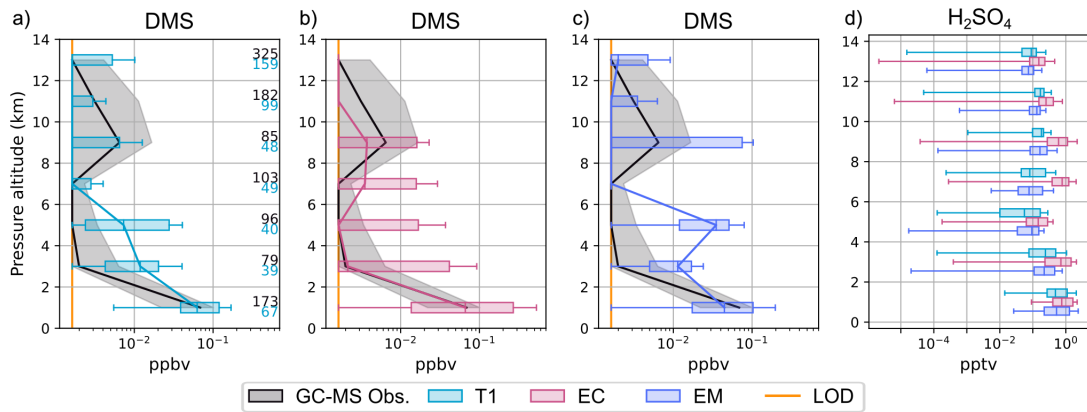


Figure 4.9.: Vertical distribution of DMS and sulfuric acid (H_2SO_4) from EMAC simulations using different convection parameterisations compared to the GC-MS over-ocean DMS observations: a) Tiedke-Nordeng scheme (T1), b) ECMWF scheme (EC), c) Emanuel and Živković-Rothman scheme (EM). The solid lines correspond to the median in each altitude bin; the grey area indicates the 25th–75th percentile range of the observations. Values below the LOD were set to the LOD for both observed and simulated DMS data to facilitate direct comparison. d) Simulated H_2SO_4 for all three convection schemes. Data are binned in 2 km intervals, and the number of observations (black) and respective simulations (blue) in each altitude bin are given on the right side of panel a).

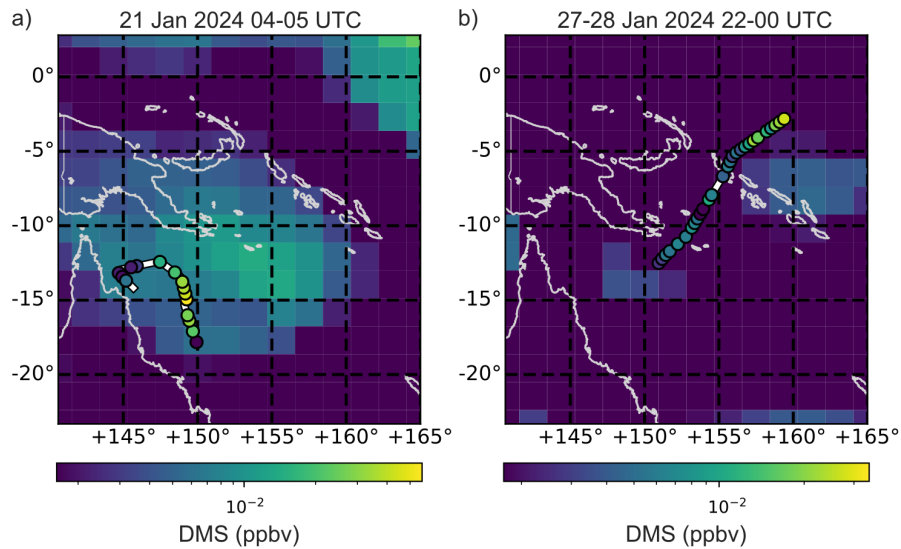


Figure 4.10.: Upper tropospheric DMS mixing ratios (12–14 km) measured during CAFE Pacific plotted on top of the corresponding gridded maximum values from the EMAC simulations for the same time period and altitude range. a) Flight segment of RF7 (see also Figure 4.4); b) flight segment of RF10 (see also Figure 4.5). Measurements below the LOD have been replaced with the LOD. Simulations are binned into $1.875^\circ \times 1.875^\circ$ intervals. Please note that both panels have their own colour bars indicated below.

the results underscore the need to re-evaluate and improve convection parametrisations in global models to obtain a more realistic representation of DMS transport and its climatic impacts.

4.4. Conclusions

In this study, we present airborne, in situ measurements of DMS from the CAFE-Brazil and CAFE-Pacific campaigns that span the tropospheric column from 0.3 km to 14 km over the Amazon rainforest and the eastern Indo Pacific Ocean. The boundary layer mixing ratios and the vertical profile of DMS in the lower troposphere are consistent with earlier gas chromatographic observations above tropical rainforest (M. O. Andreae and T. W. Andreae, 1988; M. O. Andreae; Berresheim, et al., 1990). In the upper troposphere, DMS was generally below the LOD in deep convectively up-drafted air masses above the Amazon Basin. The boundary layer data confirm the existence of a terrestrial source and the previously reported east-west gradient, which may be linked to a geocological gradient rather than to transport of marine DMS.

The vertical profile of DMS in the lower and mid-troposphere over the eastern Indo Pacific Ocean agrees well with previous measurements, for example, those measured aboard the DC-8 during the PEM Tropics-B campaign. In the upper troposphere (9-14 km), we frequently observed elevated DMS in deep convective outflows, reaching up to 56 pptv, a phenomenon that has been previously observed only rarely (Marandino et al., 2013; Thornton et al., 1997). These observations highlight the need for further research on the fate of lofted DMS and its role in new particle formation at low temperatures and pressures typical of the upper troposphere and stratosphere.

For the season and region sampled during the CAFE-Pacific campaign, the marine emission inventory of Hulswar et al. (2022) provides the most accurate simulated DMS mixing ratios, although further refinements are necessary. Among the convection parameterisations tested, the Tiedtke-Nordeng scheme (Nordeng, 1994; Tiedtke, 1989) yields the closest agreement with the observed vertical distribution, although it overestimates mixing ratios in the mid-troposphere. In the upper troposphere, the simulated lofted DMS mixing ratios match the observed magnitudes, but the model often predicts the updrafts slightly displaced from the aircraft trajectory.

Comparison of EMAC simulations that employ the terrestrial DMS inventory of Spiro et al. (1992) with the CAFE-Brazil shows that this climatology overestimates Amazon rainforest emissions by roughly a factor of three. Although the oceanic source dominates the global DMS budget and terrestrial emissions contribute only a minor fraction, such an overestimate can produce a regional excess of DMS throughout the troposphere, with potential consequences for regional sulfur chemistry. Our work, therefore, motivates the development of a refined parameterisation for terrestrial DMS emissions in the EMAC model. Future work should focus on improving the understanding of terrestrial, particularly plant-derived, DMS sources and obtaining additional atmospheric observations in continental, forested regions.

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Author contributions. BEK, JL, and JW designed the study. BEK conducted the measurements and processed the flight data, with contributions from JB and AG. MK and AM prepared the EMAC simulations, with supervision from AP. MH retrieved and processed the satellite data. BEK analysed and interpreted the data and wrote the manuscript with contributions from all co-authors.

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Chapter 5

Impacts of convection, chemistry, and forest clearing on biogenic volatile organic compounds over the Amazon

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Abstract. The Amazon rainforest is the largest source of biogenic volatile organic compounds (BVOCs) to the atmosphere. To understand the distribution and chemistry of BVOCs, airborne and ground-based measurements of BVOCs are conducted over the Amazon rainforest in the CAFE-Brazil campaign (December 2022–January 2023), including diel (24-hour) profiles between 0.3–14 km for isoprene, its oxidation products, and total monoterpenes. Although daytime deep convective transport of BVOCs is rendered ineffective by photochemical loss, nocturnal deep-convection exports considerable BVOC quantities to high altitudes, extending the chemical influence of the rainforest to the upper troposphere, and priming it for rapid organic photochemistry and particle formation at dawn. After contrasting pristine and deforested areas, a BVOC sensitivity analysis is performed using a chemistry-climate model. Here we show that reducing BVOC emissions, decreased upper tropospheric ozone, increased lower tropospheric hydroxyl radicals, shortened the methane lifetime, with the net effect of enhancing climate warming through ozone and aerosols.

5.1. Introduction

Emissions of biogenic volatile organic compound (BVOC) from the Amazon rainforest occur through diverse processes such as photosynthesis, respiration, and stress responses of the vegetation, but also from microbial activities in the forest soil (Edtbauer et al., 2021; Guenther et al., 2012; Hewitt, 1999; Laothawornkitkul et al., 2009; Pfannerstill et al., 2018; Pugliese et al., 2023). The main primary BVOC emissions are isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) with estimated Amazonian emissions of 150 Tg y^{-1} and 60 Tg y^{-1} , respectively (H. Wang et al., 2024). Once released, BVOCs are oxidized rapidly by OH radicals, ozone (O_3), and, to a lesser extent, NO_3 radicals, into multiple secondary volatile oxidized products and aerosol particles. Therefore, BVOC emissions can influence the atmospheric oxidation capacity, the radiative budget, and regional precipitation by generating secondary organic aerosols and cloud condensation nuclei, respectively (Atkinson, 2000; Lelieveld; Butler, et al., 2008; Machado; Unfer, et al., 2024). Due to the short atmospheric lifetimes of most BVOCs (minutes–hours), their influence is generally thought to be primarily confined to the boundary layer. Indeed, a strong concentration gradient has been observed by day at the entrainment zone between the top of the planetary boundary layer (0–2.5 km) and the free tropical troposphere (2.5–18 km) (Williams et al., 2001). Nevertheless, late afternoon shallow cumulus lift BVOC emissions to around 3 km before the onset of the nocturnal boundary layer at 100–200 m, which strands them aloft overnight in the so-called residual layer (Henkes et al., 2021). Here, they can persist since the photochemically generated OH radicals that initiate oxidation by day are negligible at night, and their reaction with O_3 is relatively slow. However, frequent deep convection events impact the entire Amazon region, which can potentially transport boundary layer and residual layer air up to high altitudes within 0.5–2 hours (Bardakov; Thornton; Riipinen, et al., 2021; Chatfield and Crutzen, 1984). Substantial nocturnal vertical transport to mid-altitudes (6–8 km) has been proposed based on model and satellite data assessments of aerosol distributions, although this has not been confirmed with in-situ data (Palmer et al., 2022). A recent case study from the same Chemistry of the Atmosphere Field Experiment, Brazil (CAFE-Brazil) campaign and associated modeling have shown that prodigious particle production occurs just after dawn at much higher altitudes (12–14 km) and is related to the oxidation of isoprene (Bardakov; Thornton; Ekman, et al., 2024; Curtius et al., 2024). Despite evidence for potentially profound atmospheric effects of BVOC on the oxidation capacity, particle production, and precipitation, a full spatial and temporal assessment of these BVOC compounds above their largest global terrestrial source is yet to be determined.

Globally, the emission of BVOCs from terrestrial vegetation is estimated to be $\sim 760 \text{ Tg C yr}^{-1}$, of which isoprene and monoterpene contributions are 70 % and 11 %, respectively (Guenther et al., 2012; Sindelarova et al., 2014). The Amazon accounts for 40 % of all BVOC emissions (Guenther et al., 2012) and is therefore a significant component of the global carbon cycle. In the past few decades, the Amazon rainforest has experienced significant changes driven by human activities, including deforestation, climate change, and natural disturbances like El-Niño. The Amazonian deforestation is still increasing due to human activities, notably by conversion of forested land for agriculture (cropland, pasture, and plantation) and logging (Durieux et al., 2003; Nobre

et al., 2016; Pendrill et al., 2019). Wright et al. (2017) reported that the dry season had been extended by deforestation in the southern Amazon, and Leite-Filho et al. (2021) suggested that rainfall reductions could be attributed to deforestation through analysis of historical records, thus also connecting BVOC emissions to the hydrological cycle. It is estimated that since the 1960s, approximately 20 % of the rainforest has been converted to farmland, resulting in a net release of CO₂. In addition to deforestation, climate change has emerged as another major driver of transformation in the Amazon. Global warming has increased tree mortality rates, forest fires and exacerbated drought or water stress across the Amazon rainforest (Brienen et al., 2015; Feldpausch et al., 2012). These factors may lead to variations in BVOC emissions, either increasing or decreasing them. To assess the full atmospheric effects of deforestation and climate change, the chemical and physical impacts of BVOC must be characterized and understood (Ganzeveld and Lelieveld, 2004; Weber; Archer-Nicholls, et al., 2022).

The main objective of the CAFE-Brazil campaign was to investigate the distribution and atmospheric processing of biogenic chemicals, as well as their role in upper tropospheric chemistry following convective transport over the Amazon rainforest during the dry to wet transition periods. Although a previous study reported the strong seasonal variation in the BVOC emissions at the surface over the Amazon rainforest (Yáñez-Serrano; Nölscher; Williams, et al., 2015), Machado; Laurent, et al. (2004) reported the strong intensity of convection during the dry-to-wet transition periods and the onset of the wet season. This campaign primarily focused on BVOC measurements over pristine areas to minimize the influence of urban plumes and biomass burning (which was less prevalent during this period) (Duncan et al., 2003; Gonzalez-Alonso et al., 2019; Kirchhoff et al., 1989). Previous studies have shown that urban plumes can significantly influence photochemistry and the oxidation capacity in the downwind forest regions (Nascimento et al., 2022; Shilling et al., 2018). However, the low median value of benzene (24 ppt) in the boundary layer measured near the limit of detection (LOD, 12 to 22 ppt for different flights) further indicates that urban emissions were not a significant source in the area covered during this study (Supplementary Figure 1).

By exploiting the extended range (8000 km), high altitude (14 km) and long flight duration (10 hours) capability of the High Altitude and Long-range (HALO) research aircraft, data coverage extended between 4.5°N to 11.5°S and 33° to 72°W, see Figure 5.1. By varying the take-off times of the 15 research flights, full 24-hour profiles of BVOC mixing ratios could be characterized at multiple altitudes from the campaign data. In addition to the airborne data, measurements from the Amazon Tall Tower Observatory (ATTO) ground site, situated in the pristine rainforest 150 km northeast of Manaus (2.1°S, 59.0°W), allowed 24-hour data coverage at 320 m over the two-month CAFE-Brazil campaign. The combination of airborne and ground-based datasets gives an unprecedented view of the vertical (0.3–14 km), temporal (24-hour profiles at multiple altitudes) and spatial distribution of BVOCs over the Amazon rainforest. Here, we focus on isoprene, its combined oxidation products methyl vinyl ketone, methacrolein, isoprene-hydroxy-hydroperoxides, (hereafter termed isoprene-OP), and monoterpenes. These data were measured using two near identical Proton-Transfer-Reaction Time Of Flight mass Spectrometers (PTR-TOF-MS), one at the ATTO ground site and one operated in the aircraft. The instruments were cross-calibrated and validated with a Gas chromatography-mass spectrometer (GC-MS) (see Section 5.3). A low-

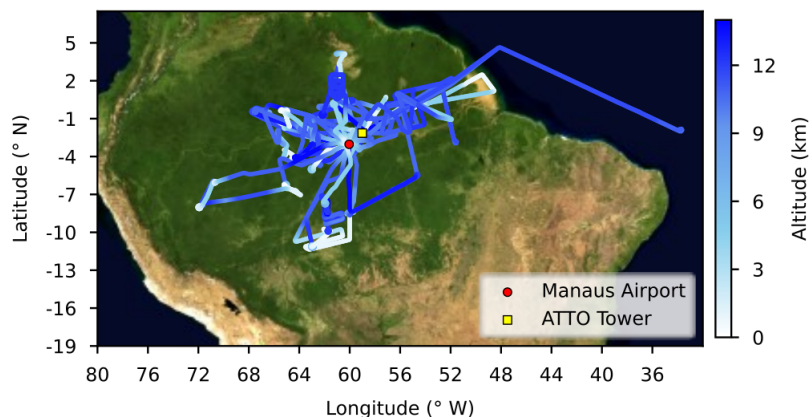


Figure 5.1.: The flight tracks during the CAFE-Brazil campaign over the Amazon rainforest. The flight track is color-coded by altitude. All flights were performed from manaus airport (red circle), Brazil (3°S, 60°W). The location of the Amazon Tall Tower Observatory (ATTO) ground-based forest site is marked with a yellow square. Satellite picture data in this figure obtained from <https://wvs.earthdata.nasa.gov>, NASA Worldview Snapshots.

altitude flight (900 m) contrasting pristine forested and deforested areas provided us an additional motivation to perform a BVOC sensitivity study using the global atmospheric chemistry model EMAC. This study aims to investigate the atmospheric impacts of the Amazon rainforest's current BVOC emissions and explores impacts of potential changes of these emissions. The model was then used to assess the atmospheric chemistry of BVOCs over the Amazon rainforest and the impact of changes associated with their modulation.

5.2. Result and discussion

5.2.1. Vertical profile of trace gases

The vertical profiles of isoprene, isoprene-OP, and monoterpenes for all flights are shown in Figure 5.2 and Supplementary Figure 2. The vertical distributions of these gases show similar characteristics, an approximately exponential decrease from 0.3 to 3 km in the lower troposphere (LT), a central mid-troposphere section (MT) from 3–9 km with consistently low mixing ratios, and then increased levels at higher altitudes in the upper troposphere (UT) peaking between 9 to 14 km. The higher mixing ratios at lower altitudes result from direct emissions (isoprene and monoterpenes) by the rainforest ecosystem into the well-mixed boundary layer and subsequent rapid oxidation to isoprene-OP. The primary VOCs (isoprene and monoterpenes) declined more rapidly than isoprene-OP with increasing altitude in the LT, in accord with their respective reaction rates with OH. Within the LT, mixing ratios decrease rapidly with height through both turbulent mixing dilution from above and chemical loss (oxidation). The mean mixing ratios of isoprene (2.25 ± 1.35 ppbv) and monoterpenes (0.23 ± 0.14 ppbv) between 0.3 to 1 km are ~ 2.5 times higher

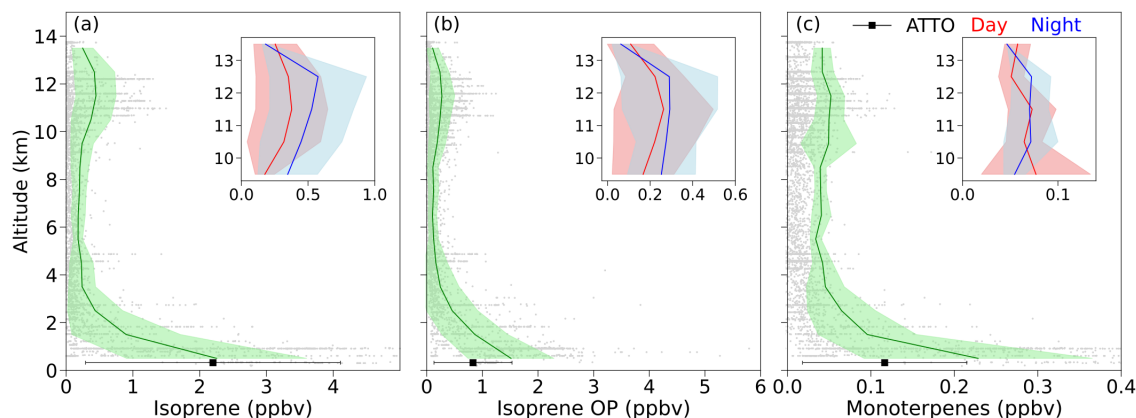


Figure 5.2.: Vertical profiles of biogenic volatile organic compounds (BVOCs) during the CAFE Brazil campaign. Vertical profiles of a) isoprene, b) isoprene oxidation products (OP) and c) monoterpenes during the CAFE Brazil campaign. Gray dots are 1 min-averaged data, while mean values are represented by a solid green line (1 km bin); the shaded light-green area shows the standard deviation. Note the mean value is calculated only for values above the limit of detection (LOD). The black square with error bars represents the mean value of Amazon Tall Tower Observatory (ATTO) data measured during the flight days. The inset plots show the mean vertical profiles of BVOCs at higher altitudes (9–14 km) during day- and nighttime in red and blue, respectively.

than the mean value measured between 1 to 2 km altitude. The isoprene-OP (1.51 ± 0.77 ppbv) decline less steeply to 0.87 ± 0.59 ppbv over the same height due to its secondary production from isoprene photooxidation during upward transport and subsequent advection aloft. In the mT, the mean mixing ratios of all BVOCs are very low, and the levels are generally constant except for a few outliers. Such short spike-like events may be due to outflow from occasional cloud convection to this height or mid-level detrainment from deeper convective systems (Williamson et al., 2019). However, the predominantly low mixing ratios in this altitude range suggest such events are rare.

The UT data showed elevated levels of isoprene, isoprene-OP and monoterpenes, with mixing ratios peaking between 11 and 12.5 km. The elevated mixing ratios of isoprene, isoprene-OP and monoterpenes in the UT provide clear evidence of extensive rapid transport to this altitude associated with deep convection. Supplementary Figure 5.3 depicts an example of the deep convection of isoprene in the UT for Flight 10. The aircraft sought and captured multiple deep convection outflow events in the UT during day and night, although mixing ratios for all three species at ~ 12.5 km were consistently higher at night (see inset Figure 5.2 and Supplementary Figure 4). The detrainment of trace gases from convective clouds is known to depend on various parameters, including the lapse rate minimum, which determines the height of the horizontal outflow of the air emerging from the convective cloud. Gettelman and Forster (2002) reported a lapse rate minimum height of 10–12 km for active convective (deep convection) regions in the tropics, in good agreement with the observed higher BVOCs at this altitude range presented here. In the present study, on average, approximately 20 % of the boundary layer isoprene reaches the UT during the convective outflow, while Bardakov; Thornton; Riipinen, et al. (2021) estimated

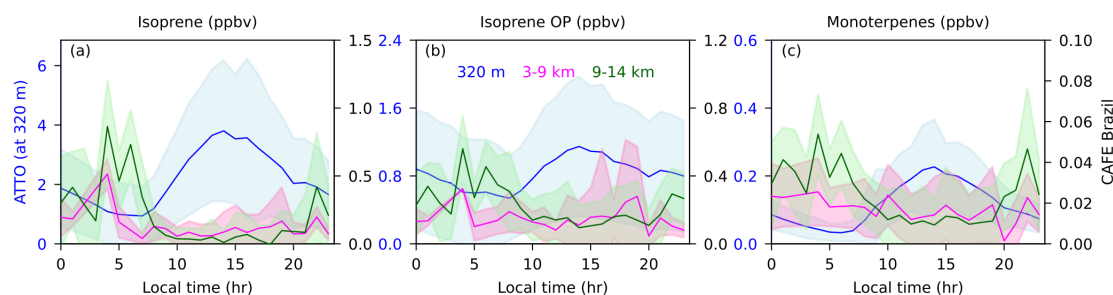


Figure 5.3.: Diel cycle of biogenic volatile organic compounds (BVOCs) for three altitudes over the Amazon rainforests. Diel cycles of a) isoprene, b) isoprene oxidation products (OP) and c) monoterpenes for three different altitude regimes of 320 m (left side y-axis) at Amazon Tall Tower Observatory (ATTO), 3–9 km, and 9–14 km (right side y-axis) during the CAFE-Brazil campaign.

from model calculations that $\sim 30\%$ of the boundary layer isoprene would be transported to the UT during an hour of convection. Jo et al. (2021) measured on average $\sim 25\%$ of isoprene from the boundary layer was transported to the UT during the SEAC4RS campaign over the southeastern US.

Relative to the boundary layer, the mixing ratios of isoprene, isoprene-OP and monoterpenes measured after deep convective transport are significantly lower. This can result from: oxidation reactions with OH and O_3 ; partial uptake into the cloud for the more soluble isoprene-OP; or dilution through the entrainment of mid-tropospheric air masses. These processes also contribute to the large variability of BVOC mixing ratios observed in the UT, and the stochastic nature of the convective events. Significantly, the nighttime profiles show a pronounced enhancement in the mixing ratios of isoprene (0.57 ± 0.36 ppbv), its oxidation product (0.29 ± 0.22 ppbv) and monoterpenes (0.053 ± 0.018 ppbv) in the UT between 12 to 13 km. During the daytime, the highest UT mean mixing ratios of isoprene (0.38 ± 0.27 ppbv), its OP (0.26 ± 0.22 ppbv) and monoterpenes (0.053 ± 0.02 ppbv) are observed between 11 to 12 km. Due to active photochemistry during daytime, the mean product/precursor ratio for isoprene-OP/isoprene (1.58 ± 1.09) is almost double that observed at nighttime (0.83 ± 0.62) (Supplementary Figure 5). At night, approximately 21 % and 27 % of the mean boundary layer values of isoprene and monoterpenes remain in the UT. In comparison, only 15 % of boundary layer isoprene-OP reached the UT, presumably due to in-cloud losses associated with its higher solubility and possible subsequent enhanced removal through in-cloud aqueous oxidation chemistry (Y. Li et al., 2017). X. Wang et al. (2021) investigated the ozonolysis of methyl vinyl ketone (MVK) and methacrolein (MACR) at the air-water interface, and observed that interfacial water molecules act as a catalyzer for the reaction between MVK and O_3 . Thereby, the primary isoprene oxidation products (MVK and MACR) can potentially undergo aqueous phase chemistry to produce further even more soluble carbonyl compounds, including oxalate, glyoxal, and methylglyoxal (Ervens et al., 2011; Y. Li et al., 2017; X. Wang et al., 2021). Our results support the notion that isoprene-OP is preferentially removed in convection relative to isoprene, and the more soluble second-generation oxidation products were not observed at high altitudes. During the daytime, the monoterpenes reaching the UT constitute 23 % of the boundary

layer values. These values are comparable to, but higher than, the convectively transported isoprene, which was 17 % of its boundary layer value. The loss of monoterpenes during day and night during transport from the boundary layer to UT is, therefore, also lower than that of isoprene. This can be due to the slower reaction rate with OH compared to isoprene and the tendency for the reaction rates of some monoterpenes with O₃ to decrease under low-temperature conditions (Gaona-Colmán et al., 2016; Sun et al., 2011) in the UT.

From the measurements presented here, it is clear that elevated levels of the surface emitted primary BVOCs (isoprene and monoterpenes) and their photochemical products are present in the Amazonian UT (9-13 km). This is important because the oxidation of these species takes place in the UT, where low temperature (~60°C), low pressure (200 mbar), and limited particle surface area for condensation create favorable conditions for new particle formation. Curtius et al. (2024) have reported extremely high particle production rates for a convective system, and the NASA Atmospheric Tomography (ATom) mission have reported unexplained high particle numbers emerging from the Amazon region (Kupc et al., 2020; Williamson et al., 2019; Zha et al., 2024). It should be noted that in time, a fraction of these newly formed particles can grow into larger sizes through coagulation and condensation and generate cloud condensation nuclei.

5.2.2. Diel variations

A remarkable feature of this dataset is that it allows investigation of the diel (24-hour) variation of the three selected species at multiple altitudes, namely in the Lower Troposphere (LT), middle troposphere, and Upper Troposphere (UT). The diel variations of isoprene, isoprene-OP, and monoterpenes at three altitude regimes of 320 m, 3-9 km, and 9-14 km are shown in Figure 5.3 and Supplementary Figure 6. The ATTO data, measured at 320 m during the flight days was used to determine a diel (24-hour) variation at low altitudes. In the lowest altitude regions, all presented BVOCs exhibit strong diurnal variations with peak mixing ratios of isoprene and monoterpenes measured in the afternoon (12:00–16:00), coinciding with the highest solar radiation and temperature. This is consistent with fresh biogenic emissions entering the well-mixed boundary layer, both from photosynthetically driven de-novo emissions and temperature-driven release from storage pools with the plants. Similar temporal patterns were observed for mixing ratios of isoprene-OP, indicating its rapid formation through the photochemical oxidation of isoprene by OH. Estimates of OH radical concentrations at this site indicate that they also peak between 14:00 and 15:00 (Ringsdorf et al., 2023). High secondary production of isoprene-OP at this time causes a slower decline of isoprene-OP than the precursor isoprene. For the measurements at 320 m, the lowest values of BVOCs occur in the early morning (04:00-06:00). In the middle troposphere, we observe substantially lower values for all three species, with a modest peak in isoprene visible at 04:00, while isoprene-OP shows peaks both at 04:00 and later and with more variability between 15:00-19:00 local time. The early morning peaks may be associated with the re-assimilation of the residual layer that is left isolated aloft when the nocturnal boundary layer forms lower down. The levels of isoprene and monoterpenes are very low during the daytime in the middle troposphere. This is consistent with model predictions for the altitude of maximum

OH being around 3-4 km (Lelieveld; Gromov, et al., 2016; M. Li et al., 2018) and, therefore, efficient loss through oxidation during daytime. The same processes are responsible for the late afternoon elevated OP.

Most interestingly, a diel cycle is also observed in the UT (9-14 km), but in contrast with the near-surface values which peaked between 14:00-15:00, the high-altitude maxima occur shortly before dawn between 03:00-06:00. It is important to note that deep convection events were widespread and frequent throughout the Amazon basin both by day and night (Supplementary Figure 7). Within such convection, air from the boundary and residual layers may be transported rapidly to higher altitudes on timescales of 0.5-2 hours. However, the atmospheric lifetime of isoprene with respect to OH by day is also 1-2 hours. This means that isoprene (and the other BVOCs) will undergo considerable photochemical loss during the horizontal transport following outflow from the cloud by day. In contrast, at night, any convection occurring from sunset to sunrise can export unreacted residual isoprene (and other BVOCs) to high altitudes without subsequent loss from OH. O₃, which is still present by night, reacts much slower with isoprene (lifetime about 2 days at 20 ppbv O₃) (Karl et al., 2004; Paulson and Orlando, 1996) and boundary layer O₃ levels in the Amazon are typically low 10-20 ppbv (Bela et al., 2015; Kuhn et al., 2010). In the UT, the highest mean mixing ratios of isoprene, its oxidation products and monoterpenes are measured at 0.86 ± 0.34 , 0.56 ± 0.20 and 0.05 ± 0.02 ppbv, respectively, at 04:00 local time, two hours before dawn. The mean mixing ratio of monoterpenes in the UT at this time is closely comparable to those measured in the boundary layer at 320 m between 04:00 and 06:00 local time, suggesting that very efficient nighttime vertical transport has occurred. Isoprene transported by convection at night can accumulate in the UT since O₃ in the outflow will be low and OH is not present. However, from dawn onwards, the influx of solar energy increases, promoting outflow plume dispersion, in-mixing of O₃, and the photochemical formation of OH. The nocturnally transported isoprene and monoterpenes decline rapidly to low mixing ratios after 08:00 local time when OH production increases. In contrast, isoprene OP decreased more slowly due to its secondary production from the isoprene oxidation, partially offsetting loss through reaction with OH. The higher mean mixing ratios of isoprene-OP in the UT result from both the updraft during nighttime and their in-situ formation from isoprene. It is remarkable that not only do the emissions from the Amazon rainforest biome extend to 14 km and influence the UT, but we also observe distinct diel cycles in the BVOCs at different altitudes. The buildup of highly reactive species, such as isoprene and monoterpenes during the night primes the upper atmosphere for vigorous photochemistry at dawn (Palmer et al., 2022).

5.2.3. BVOCs sensitivity analysis in the Amazonian atmosphere

The EMAC model simulations were performed to investigate the sensitivity of atmospheric chemistry above the Amazonia basin and the radiative effects to changes in BVOC emissions. The motivation of the sensitivity study is the elevated levels of BVOCs measured in the UT associated with convection and addressing how changes in the BVOC emission at the surface will impact the atmospheric chemistry from the boundary layer to the UT (9-14 km). Flight 06 provides notable

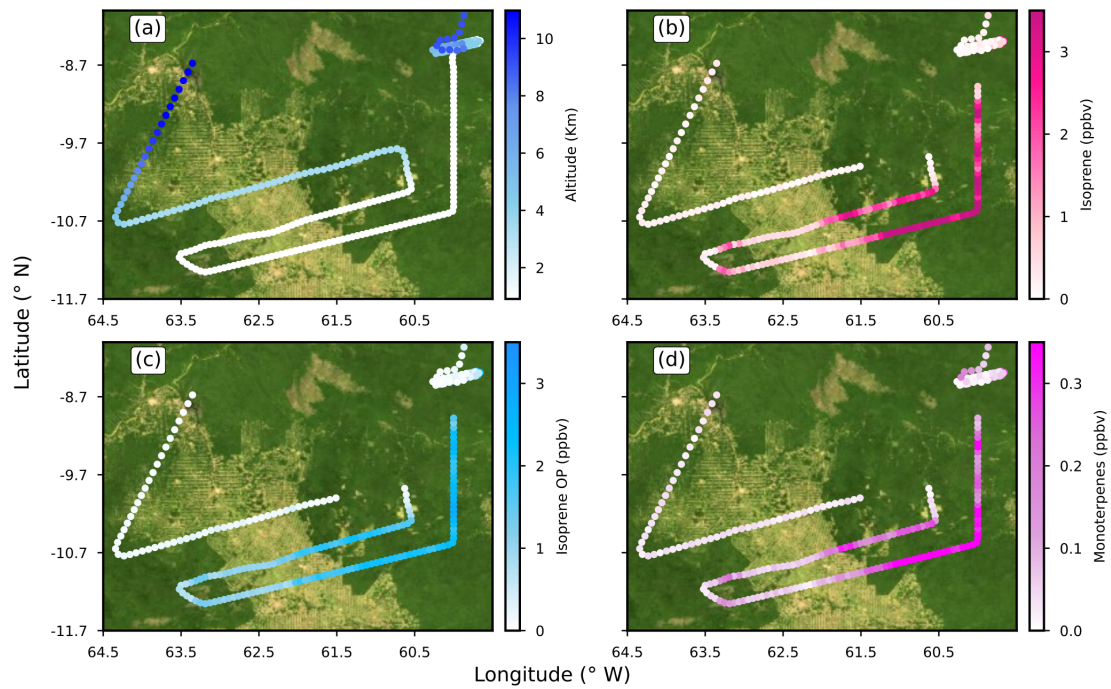


Figure 5.4.: Flight tracks of flight 06 over forested and deforested regions. Flight tracks of flight 06 with color bar a) altitude in meters and mixing ratios of b) isoprene c) isoprene oxidation products (OP) and d) monoterpenes over the Amazon rainforest. Green and tan colors on the map show the forested and deforested regions, respectively. Satellite picture data in this figure obtained from <https://wvs.earthdata.nasa.gov>, NASA Worldview Snapshots.

motivation for this sensitivity study. In this flight, in fact, the measurements documented BVOCs over deforested areas converted to pasture, and contrasted to nearby pristine forests sampled at relatively low altitudes (~ 900 m) in the boundary layer over Rondônia, Brazil. Figures 5.4 a-d depict the variations in the altitude and mixing ratios of isoprene, isoprene-OP and monoterpenes along flight 6 over forested and deforested regions, respectively.

The flight 06 data show a steep spatial gradient of isoprene mixing ratio over forested and pasture regions. The mean mixing ratios of isoprene, isoprene-OP, and monoterpenes over deforested regions were 0.75 ± 0.45 , 1.2 ± 0.36 and 0.08 ± 0.04 ppbv, respectively. In contrast, the mean mixing ratios of isoprene (2.96 ± 0.72 ppbv), and monoterpenes (0.31 ± 0.09 ppbv) over forested regions were approximately four times higher than the pasture regions. While mixing ratio of isoprene-OP (2.12 ± 0.41 ppbv) were only ~ 1.7 times higher than over the deforested regions. The lower spatial gradients of isoprene-OP are likely due to the transport of the longer-lived isoprene-OP from adjacent forested regions.

Deforestation has been reported as a primary driver of the reduction in BVOC emissions in tropical forests although other factors, such as biomass burning and climate change, also play significant roles. On the other hand, several studies suggested that global BVOC emissions will likely increase with climate change, potentially by up to 50% under scenarios with doubled CO_2 concentrations (Vella; Forrest; Lelieveld, et al., 2023; Yáñez-Serrano; Nölscher; Bourtsoukidis, et al., 2018). As a result, the future Amazonian atmosphere could experience dramatic positive or negative variations in BVOC emissions. Therefore, we evaluate the atmospheric response in scenarios where Amazonian BVOC emissions are reduced by 50% and 75%, and increased by 50% using the EMAC model.

EMAC is a general circulation model, here used at roughly 200×200 km horizontal resolution and 90 vertical levels up to 80 km. BVOCs are emitted using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2012) and a comprehensive atmospheric chemistry mechanism (Mainz Isoprene Mechanism, MIM) (Jöckel; Tost; Pozzer; Brühl, et al., 2006) is used. Details of the model are provided in the method section. We performed a base-case scenario and three sensitivity runs with perturbed BVOC emissions, as stated above. The base-case EMAC run generally agreed with the isoprene measured during the CAFE-Brazil campaign, especially in the LT (see Supplementary Figure 8). While monoterpenes are somewhat underestimated in the boundary layer, most probably due to their reactions with O_3 , which is known to be overestimated in EMAC, especially in the tropics (Jöckel; Tost; Pozzer; Kunze, et al., 2016), as well as in other global chemistry-climate models (Young et al., 2013). The measurements show higher BVOC levels in the UT than the model, which can be expected since the aircraft actively sought convective outflow. These sub-grid scale processes are parametrized in the model and averaged over the horizontal extent of the grid box. However, surface monoterpene and isoprene mixing ratios were evaluated with measurements from the ATTO tower, and simulated ozone, OH and organic aerosol were additionally evaluated with background aircraft observations, showing good agreement (supplementary Figures 9-12). Moreover, previous studies have evaluated the EMAC model with similar setups for aerosols (Kohl et al., 2023; Pozzer; Meij, et al., 2012; Pozzer; Reifenberg, et al., 2022; Tsimpidi et al., 2014), ozone and OH (Jöckel; Tost; Pozzer; Kunze, et al.,

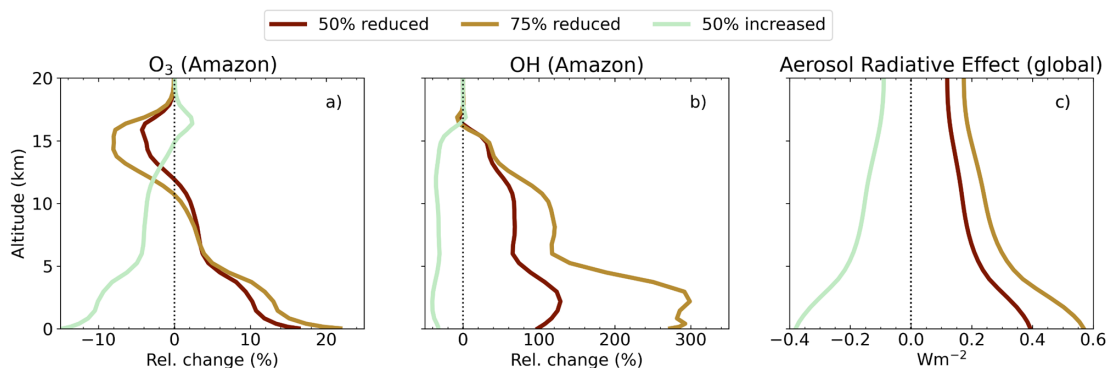


Figure 5.5.: The relative change in the vertical profiles of ozone, OH radical and aerosol radiative effect due to change in the biogenic volatile organic compounds (BVOCs) emission at the surface. The vertical profiles of relative changes in a) O_3 and b) OH and of absolute changes in c) the global radiative effect due to aerosol between the base simulation and the simulation with 50% and 75% reduction and a 50% increase in the BVOCs emission. The radiative effect is the imbalance between incoming and outgoing radiation and is calculated at each vertical level.

2016). The simulated diurnal cycle of isoprene mixing ratios (Supplementary Figure 13) supports our findings observational analysis. The highest isoprene mixing ratios in the BL are simulated in the afternoon hours, with delayed transport to the residual layer, and the highest UT isoprene mixing ratios in the early morning, following night-time convection. Isoprene mixing ratios react non-linearly to changes in BVOC emissions, with a positive feedback due to the increased (decreased) OH availability, the main sink of isoprene, following decreases (increases) in BVOC emissions (Figure 5.5).

The annual and seasonal changes in the Amazonian region over 0-20 km altitude, relative to the base case, for the oxidants OH radicals, O_3 , and the global radiative effect due to aerosol, are illustrated in Figure 5.5 and Supplementary Figure 14, respectively. Each panel in Figure 5.5 indicates the relative change across the atmospheric column. The results show that BVOCs strongly influence the oxidation capacity of the atmosphere, even up into the UT. Annually, the strongest effects on OH (changes of 300% relative to the base case, when BVOC emissions were lowered to 25%), occurred in the boundary layer at 0-3 km altitude. The highest relative change in OH (~400%) in the LT (0-3 km) during the dry season suggests a higher loss rate of OH, driven by elevated BVOC emissions over the Amazon basin during this period (Supplementary Figure 14). In the mid-troposphere (5-10 km), a 75% decrease in BVOC emissions leads to a 100-150% relative increase in OH mixing ratios. On the other hand, OH only decreases by 15-40% after increasing BVOC emissions by 50% at these altitudes. This relative change in OH after reducing and increasing BVOC emission shows a non-linear dependency (Figure 5.5 b). An increase in BVOC emissions can lead to a reduction in OH levels; however, the sensitivity of OH to increases in BVOC is buffered, as other sinks and competing processes also play a significant role (Lelieveld; Gromov, et al., 2016). It should be noted that such significant increases of OH in this region will also affect the lifetimes of longer-lived radiatively active gases such as methane and reactive halocarbons. Indeed, the model estimates that the methane lifetime will decrease by ~0.3-0.4 years globally

if forest BVOC emissions over the Amazon are reduced by 75%. Scott et al. (2018) estimated a 0.5-year reduction in methane lifetime reduction due to global deforestation, in close agreement with these results.

Interestingly, the net annual changes in O_3 vary strongly with altitude. When Amazonian BVOC emissions are reduced by 75% in the model, O_3 increases by circa 22% in the LT (0-4 km) averaged over the Amazon basin (Figure 5.5 a), with local increases exceeding 30% (Supplementary Figure 15), but decreases by 10% in the UT (between 13-16 km). Seasonally, the strongest influence on O_3 at the surface is observed during the dry season (> 25% relative change), while this impact is more pronounced (~ -10%) in the UT during the wet season and the transition from dry to wet periods (Dec-Jan, Supplementary Figure 14). This indicates that the significant convective transport of BVOCs during the wet seasons plays a pivotal role in the production of O_3 in the UT. The O_3 increase in the lower troposphere can be attributed to lower rates of direct BVOC- O_3 reactions, particularly for monoterpenes that react faster with O_3 than isoprene (Atkinson, 2003). Therefore, we infer that BVOCs act mainly as the sink for O_3 (Supplementary Figure 15) because the rainforest boundary layer is a NO_x poor environment, where photochemical O_3 production is limited by extremely low NO (Bela et al., 2015; Kuhn et al., 2010). In contrast, the high-altitude regions are enriched in NO_x by lightning, and the reduction in O_3 in the UT due to the reduction in BVOC levels reveals that O_3 production is limited by BVOCs, and that lower surface emissions mean less BVOC is available aloft to drive photochemical O_3 production.

We also estimate the radiative effect of perturbations in BVOC emissions over the Amazon region specifically due to the changes in O_3 and aerosol. The changes in radiative forcing due to aerosol are also shown in Figure 5.5 c as a function of altitude. It is remarkable that a 75% BVOC emission reduction on the Amazon leads to a very strong regional warming, with aerosol radiative effect of $\sim 6 \text{ W m}^{-2}$ at the surface over the Amazon Basin and a lower but significant $\sim 0.6 \text{ W m}^{-2}$ globally. In contrast, a 50% increase in BVOC emissions has a substantial global cooling effect of -0.4 W m^{-2} (Figure 5.5 c). By performing additional sensitivity studies reducing only isoprene and only monoterpenes (supplementary Figure 16), we learn that isoprene dominates the observed changes in the gas phase oxidants. In contrast, the monoterpenes play a main role in the aerosol radiative forcing. By reducing regional BVOCs up to 75%, a small radiative cooling occurs in the global upper troposphere ($\sim 0.03 \text{ W m}^{-2}$), due to ozone, which is relatively insignificant compared to the changes caused by aerosols.

Previous modelling studies have reported a latitudinal sensitivity to deforestation, with tropical deforestation accounting for 80% of the direct radiative forcing. Scott et al. (2018) have also reported that BVOCs can impact short-lived tracers, especially aerosol, O_3 and methane, noting the negative radiative forcing resulting from the reduction in O_3 and methane concentrations while noting positive radiative forcing attributable to low aerosols (Vella; Forrest; Pozzer, et al., 2025). The aforementioned modelling results were conducted with a different model and methodical approaches, but nevertheless, the general results are in good agreement with those shown here. The results of BVOC sensitivity study emphasize the importance of the Amazon rainforest for the global climate system.

This study highlights the role of convection in shaping the atmospheric distribution of BVOCs and their contribution to upper tropospheric chemistry, including O_3 production, and OH loss. However, the radiative warming that occurs when monoterpene-generated aerosol is reduced overwhelms the small (5%) changes from the methane lifetime change. It should also be noted that the Amazon rainforest stores approximately 108 Pg C in living aboveground biomass (Feldpausch et al., 2012; Rosan et al., 2024). According to this study, if deforestation through burning accounts for the 50% reduction in Amazonian biomass, it would additionally release approximately 54 Pg C (equivalent to a global increase of 25 ppm CO_2) into the atmosphere, leading to a strong positive radiative forcing and warming, as well as a long-term perturbation of the global hydrological and carbon cycles. The potential effects of deforestation and afforestation on the Earth's atmosphere are further discussed elsewhere, e.g., in Weber; King, et al. (2024). Our BVOC sensitivity study highlights the role these species play in the atmosphere. In short, by storing carbon and releasing BVOCs, the Amazon rainforest modulates atmospheric CO_2 concentrations and regulates oxidation processes in the upper and lower troposphere.

This study describes a unique and comprehensive dataset for isoprene, its oxidation products (isoprene-OP), and total monoterpenes over the Amazon rainforest from 300 m to 14 km altitude during a two-month airborne and ground-based field campaign (CAFE-BRAZIL, December 2022–January 2023). The data reveal that tropical deep convection has a strong impact on the distribution of these short-lived trace gases, with little influence in the mid-troposphere (3–9 km) but elevated levels in the upper troposphere (UT, 9–14 km). Moreover, we show that nocturnal convection effectively transports biogenic species to the UT, where they accumulate through the night without effective oxidation, and then rapidly oxidize at daybreak. The results support the conclusions of Palmer et al. (2022), who used a combination of satellite and model data to infer nocturnal vertical transport of isoprene (6–8 km), although our in-situ data shows vertical transport and outflow through convection occurring at significantly higher altitudes (10–12 km). These results also show that the UT isoprene values highlighted by Curtius et al. (2024) in a dawn-flight convective outflow case study with associated strong particle production are widespread over the region.

By comparing surface and UT levels of isoprene, isoprene-OP and monoterpenes, we note that convection preferentially removes the more oxidized and soluble isoprene-OP, relative to the primary emissions. Here we provide the vertical and diel (24-hour) resolved distribution of these species, showing that the daily peak in the concentration of isoprene shifts from 12:00–14:00 at the surface to around 04:00 at 10 km, again due to deep nocturnal convection and absence of photochemical degradation. By selecting realistic values based on measured BVOC mixing ratios over deforested regions during this campaign and previously reported projections, the sensitivity study highlights that a reduction in BVOC emissions over the Amazonian region would lead to a decrease in upper tropospheric O_3 , an increase of lower tropospheric OH, a shortening of the methane lifetime, and a strong net increase in radiative cooling forcing through O_3 and aerosols. An underestimation of the model results compared to the observations suggests that the effects of BVOCs on O_3 , OH, and radiative forcing in the UT may be stronger than the relative changes presented in this study. This highlights the need to include BVOC chemistry in global models when simulating global change and their potential contributions to radiative forcing.

5.3. Methods

5.3.1. Instrumentation

The high time- and mass-resolved BVOC measurements of isoprene, isoprene oxidation products (OP) and total monoterpenes were performed using PTR-TOF-MS (Ionicon 8000, Analytik GmbH, Austria). In the aircraft, a 2 m long 1/8-inch sulfonert inlet tube was used for sampling and was permanently heated to 40°C. Hydronium ions (H_3O^+) were used as a reagent ion to ionize molecules with sufficient proton affinity in the ambient air molecule within the PTR-drift tube. The instrument is operated with a drift pressure of 2.2 mbar, E/N 137 Td, drift voltage of 600 V, and reactor temperature of 60°C, running at time resolution of 1 s. An air molecule (R) is ionized in the drift tube by the following proton transfer equation:



Molecules with proton affinities higher than that of water (693 kJ mol^{-1}), can be ionized in the drift tube and therefore measured by the detector. In flight background measurements were conducted for 10 minutes at every 1–2 km of altitude using pressurized synthetic air in the aircraft. The ionicon data analyser (IDA) 2.2.0.4 software was used to analyze the raw data. The instrument was calibrated the day before each flight. Isoprene, Isoprene-OP and monoterpenes were calibrated with a commercial gravimetrically prepared standard (Apel-Riemer Environmental Inc) containing isoprene, methacrolein, α -pinene and other compounds. The calibration was performed for both dry and humid air conditions and humidity dependencies were factored into the final data. The limit of detection (LOD, 3σ) of averaged 1 min data for isoprene, isoprene OP (MVK, MACR and ISOPOOH) and monoterpenes ranges from 85 to 180 ppt, 13 to 56 ppt, and 24 to 43 ppt for different flights, respectively. Data below the detection limit were filtered out during the averaging. The total uncertainty, including both precision and calibration error, was estimated to be approximately 10–20%. Several studies have shown that isoprene detection by PTR-TOF-MS can be compromised by interferences caused by the fragmentation of larger molecules or ozone generated species. Therefore, we used data measured by the fast Gas chromatography-mass spectrometer (GC-MS) onboard to validate isoprene values and to assess the degree of interference in ambient air over the Amazon. PTR-TOF-MS isoprene validation with the GC-MS and associated correction are discussed in detail in supplementary text 1. The detailed information of GC-MS is discussed in Supplementary Text 2.

5.3.2. Model

Model calculations were performed using the ECHAM/MESSy Atmospheric Chemistry-climate Model (EMAC) (Jöckel; Kerkweg, et al., 2010; Jöckel; Tost; Pozzer; Brühl, et al., 2006). Simulations were conducted at a horizontal resolution of T63, equivalent to $1.875^\circ \times 1.875^\circ$ (approx. $200 \times 200 \text{ km}$) with 90 hybrid, terrain-following vertical levels extending up to 0.01 hPa ($\sim 80 \text{ km}$).

Simulations were nudged towards meteorological reanalysis data (ERA5) (Hersbach et al., 2020) to represent actual meteorological conditions. Gas-phase chemistry was simulated using the MECCA (Sander; Baumgaertner, et al., 2019) submodel with MIM1 (Jöckel; Tost; Pozzer; Brühl, et al., 2006; Pöschl et al., 2000) chemistry. Photochemical J-values were calculated using the JVAL (Sander; Jöckel, et al., 2014) submodel. Lightning NO_x emissions were computed using Grewe's algorithm (Grewe et al., 2001), while dry deposition, wet deposition, and sedimentation were modeled with the DDEP (Kerkweg et al., 2006), SCAV (Tost et al., 2006), and SEDI (Kerkweg et al., 2006) submodels, respectively.

Anthropogenic surface emissions of reactive gases and primary aerosols were sourced from the CEDS database (McDuffie et al., 2020) for the year 2019, supplemented by aircraft emissions from the CAMS global aviation dataset (Granier et al., 2019). Natural emissions of biogenic VOCs were calculated using the MEGAN submodel (Guenther et al., 2012). For the sensitivity studies, BVOC emissions were scaled down to simulate the impact of deforestation. For the sensitivity studies, BVOC emissions were simply scaled with a factor of 0.5 (50% reduction), 0.25 (75% reduction), and 1.5 (50% increase) without further changes to the simulation. The model's aerosol microphysics rely on seven interactive log-normal modes, comprising four hydrophilic and three hydrophobic modes, to represent the aerosol size distribution. All aerosols are treated as spherical particles (Pringle et al., 2010). While aerosols are externally mixed across size modes, they are internally mixed within each mode based on contributing species. Gas-aerosol partitioning is determined using ISORROPIA for inorganic species (Fountoukis and Nenes, 2007) and ORACLE for organic species, based on their sources and volatility (Tsimpidi et al., 2018). Radiative calculations are performed with the RAD submodel (Dietmüller et al., 2016), comparing the sensitivity to the reference simulation, with aerosol optical properties calculated with the AEROPT submodel (Dietmüller et al., 2016).

Data Availability. All data that support the findings of this study are publicly available on FigShare (<https://doi.org/10.6084/m9.figshare.28692260.v1>) (Tripathi et al., 2025). Source data are provided with this paper.

Code Availability. The Modular Earth Submodel System (MESSy, <https://zenodo.org/doi/10.5281/zenodo.8360186>) (Consortium, 2025) is continuously further developed and applied by a consortium of institutions. The usage of MESSy and access to the source code is licenced to all affiliates of institutions which are members of the MESSy Consortium. Institutions can become a member of the MESSy Consortium by signing the MESSy Memorandum of Understanding. More information can be found on the MESSy Consortium Website (<http://www.messy-interface.org>).

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Chapter 6

Conclusions and future perspectives

In this doctoral project, Fast Gas Chromatography-Mass Spectrometry (Fast GC-MS), Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS), and the EMAC (ECHAM5/MESSy2) atmospheric chemistry model were used to study the vertical (0.2–14 km) and spatial distribution of BVOC in two contrasting tropical settings: (i) above the "green ocean" of the Amazon rainforest, and (ii) above the "blue ocean" of the Pacific. The measurements were conducted during two campaigns of the Chemistry of the Air Field Experiment (CAFE) in Brazil (CAFE-Brazil; Dec 22–Jan 23) and in Australia (CAFE-Pacific; Jan–Feb 24) that together comprise more than 180 flight hours of data. The dissertation focuses on identifying and quantifying the spatial emission patterns and atmospheric fate of three key BVOCs—*isoprenoids*, DMS and CH_3Cl . Special emphasis lies on quantifying the efficiency of their deep convective transport from the planetary boundary layer to the upper troposphere (UT), which depends on losses during transport due to gas-phase oxidation, dilution, and uptake by liquid cloud droplets. Below, the central conclusions are summarised and future perspectives are explored separately for each studied compound.

Chloromethane. Tropical plants are known as dominant source of CH_3Cl globally, and the Fast GC-MS datasets presented here cover two different rainforests, the Amazon and the rainforest of Papua New Guinea. The enrichment with CH_3Cl relative to its tropical background mixing ratios (MLO, RPB, SMO), indicative of the regional source strength, was significantly positive above both rainforests, confirming tropical rainforests as dominant source of CH_3Cl during both campaigns. Surprisingly, a fourfold higher enrichment was found above the Papua New Guinean rainforest compared to the Amazon, revealing substantial variability of emission rates across different rainforest ecosystems. A plausible driver of this disparity is the substantially higher abundance of high- CH_3Cl -emitting taxa (e.g., dipterocarp and fern trees) in Southeast Asian forests, potentially linked to adaptation to greater chlorine availability on tropical islands and coastal regions. Future work should employ long-term, ecosystem-scale flux measurements and targeted experiments to identify the specific sources (e.g., tree compartments, fungi, soils, phyllosphere microbes, dead plant material) that control CH_3Cl emissions across different rainforest environments. Combining the CAFE measurements with ten earlier airborne campaigns (GABRIEL, HIPPO 1–5, ATom 1–4) confirms that the tropics constitute the principal global source of CH_3Cl , but the longitudinal distribution is far from uniform: marked enrichments occur throughout the whole tropospheric column over continents and large islands. In the western-Pacific sector, the main conduit for troposphere-to-stratosphere transport, upper-tropospheric CH_3Cl exceeds the tropical background by 50–90 pptv. Consequently, the mixing ratios measured at the existing network of remote-site observatories cannot be simply interpolated to represent the whole atmosphere. Due to the longitudinal variability, air masses entering the stratosphere likely carry up to 10% more CH_3Cl than indicated by the current monitoring stations. Stratosphere-resolving global models such as EMAC currently don't account for the longitudinal variability, despite its potential relevance to stratospheric chlorine levels. Future work should aim at developing a more realistic emission parametrisation, perhaps based on inversion-modelling results such as those by Xiao et al. (2010), and assess its impact on stratospheric chlorine loading and ozone recovery trajectories. Moreover, the global monitoring network should be extended with stations in the outflow regions

of tropical continents to better capture the true CH_3Cl distribution.

Dimethyl sulfide. Two extensive airborne in-situ DMS datasets obtained with Fast GC-MS during the CAFE-Brazil and CAFE-Pacific campaigns were presented. The planetary boundary layer DMS mixing ratios over the Pacific Ocean were approximately one magnitude higher than over the rainforest, confirming the well-established dominance of marine sources in the global DMS budget. The lower tropospheric vertical gradients above the Amazon and Indo-Pacific agree well with earlier observations in comparable regions. In deep convective outflows in the Amazonian UT, the present work provides the first in-situ measurements. DMS mixing ratios were consistently below the detection limit, indicating that DMS likely plays a minor role in the atmospheric chemistry there. In contrast, over the Indo-Pacific, DMS enrichments of up to 56 pptv were frequently observed in convective outflows between 9–14 km, a phenomenon that has been captured only rarely by previous in-situ measurements. These results underscore the need to investigate the fate of lofted DMS and its contribution to new particle formation (NPF) under the low-temperature, low-pressure conditions of the UT.

Comparison of the airborne observations with EMAC simulations that employ three different sea-surface DMS inventories shows that the inventory of Hulswar et al. (2022) provides the closest match to the CAFE-Pacific measurements, although further refinements are still required. Among the three convection schemes tested, the EMAC standard Tiedtke-Nordeng parameterisation (Nordeng, 1994; Tiedtke, 1989) reproduces the observed vertical distribution best, albeit with a modest over-estimate in the mid-troposphere. The sensitivity analysis shows that the choice of convection parameterisation also affects distributions of DMS oxidation products, such as sulfuric acid, that are relevant to aerosol formation in the marine atmosphere.

Over the Amazon, the sole terrestrial DMS inventory of Spiro et al. (1992) overestimates rainforest emissions by roughly a factor of three. Although oceanic sources dominate the global DMS budget, this overestimate generates a regional excess of DMS throughout the troposphere in the model, potentially altering local sulfur chemistry. Future work should refine the parametrisation of terrestrial DMS emissions, for example, by incorporating light- and temperature-dependent plant emissions from the MEGAN submodel. Additional long-term atmospheric observations in continental, forested environments and targeted studies of the drivers of DMS production in plants and other forest components will improve our understanding of forest DMS emissions.

Isoprenoids. Airborne and ground-based measurements were used to characterise diel variations in the vertical distribution of isoprene, its oxidation products, and monoterpenes during the CAFE-Brazil campaign. Two near-identical PTR-TOF-MS instruments were employed aboard the research aircraft HALO and on ground at the Amazon Tall Tower Observatory (ATTO), and the airborne measurements were validated with the Fast GC-MS data. The first part of the study investigates the deep-convective uplift of BVOCs from the planetary boundary layer into the UT. Although deep convection occurs both day and night, transport efficiency peaks at night when photo-oxidants are low: 21% of the boundary layer isoprene, 15% of its oxidation products, and 27% of monoterpenes are detected in the UT. These results confirm recent satellite-based and

modelling predictions (Palmer et al., 2022). Moreover, the data support a complementary study showing that the nocturnally lofted isoprene, together with lightning-generated NO_x , serves as a key precursor for NPF in the Amazonian UT (Curtius et al., 2024).

A low altitude flight above a deforested area that recorded roughly four times lower isoprenoid levels than over pristine rainforest motivated a sensitivity analysis of atmospheric chemistry to changes in isoprenoid emissions using the EMAC model. The base-case, representing present-day conditions, reproduces the observations reasonably well. Three perturbation scenarios were examined: a 50% and a 75% reduction in isoprenoid emissions to simulate deforestation, and a 50% increase to represent a warming climate. Reductions in emissions lead to markedly higher OH and O_3 concentrations over the Amazon, shortening the methane lifetime by 0.3–0.4 yr for the 75% reduction case. However, the isoprenoid reductions also produce a significant warming aerosol radiative effect because of the associated decrease in secondary organic aerosol formation. Conversely, the emission increase scenario yields the opposite chemical response, with lower OH and O_3 and a lengthened methane lifetime, but a cooling aerosol radiative effect owing to enhanced aerosol loading. The results show that changes in isoprenoid emissions exert a pronounced impact on atmospheric processes in the Earth System.

Future work should deepen our understanding of isoprenoid chemistry throughout the troposphere, with particular focus on its role in new-particle formation (NPF). Although Curtius et al. (2024) showed that isoprene nitrates drive NPF in the upper troposphere, open questions remain regarding the detailed reaction pathways, their pressure- and temperature-dependences, and the fate of the nitrates (e.g., photolysis rates). The influence of other species, such as sulfur compounds, on isoprene-related NPF at these altitudes is also unclear. Moreover, under the higher temperature and pressure conditions of the lower troposphere, where most isoprenoid oxidation occurs, the contribution of isoprenoids to NPF is still insufficiently quantified. Incorporating these newly identified mechanisms into Earth system models will be essential for improving predictions of aerosol loading, cloud microphysics, and the associated radiative effects.

Overall, the combined airborne measurements and model analyses demonstrate that deep convective transport critically shapes the vertical distribution and atmospheric impact of BVOCs, that tropical ecosystems exhibit large spatial variability in emissions, and that current global-scale emission inventories and convection schemes require substantial improvement to accurately represent BVOC-driven chemistry, aerosol formation and their climate feedbacks.

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Appendix A

Abbreviations and Acronyms

ABLE	Atmospheric Boundary Layer Experiment
AEST	Australian Eastern Standard Time
AGAGE	Advanced Global Atmospheric Gases Experiment
AMT	Amazon Time
AMZ	Pristine Amazon PBL cluster
AMZ+BB	Pristine Amazon PBL with BB background cluster
ATom	Atmospheric Tomography Mission
ATTO	Amazon Tall Tower Observatory
BAHAMAS	Basis HALO Measurement and Sensor System
BB	Biomass burning
Br	Bromine atom
BrO	Bromine oxide radical
BVOC	Biogenic volatile organic compound
C ₁₀ H ₁₆	Monoterpenes
C ₅ H ₈	Isoprene (2-Methylbuta-1,3-diene)
CAFE	Chemistry of the Atmosphere Field Experiment
CAMS	Copernicus Atmosphere Monitoring Service
CCN	Cloud condensation nuclei
CFC	Chlorofluorocarbon
CFC-11	Trichlorofluoromethane (CCl ₃ F)
CFC-113	1,1,2-Trichloro-1,2,2-trifluoroethane (CClF ₂ CCl ₂ F)
CFC-12	Dichlorodifluoromethane (CCl ₂ F ₂)
CH ₃ Cl	Chloromethane
CH ₄	Methane
Cl	Chlorine atom
CO ₂	Carbon dioxide
CST	Coastal PBL cluster
CT	Cloud type
CTT	Cloud top temperature
DECAFE-88	Dynamique et Chimie de l'Atmosphere en Foret Equatoriale 1988

DJF	December, January, February
DLR-FX	Deutsches Zentrum für Luft und Raumfahrt – Flugexperimente
DMS	Dimethyl sulfide
DMSP	Dimethylsulfoniopropionate
ECD	Electron capture detector
ECHAM	General circulation model by ECMWF and MPI for Meteorology HAMBURG
ECMWF	European Centre for Medium-Range Weather Forecast
EI	Electron impact
EMAC	ECHAM5/MESSy2 Atmospheric Chemistry model
ERA5	ECMWF Re-Analysis 5
ESM	Earth system model
FAIRO	Fast Airborne Ozone instrument
FID	Flame ionisation detector
FLEXPART	Flexible particle dispersion model
FT	Free troposphere
GABRIEL	Guyanas Atmosphere-Biosphere exchange and Radicals Intensive Experiment with the Learjet
GC	Gas Chromatograph
GC-MS	Gas Chromatography-Mass Spectrometry
H ₂ O	Water
H ₂ SO ₄	Sulfuric acid
HALO	High Altitude Long Range research aircraft
HIAPER	High-performance Instrumented Airborne Platform for Environmental Research
HIPPO	HIAPER Pole-to-Pole Observations
HO ₂	Hydroperoxy radical
HO _x	Sum of OH and HO ₂
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory model
I	Iodine atom
ISOPOOH	Isoprene hydroxy hydroperoxide
Isoprene-OP	Sum of isoprene oxidation products (MVK, MACR, ISOPOOH)
LCA	Latent class analysis
LOD	Limit of detection
LT	Lower troposphere
M/O	Median model to observation ratio
<i>m/z</i>	Mass-to-charge-ratio
MACR	Methacrolein (2-methylprop-2-enal)
MECCA	Module Efficiently Calculating the Chemistry of the Atmosphere
MEGAN	Model of Emissions of Gases and Aerosols from Nature
MESSy	Modular Earth Submodel System
MIM1	Mainz Isoprene Mechanism
MLO	Mauna Loa Observatory

MODIS	Moderate-resolution Imaging Spectroradiometer
MS	Mass Spectrometer
MSA	Methanesulfonic acid
MT	Mid-troposphere
MVK	Methyl vinyl ketone (but-3-en-2-on)
N ₂ O	Nitrous oxide
NASA	US National Aeronautics and Space Administration
NCAR EOL	US National Center for Atmospheric Research – Earth Observing Laboratory
NMVOC	Non-methane VOC
NO	Nitrogen oxide
NO ₃	Nitrate radical
NOAA	US National Oceanic and Atmospheric Administration
NO _x	Sum of NO and NO ₂
NPF	New particle formation
NSF	US National Science Foundation
O(¹ D)	Singlet Oxygen
O(³ P)	Triplet Oxygen
O ₃	Ozone
OCI	Ocean color index
OH	Hydroxyl radical
OVOC	Oxygenated volatile organic compound
PAC	Pacific ocean PBL cluster
PANTHER	PAN and other Trace Hydrohalocarbon ExpeRiment
PBL	Planetary boundary layer
PD	Present-day
PEM	Pacific Exploratory Missions
PFA	Perfluoralkoxy polymer
PI	Pre-industrial
PNG	Papua New Guinea PBL cluster
ppbv	Parts per billion by volume (10 ⁻⁹ mol mol ⁻¹)
pptv	Parts per trillion by volume (10 ⁻¹² mol mol ⁻¹)
PTR-ToF-MS	Proton Transfer Reaction-Time of Flight-Mass Spectrometer
R ²	Coefficient of determination
rBC	Refractory black carbon
RF	Research flight
RO ₂	Peroxy radical
ROOH	Organic hydroperoxide
RPB	Ragged Point Barbados Observatory
S4D	Sampling in 4 dimensions
SAM	S-adenosyl-L-methionine
sccm	Standard cubic centimeters per minute

SEAC4RS	Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys
SIM	Selected ion monitoring
SMM	S-methylmethionine
SMO	American Samoa Observatory
SO ₂	Sulfur dioxide
SOA	Secondary organic aerosol
SOFIA	System for Organic Fast Identification Analysis
SP2	Single Particle Soot Photometer
TGI	Trace Gas Inlet
TIC	Total ion count
TST	Troposphere-to-stratosphere transport
TTL	Tropical tropopause layer
UT	Upper Troposphere
UTC	Coordinated Universal Time
UV	Ultraviolet radiation
V25	In-house developed controlling system based on a V25 processor
VOC	Volatile organic compound
WMO	World Meteorological Organisation
XVOC	Halogenated volatile organic compound

Appendix B

Use of AI-tools

AI-tool	Used for	Why	When
OpenAI OSS 120 B	Reformulation of my draft texts	Improve wording, clarity and conciseness	Throughout the entire work
	Reformulation and extension of Python code	Improve code efficiency and readability	Sometimes during coding
Grammarly browser add-on	Correct my spelling and punctuation	Improve sentence structure	Throughout the entire work
Nature Research Assistant (beta)	Reformulation of my draft texts	Improve clarity, identify and reduce overstated claims	Chapter 4
	Summarize papers, find related papers	Get quick overview of new literature	Sometimes during literature research

Appendix C

Curriculum Vitae

Bianca Elena Krumm

Date of birth: 10/01/1996

Languages: German (native), English (C1), French (A1)

Education

01/2022–present **Doctoral researcher in atmospheric chemistry**
Max Planck Institute for Chemistry (Mainz, Germany)
Thesis title: "Biogenic volatile organic compounds from green and blue oceans"

04/2019–11/2021 **M.Sc. in chemistry**
Karlsruhe Institute of Technology (Germany) and
Université de Lille (France)
Thesis title: "Kinetic Study of the Reaction between 1,3,5-Trioxane and Hydroxyl Radicals"

10/2014–04/2019 **B.Sc. in chemistry**
Karlsruhe Institute of Technology (Germany)
Thesis title: "Bestimmung der Reaktionsvolumina durch Messung der Druckabhängigkeit des elektrochemischen Potentials für die Kupfer-Unterpotentialabscheidung und Sulfat-Adsorption auf Au(111)"

Professional Experience

05–10/2020 **Student research assistant** (HiWi)
Karlsruhe Institute of Technology (Germany)
Institute of Meteorology and Climate Research (IMK)
Analysis of photolysis and reaction rates in AIDA chamber experiments using the kinetic simulation tool KinSim

- 11/2019–02/2020 **Research intern** (part of M.Sc. program)
 Université de Lille (France)
 Study of the humidity dependence of the reaction between ethanol and
 OH radicals using OH-LIF

Teaching

- 04–07/2025 **Laboratory course in general inorganic chemistry**
 Johannes Gutenberg Universität, Dept. Inorganic Chemistry
- 10/2018–10/2019 **Tutorial of mathematical methods in physical chemistry**
 Karlsruhe Institute of Technology, Dept. Physical Chemistry

Field Campaigns

- 12/2022–02/2023 **Chemistry of the Air Field experiment (CAFE) Brazil**
 HALO campaign based in Manaus, Brazil
- 01–03/2024 **Chemistry of the Air Field experiment (CAFE) Pacific**
 HALO campaign based in Cairns, Australia

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