

Total OH reactivity in pristine and polluted environments

Investigating atmospheric chemistry in the Anthropocene

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“The atmosphere is the key symbol of global interdependence.”
Margaret Mead

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Summary

Since the start of industrialization and increasingly since the 1950s, anthropogenic activities have altered the Earth's atmospheric composition significantly with consequences for climate, weather, and the health of both humans and ecosystems. Reactive trace gases are, on the one hand, part of the anthropogenic emissions that fuel air pollution and impact climate, and on the other hand, are impacted by the man-made changes in environmental conditions in a feedback loop. A way to quantify the total atmospheric load of reactive trace gases is the measurement of total OH reactivity, i.e. the loss rate of the most important tropospheric oxidant, the hydroxyl (OH) radical.

In this doctoral project, total OH reactivity measurements were used to investigate two points in the feedback loop of human activity and atmospheric reactants: Firstly, the *indirect* impact of anthropogenic climate change and deforestation, which will lead to an increasing frequency of drought and heat events in the Amazon rainforest, is thought to influence biogenic trace gas emissions. This was investigated using total OH reactivity observations during an extreme El Niño event. Secondly, *direct* human impact above the seaways around the Arabian Peninsula, detectable by anthropogenically emitted trace gases from ships and oil/gas production, was studied with total OH reactivity observations and a regional ozone formation assessment. The method-oriented part of this doctoral project was based on the need for robust, accurate long-term observations of total OH reactivity for understanding atmospheric photochemistry in the Anthropocene epoch.

During the drought and heat conditions of the extreme 2015/16 El Niño event, the diel cycle of total OH reactivity in the Amazon rainforest exhibited a striking difference to "normal" diel behavior. After the usual early afternoon OH reactivity maximum, a second, higher peak was observed during the sunset hours. A possible explanation for the increased sunset reactivity was found in stronger turbulent transport inside and above the canopy related with the changed meteorological conditions, combined with a stress-related release of monoterpenes and other (unmeasured) BVOCs by vegetation.

Total OH reactivity measured around the Arabian Peninsula was comparable to highly populated urban areas, due to a combination of shipping emissions and petrochemical pollution. The extreme regional ozone concentrations could be explained by a favorable mixture of NO_x and VOCs coupled with intense solar irradiation, causing rapid photochemical reactions.

A new Comparative Reactivity Method (CRM) instrument for long-term autonomous measurements of total OH reactivity was successfully characterized and tested in Helsinki. Interferences were quantified and compared to a model of the CRM reactor

chemistry. The total OH reactivity observed in winter in Helsinki was with an overall median of 7.6 s^{-1} at the lower end of worldwide urban observations.

In the first comprehensive intercomparison of OH reactivity measurements, the CRM method was compared to all other available instrument types by simultaneous measurements at an atmospheric simulation chamber. Results showed that the CRM device is suited for a range of atmospheric mixtures. However, significant deviations were seen under terpene-dominated and high NO conditions. A sensitivity towards ozone, which also impacted the size of the NO₂ interference, was newly discovered for CRM. Photolysis inside the reactor and the HO₂ concurrently produced with OH were identified as major sources of interferences and uncertainties. With the aim of improving the method, laboratory studies were conducted in the aftermath of the intercomparison, focusing on reducing photolysis and increasing CRM sensitivity.

Zusammenfassung

Seit Beginn der Industrialisierung und vermehrt seit den 1950er Jahren haben anthropogene Aktivitäten die Zusammensetzung der Erdatmosphäre signifikant verändert, was sich auf das Klima, das Wetter und die Gesundheit von Mensch und Ökosystemen auswirkt. Reaktive Spurengase sind einerseits Teil der anthropogenen Emissionen, die Luftverschmutzung verursachen und das Klima beeinflussen können, und andererseits werden sie in einem Rückkopplungskreislauf durch menschengemachte Änderungen der Umweltbedingungen beeinflusst. Eine Möglichkeit zur Quantifizierung der Gesamtheit reaktiver Spurengase in der Atmosphäre ist die Messung der OH-Gesamtreaktivität, also der Verlustrate des wichtigsten troposphärischen Oxidationsmittels, des Hydroxylradikals (OH).

In diesem Promotionsprojekt wurden Messungen der OH-Gesamtreaktivität verwendet, um zwei Punkte im Rückkopplungskreislauf zwischen menschlichen Aktivitäten und Spurengasen in der Atmosphäre zu untersuchen: Die *indirekten* Auswirkungen von anthropogenem Klimawandel und Entwaldung im Amazonasregenwald führen dort zu häufigeren Dürre- und Hitzeperioden. Es wird erwartet, dass diese sich auf biogene Spurengasemissionen auswirken, was mittels Messungen der OH-Gesamtreaktivität während eines extremen El Niño-Events untersucht wurde. Der *direkte* menschliche Einfluss entlang der Seewege um die Arabische Halbinsel durch anthropogen emittierte Spurengase von Schiffen sowie der Öl- und Gasförderung wurde mithilfe von Beobachtungen der OH-Gesamtreaktivität und einer Analyse der regionalen Ozonbildung charakterisiert.

Der methodenorientierte Teil dieser Doktorarbeit begründet sich in der Notwendigkeit robuster und langfristiger Beobachtungen der OH-Gesamtreaktivität mit hoher Messgenauigkeit, um atmosphärische Photochemie in der Epoche des Anthropozäns zu erfassen.

Während der Dürre- und Hitzeperiode des extremen El Niño-Events 2015/16 zeigte der Tagesgang der OH-Gesamtreaktivität im Amazonasregenwald einen auffallenden Unterschied zum „normalen“ Tagesgang: Nach dem üblichen OH-Reaktivitäts-Maximum am frühen Nachmittag wurde in den Sonnenuntergangsstunden ein zweiter, höherer Maximalwert beobachtet. Eine mögliche Erklärung für die erhöhte abendliche Reaktivität wurde in verstärktem turbulenten Transport in und über den Baumkronen, verursacht durch die veränderten meteorologischen Bedingungen, kombiniert mit stressinduziert durch die Vegetation freigesetzten Monoterpenen und anderen (nicht gemessenen) biogenen Spurengasen, gefunden.

Die entlang der Seewege rund um die Arabische Halbinsel gemessene OH-Gesamtreaktivität war vergleichbar mit der in dicht bevölkerten urbanen Regionen, was sich auf eine Kombination aus Schiffsemissionen und petrochemischer Luftverschmutzung zurückführen lässt. Die hohen Ozonkonzentrationen in der Region konnten

durch eine die Ozonbildung befördernde Mischung von NO_x und VOCs, gekoppelt mit beschleunigten photochemischen Reaktionen durch intensive Sonneneinstrahlung, erklärt werden.

Ein neues Comparative Reactivity Method (CRM)-Gerät für autonome Langzeitmessungen der OH-Gesamtreaktivität wurde erfolgreich charakterisiert und in Helsinki getestet. Interferenzen wurden quantifiziert und mit einem Modell der CRM-Reaktorchemie verglichen. Die im Winter beobachtete OH-Gesamtreaktivität in Helsinki war mit einem Median von 7.6 s^{-1} im unteren Bereich der Messwerte aus Städten weltweit.

Im ersten umfassenden Vergleich von OH-Reaktivitätsmessgeräten wurde mittels simultaner Messungen an einer Atmosphären-Simulationskammer die CRM-Methode mit allen anderen verfügbaren Messverfahren verglichen. Die Ergebnisse zeigten, dass CRM für eine Bandbreite atmosphärischer Zusammensetzungen geeignet ist. Signifikante Abweichungen wurden allerdings unter terpendominierten Bedingungen und bei hohen NO -Werten beobachtet. Eine Ozon-Interferenz im CRM, welche auch die Stärke der NO_2 -Interferenz beeinflusste, wurde entdeckt. Photolyse im Reaktor sowie das gleichzeitig mit OH produzierte HO_2 wurden als Hauptquellen der Interferenzen und Messunsicherheiten identifiziert. Mit dem Ziel, die Methode zu verbessern, wurden im Nachgang der Vergleichsmessungen Laborstudien mit einem Fokus auf die Verringerung der Photolyse und die Erhöhung der CRM-Sensitivität durchgeführt.

CHAPTER 1

Introduction: The complex chemical cocktail of the atmosphere

“In the course of my enquiries, I was (...) soon satisfied that atmospherical air is not an unalterable thing (...).”

Joseph Priestley (1775)

1.1 Atmospheric chemistry of reactive trace gases

Until the late 18th century, it was believed that “air” was an element. Pioneers like Karl Wilhelm Scheele, Antoine de Lavoisier, Henry Cavendish and Joseph Priestley were the first to find out that air consists of more than one chemical compound and that its composition is alterable. Nowadays, school children learn about the main components of the atmosphere that surrounds us (nitrogen [$\approx 78\%$], oxygen [$\approx 21\%$] and argon [$\approx 1\%$]). However, tens of thousands of important players in atmospheric chemistry are present at much lower concentrations than the % ranges - in the parts per billion (ppb) levels and below. These reactive trace gases are emitted by nature and by almost all human activities: Living organisms produce them by life processes and decay, and anthropogenic sources include fossil fuel combustion, biomass burning, solvents, agriculture and even household and personal care products (Hoesly et al., 2018; Koppmann, 2007; McDonald et al., 2018).

As the name suggests, reactive trace gases are everything but inert, and participate in complex atmospheric reaction processes (a simplified scheme is shown in Fig. 1.1). As toxic compounds, some reactive trace gases have direct human health effects. Through oxidation processes, reactive trace gases impact the formation of ozone and particles, and alter the oxidative capacity of the atmosphere - which in turn influences the lifetime of greenhouse gases such as methane. Therewith, they influence the Earth’s climate, and the health of both ecosystems and humankind.

Organic reactive trace gases: Volatile organic compounds (VOCs)

Volatile organic compounds (VOCs) are carbon containing trace gases including all vapor phase organics except carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4). The existence of organic trace gases in ambient air was known already at the beginning of the 20th century (Gärtner, 1922), but chemical identification was limited to few compounds like formaldehyde, methane and CO_2 (Glueckauf, 1951; Kersey et al., 1940). Shepherd et al. (1951) succeeded to identify 20 different hydrocarbons from Los Angeles smog. By 1978, 606 VOC species had been discovered and the number increased to 2857 in 1978. Nowadays, the estimated number of so far observed VOCs is 10^4 – 10^5 , and a far greater sum is thought to remain unknown to date (Goldstein and Galbally, 2007).

On a global scale, biogenic VOCs (BVOCs) dominate the total VOC emissions with 760 – $1000 \text{ Tg(C)} \cdot \text{yr}^{-1}$ (Guenther et al., 2012; Sindelarova et al., 2014). BVOCs have ecological and physiological roles ranging from carbon metabolism to abiotic and biotic stress mitigation or signaling (Loreto et al., 2004). Anthropogenic VOC emissions are ca. a factor of 6 lower with a recent estimate of 150 – $160 \text{ Tg(VOC)} \cdot \text{yr}^{-1}$ globally (Hoesly et al., 2018). However, the distribution of sources is not uniform: anthropogenic emissions occur mostly between 40° and 50° North, whereas BVOCs

*For better comparison with the numbers given for anthropogenic emissions: This equals ca. 860 – $1100 \text{ Tg(VOC)} \cdot \text{yr}^{-1}$.

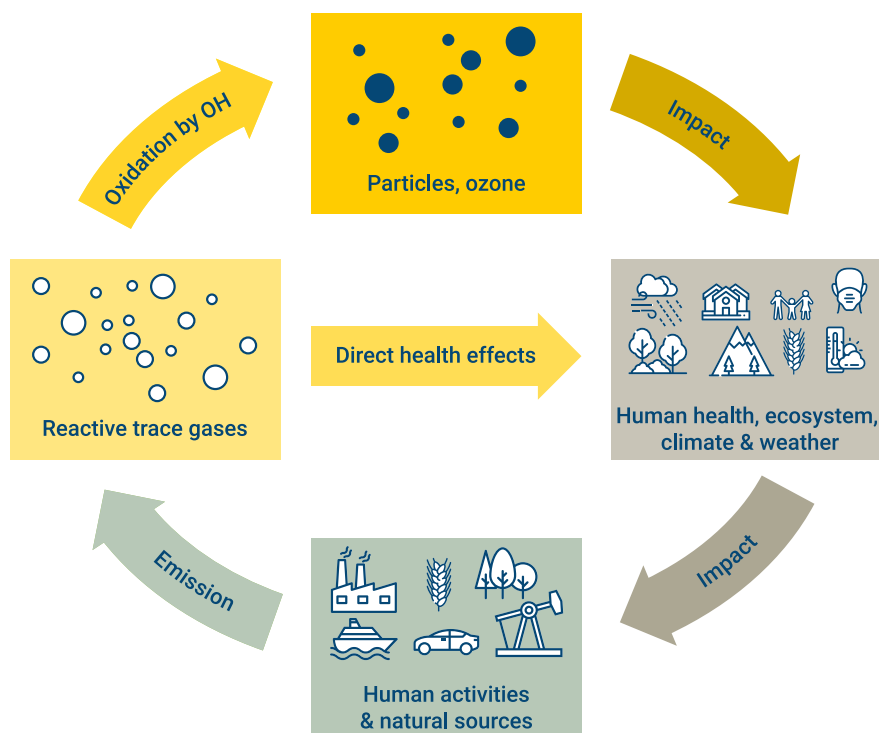


Figure 1.1: Simplified schematic of the feedback cycle connecting reactive trace gases with humans and ecosystems. Adapted from Boucher et al. (2014), Fuzzi et al. (2006), Suni et al. (2015), and Wilson et al. (2019).

are mainly emitted in the tropics. Anthropogenic VOC emissions have approximately tripled since 1950 and are still increasing in Africa and Asia while having leveled out in Europe and America (Hoesly et al., 2018).

Atmospheric oxidation of volatile organic compounds

As Priestley already noted in 1775, “atmospheric air is not an unalterable thing” – once emitted to the atmosphere, VOCs can undergo transport processes, photolyse, be removed physically by dry or wet deposition, or undergo chemical reactions.

Air pollution in large industrialized cities triggered the evolution of atmospheric chemistry research starting from the 1950s. Haagen-Smit (1952) discovered that volatile organic compounds react with nitrogen oxides (NO_x) to form ozone (O_3) – an air pollutant that causes irritation of the respiratory tract and damages plant’s leaves, therewith causing health risks, agricultural and ecosystem losses. Tropospheric ozone also is a climate relevant greenhouse gas.

The pathway of ozone formation from VOCs and NO is initiated by the hydroxyl (OH) radical, the most important* sink of organic trace gases in the atmosphere (Denman et al., 2007; Lelieveld et al., 2016b). OH is formed in the troposphere from singlet oxygen ($\text{O}(^1\text{D})$) and water vapor under the influence of sunlight:



The VOCs react with OH on different timescales (seconds to days), yielding peroxy radicals that subsequently can form peroxides, carbonyls, alcohols and other oxy-

*Other oxidants being NO_3 (mainly at nighttime), ozone and halogen radicals.

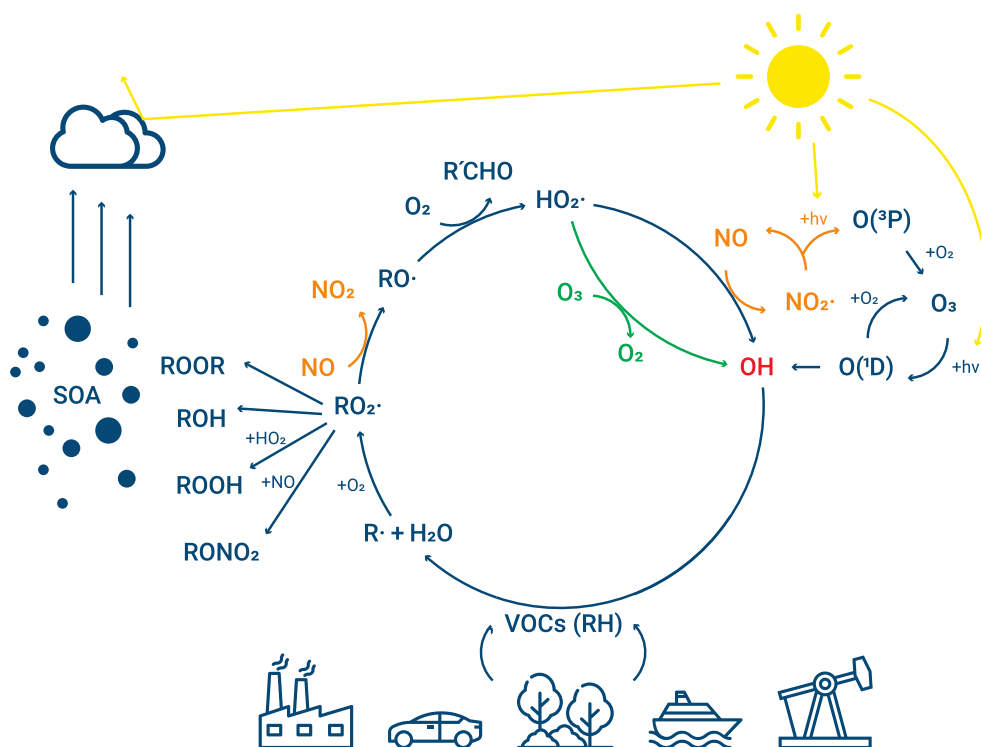
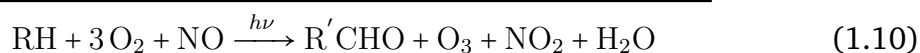
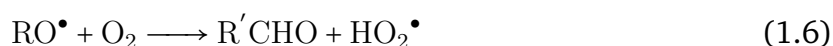


Figure 1.2: The reaction cycle of VOCs with the OH radical and its interconnection to NO_x, O₃, oxygenated VOCs and SOA (secondary organic aerosol). SOA can act as cloud condensation nuclei with implications for radiative forcing. Green arrows: ozone destruction under pristine conditions; orange arrows: NO_x presence leading to ozone formation.

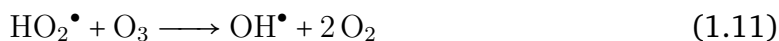
generated VOCs (OVOCs, see eqs. 1.3–1.6 and Fig. 1.2). These often have different chemical and physical properties than their precursors, mostly including a lowered vapor pressure. Depending on these properties, the OVOCs either remain available for further chemical reactions, aggregate to form secondary organic aerosol (SOA; Ahlberg et al., 2017; Donahue et al., 2012; Zhao et al., 2015), or are removed from the atmosphere by deposition. When SOA particles act as cloud/ice condensation nuclei, they influence the Earth's radiation budget and hydrological cycle. This feeds back on humans and ecosystems (Fig. 1.1).

Ozone is formed from the VOC photooxidation process when there is nitrogen oxide (NO) present (i.e. in polluted environments):



where R is an organic group and M a third body, usually N₂ or O₂.

When there is no NO present (as in very pristine environments), ozone is destroyed instead by reacting with organoperoxy or hydroperoxy radicals, e.g.:



The above discussions show that reactive trace gases are major fuels of tropospheric oxidation chemistry. Through the secondary formation of different gaseous and particulate products, VOC oxidation chemistry impacts multiple processes of physical, chemical, meteorological and climatic relevance. Through the chemical reactions described above, VOC emissions ultimately increase the concentrations of the greenhouse gases CO_2 , CH_4 and O_3 , which is why VOCs overall have an amplifying effect on global radiative forcing and, therewith, climate change (Myhre et al., 2014).

1.2 Total OH reactivity: a holistic perspective on reactive trace gases

As the main sink for VOCs and other reactive trace gases in the troposphere is the hydroxyl (OH) radical, the lifetime of a VOC is predominantly determined by its reaction rate with OH:

$$\frac{d[\text{VOC}]}{dt} = -k[\text{VOC}][\text{OH}] \quad (1.12)$$

$$\tau_{\text{VOC}} = \frac{1}{k[\text{OH}]} \quad (1.13)$$

where $[\text{VOC}]$ is the concentration of a VOC [molecules cm^{-3}], k its reaction rate coefficient with OH [$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$], and τ_{VOC} its lifetime [s].

A measure for the *combined* effect of all reactive trace gases (including VOCs and inorganic trace gases) in ambient air, i.e., the total OH sink (or OH loss frequency), is termed the total OH reactivity. Total OH reactivity is a fundamental property of the atmosphere, determining the lifetime of the OH radical and therewith influencing atmospheric oxidation capacity. As OH is the dominant oxidant, total OH reactivity also describes the total load of reactive trace gases capable of participation in tropospheric formation of ozone and SOA (see Sect. 1.1).

Total OH reactivity is, analogous with eq. 1.13 but for τ_{OH} , the sum of all individual compound OH loss rates (reactivities):

$$k_{\text{total}}[X_i] = R_{\text{total}} = R_{\text{VOC}_1} + R_{\text{VOC}_2} + R_{\text{VOC}_3} + \dots = \sum_i k_{\text{OH}+X_i}[X_i] \quad (1.14)$$

where R_{total} is the total OH reactivity [s^{-1}], R_{VOC} is the OH loss rate (or reactivity) of a VOC [s^{-1}], $[X_i]$ are trace gas concentrations [molecules cm^{-3}] and $k_{\text{OH}+X_i}$ the respective reaction rate coefficient of the trace gas with OH [$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$]. The inverse of R_{total} is the lifetime of the OH radical in the air sample.

1.2.1 Relevance of total OH reactivity

Total OH reactivity is useful in providing **a measure for the atmospheric load of OH reactants without relying on the completeness of individual observation methods**. This enables an effect-oriented perspective on VOC regulation policies for air quality: In a reactivity-based instead of a VOC mass-based approach, reactants with low concentration but large environmental effect are not overlooked, because OH reactivity directly relates to the formation of secondary pollutants, i.e. ozone and particles.

Furthermore, total OH reactivity can help in the understanding of atmospheric processes through

- ♦ Calculation of local **OH radical production** (e.g. Whalley et al., 2011) when both measurements of OH concentrations and of total OH reactivity are available. Assuming a photostationary steady state, OH production ($P(OH)$) is balanced by OH loss (i.e. OH reactivity):

$$P(OH) = [OH] \cdot R_{\text{total}} \quad (1.15)$$

This allows the investigation of radical closure. As significant missing sources for OH radicals have been found in several field measurements (Hofzumahaus et al., 2009; Lelieveld et al., 2008; Lu et al., 2013), a complete understanding of HO_x budgets is useful for constraining photochemical models.

- ♦ Determining the **OH lifetime** as the inverse of total OH reactivity, which is connected to the **atmospheric oxidation capacity** and therewith the residence time of atmospheric pollutants/greenhouse gases such as methane. The global methane budget still poses a challenge for models (Zhao et al., 2019).
- ♦ Calculation of **ozone production potential and ozone production regimes**. Total OH reactivity is needed for a quantitative understanding of ozone production and can help inferring its sensitivity to VOCs and NO_x (Kirchner et al., 2001; Pusede et al., 2014; Sinha et al., 2010; Yang et al., 2017), see chapter 3.
- ♦ Revealing the presence of **unmeasured atmospheric constituents** for atmospheric photochemistry. When compared to the OH reactivity calculated from all individually measured compounds (termed the speciated OH reactivity), total OH reactivity can be used to infer the occurrence of unmeasured atmospheric constituents (termed the unattributed or “missing” OH reactivity).

1.2.2 Total OH reactivity measurement methods

Before techniques for the direct measurement of total OH reactivity became available, it was calculated by summing the OH reactivity contributed by individually measured compounds. Knowing that typical field measurements cover a few dozens of VOCs while the actual number of different VOCs present in ambient air may be several magnitudes higher (see Sect. 1.1), it is evident that this method only provided a lower limit. The first direct measurements of total OH reactivity were conceived by two groups independently and published around 2000 (Calpini et al., 1999; Kovacs and Brune, 2001). To date, direct observation of OH reactivity has been realized with the following four methods:

- a) Direct OH loss rate measurement by flow-tube technique with laser-induced fluorescence (**flow-tube LIF**; Kovacs and Brune, 2001)

- b) Direct OH loss rate measurement by laser photolysis–laser-induced fluorescence (**LP-LIF/pump-probe LIF**; Sadanaga et al., 2004)
- c) Direct OH loss rate measurement by flow-tube technique with chemical ionization mass spectrometry (**CIMS**; Muller et al., 2018)
- d) Comparative Reactivity Method (**CRM**; Sinha et al., 2008)

The first three methods listed here are based on the direct measurement of time-dependent OH decay. They either detect OH spectroscopically (by laser-induced fluorescence; a, b) or chemically (with OH being converted to sulfuric acid and observed by mass spectrometry, c). In the flow-tube methods (a, c), OH is produced continuously and reacts with the air sample in a flow tube. The time-resolved OH decay is measured by varying the reaction time using a movable injector to produce OH. In pump-probe LIF, OH is produced by ozone photolysis not continuously but in a short laser pulse. The OH reacts with ambient reactants and its decay is followed with high time resolution.

A disadvantage of these three methods is the complexity of the setup and the large air flows needed (between 10 and 2280 L min⁻¹; Fuchs et al., 2017a). With the goal of developing a more affordable and transportable approach to total OH reactivity measurements for field measurements, an indirect method was conceived at the Max Planck Institute for Chemistry in Mainz (Sinha et al., 2008). It is called the Comparative Reactivity Method because it is based on comparing the (known) reactivity of a reference species with the reactivity of atmospheric reactants. A detailed description will follow in Sect. 1.2.3.

1.2.3 The Comparative Reactivity Method (CRM)

In the Comparative Reactivity Method, a reference species competes with the reactive species in the air sample for the reaction with artificially produced OH, and the resulting concentration change of the reference species is used to calculate the total OH reactivity (Sinha et al., 2008). The most widely used reference species is pyrrole, because it is typically not present in ambient air and reacts with OH at a similar rate as many atmospheric constituents ($k_{\text{OH}+\text{pyrrole}} = 1.26 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, rate coefficient from Dillon et al. (2012) weighted after Keßel, 2016).

Pyrrole is fed into a glass reactor (Fig. 1.3) together with humidified nitrogen ($\approx 50\text{--}90 \text{ mL min}^{-1}$) and ambient or zero air ($\approx 250\text{--}500 \text{ mL min}^{-1}$). Pyrrole concentrations (range $\approx 20\text{--}70 \text{ ppb}$) are monitored constantly by a suitable detector. In most cases, proton transfer reaction mass spectrometry (PTR-MS; Hansel et al., 1995; Lindinger and Jordan, 1998) is applied, although gas chromatography with a photo ionization detector (GC-PID) is applicable, too (Nölscher et al., 2012b; Praplan et al., 2017). A pen-ray mercury UV lamp (λ 185 nm) in the nitrogen arm of the reactor photolyzes water ($\lambda = 185 \text{ nm}$), producing OH radicals:



For determining total OH reactivity, three different measurement modes (C1–C3) are used (Fig. 1.4):

- ♦ **C1:** Pyrrole + zero air + humidified nitrogen + OH scavenger
- ♦ **C2:** Pyrrole + zero air + humidified nitrogen
- ♦ **C3:** Pyrrole + ambient air + humidified nitrogen

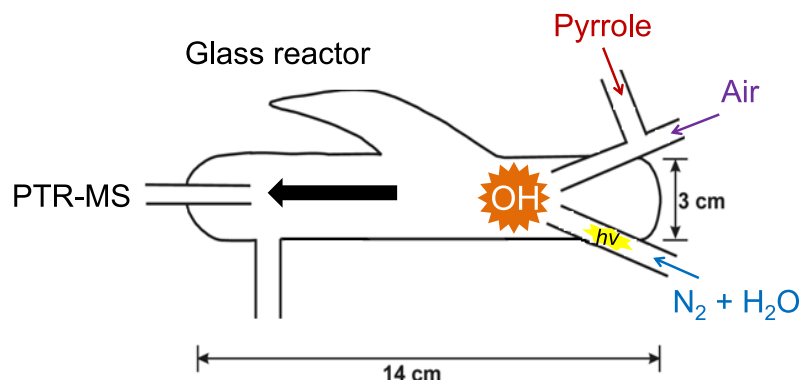


Figure 1.3: Reactor used for the Comparative Reactivity Method. " $h\nu$ " signifies the position of the UV lamp. PTR-MS is the detector (proton transfer reaction mass spectrometer).

C1 represents a maximum level of pyrrole (typically 50–70 ppb) in which no OH is present to react with. The UV lamp has to be kept on during C1 to account for pyrrole photolysis (2–15 % depending on lamp position). Instead of drying out the reactor to stop OH production, a more time efficient approach was developed by Michoud et al. (2015), where an excess concentration of propane is used as an OH scavenger. In **C2** mode, OH is not scavenged, so part of the pyrrole reacts with it, and the pyrrole level decreases to a minimum (typically 20–30 ppb). The difference between C1 and C2 represents the apparent OH concentration* in the reactor.

In **C3** mode, ambient air is introduced into the system. Reactive trace gases from the air sample react with part of the OH radicals. Due to this competition, the pyrrole level increases depending on the OH reactivity of the air sample. The total OH reactivity is then calculated from C1–C3 as follows:

$$R_{\text{total}} = C1 \cdot k_{\text{OH+pyrrole}} \cdot \frac{C3 - C2}{C1 - C2} \quad (1.17)$$

where C1, C2 and C3 are the pyrrole concentrations from the respective modes in molecules cm^{-3} and $k_{\text{OH+pyrrole}}$ is the reaction rate coefficient of pyrrole with OH in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Since its introduction, the Comparative Reactivity Method has been adopted by several research groups. Field observations made by CRM are marked in Tables 1.1 and 1.2. Recently, the method has been adapted for observation of total chlorine radical reactivity (Keßel, 2016).

Interferences and corrections in CRM

The CRM system is subject to several interferences and deviations. Therefore, the experimentally derived pyrrole levels C1–C3 cannot directly be inserted into the CRM equation (eq. 1.17). Figure 1.5 shows the whole data processing flow. In order to derive the correct total OH reactivity at the end, the raw signals need to be corrected for[†] (numbers refer to Fig. 1.5):

*During C3 mode, additional OH can be produced by aldehyde oxidation, peroxy radical photolysis (see Chapter 5) or HO_2 reactions (see Sect. 1.2.3).

[†]For an elaborate description of CRM characterizations, corrections and uncertainties, the reader is referred to Chapter 4.

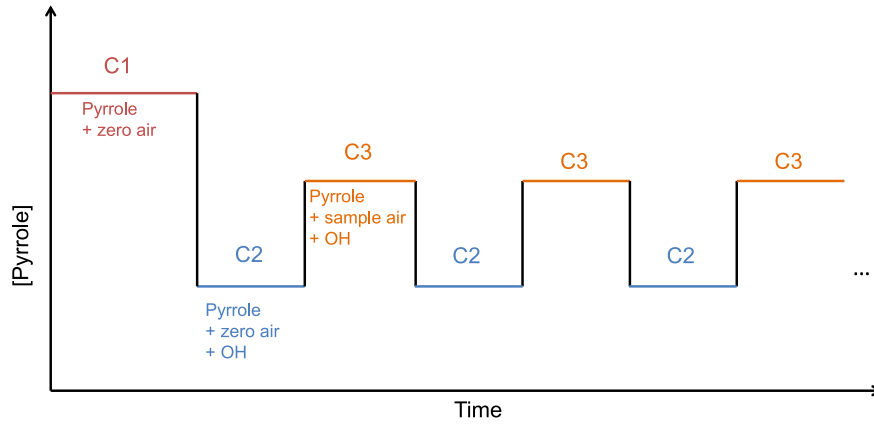


Figure 1.4: Schematic representation of measurement modes in CRM.

- 1) **Humidity dependence of the PTR-MS signal.** Following de Gouw (2003), the pyrrole signal ($m68$)* is normalized:

$$m68[ncps] = \frac{m68[cps] \cdot 10^6 \cdot p_{drift} \cdot 298.15 \text{ K}}{m21[cps] \cdot 500 + Z \cdot m37[cps] \cdot 2 \text{ mbar} \cdot T_{drift}} \quad (1.18)$$

where $m21$ and $m37$ are signals of the primary ion isotope (H_3O^{18+}) and first water cluster ($\text{H}_3\text{O}^+ x \text{H}_2\text{O}$) in the PTR-MS, respectively. p_{drift} and T_{drift} represent drift temperature and pressure, respectively. Z is an experimentally derived factor from measuring a stable pyrrole mixing ratio (while the UV lamp is off) at different humidity levels.

- 6) **Humidity difference between C2 and C3.** During C2 measurements, ambient air passes through a catalytic converter which converts all VOCs to CO_2 and water (and removes $\approx 90\%$ of NO_x , see Keßel, 2016). Humidity can differ between C2 (background) and C3 (ambient air). This difference has to be accounted for because the amount of OH radicals generated in the reactor depends on humidity (Sinha et al., 2008). C2 mixing ratios are therefore corrected using a relationship derived from an empirical test where the OH field in the reactor is varied by monitoring a stable pyrrole level at different humidity levels with the UV lamp on (Michoud et al., 2015). This results in a parametrization of the format:

$$\text{C2}_{corr} = \text{C2} + a \left(\left[\frac{m37}{m19} \right]_{C3}^2 - \left[\frac{m37}{m19} \right]_{C2}^2 \right) + b \left(\left[\frac{m37}{m19} \right]_{C3} - \left[\frac{m37}{m19} \right]_{C2} \right) \quad (1.19)$$

where C2_{corr} is the corrected C2 level in ppb, a and b are empirical factors, and $\frac{m37}{m19}$ is the ratio of the PTR-MS signals of the first water cluster ($\text{H}_3\text{O}^+ x \text{H}_2\text{O}$) versus the primary ion (H_3O^+).

- 7) **OH recycling interferences during C3.** Inside the CRM reactor, H radicals are generated alongside with OH following reaction 1.16, which leads to HO_2 (hydroperoxyl) radical production:



*i.e. mass-to-charge ratio = $m/z = 68$

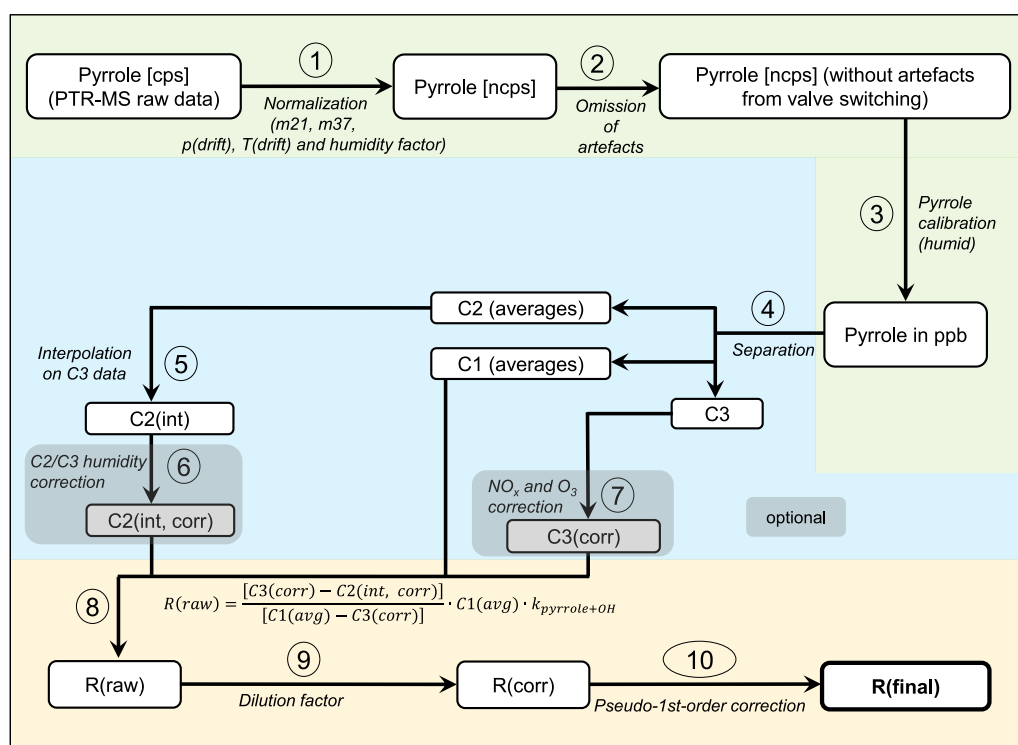


Figure 1.5: Schematic representation of the CRM data analysis procedure from raw pyrrole signal to total OH reactivity, including the corrections described in Sect. 1.2.3 (graphic adapted from Keßel, 2016). R stands for OH reactivity; corr = corrected; int = interpolated.

The HO₂ mixing ratio in the CRM reactor is estimated to be ca. 200 ppb (Keßel, 2016). This causes sensitivities towards NO_x and ozone (O₃) in the system, because their reaction with HO₂ can recycle OH radicals. This additional OH decreases the C3 level and therefore would lead to an underestimation of OH reactivity if not accounted for. Keßel (2016) investigated the effect of different VOCs present simultaneously with NO_x and found that the NO_x interference was independent from the presence of all tested VOCs.

- 7a) **NO interference.** The NO sensitivity of the CRM system can be explained by the reaction of NO with hydroperoxyl radicals, forming OH and NO₂ (eq. 1.7).
- 7b) **NO₂ interference.** NO₂ does not directly recycle OH, but is photolyzed by UV light, which partly enters the reactor, yielding NO as shown in eq. 1.8. The NO thus formed then continues with reaction 1.7. Photolysis is minimized by increasing the distance between lamp tip and reactor (Keßel, 2016).
- 7c) **Ozone interference.** When HO₂ reacts with ozone, OH and oxygen are produced (eq. 1.11). Additionally, ozone photolysis yields further OH (eqs. 1.1 and 1.2). This interference was discovered during this dissertation project and seems to depend strongly on the individual CRM reactor/lamp setup (and therewith the ozone background and HO₂ production), as it has not been observed in all systems (see chapters 4 and 5).

Corrections for ozone, NO₂ and NO are determined by feeding known amounts of these gases separately or combined* into the reactor in C3 mode while monitoring the change in pyrrole mixing ratio. The resulting parametrization is of the form:

$$C3_{corr} = C3 + c [NO]^2 + d [NO] + e [NO_2]^2 + f [NO_2] + g [O_3] \quad (1.21)$$

where $C3_{corr}$ is the corrected C3 pyrrole mixing ratio, c–g are empirically derived factors and $[X]$ are mixing ratios of the respective compounds.

- 10) **Deviation from pseudo-first-order conditions inside the reactor.** The CRM equation (eq. 1.17) assumes pseudo-1st-order conditions inside the reactor (i.e. $[pyrrole] \gg [OH]$). This condition cannot be met while preserving a reasonable sensitivity (C3–C2 difference; Sinha et al., 2008). CRM is typically operated at pyrrole/OH ratios of 1.5–3. Sinha et al. (2008) introduced a numerical modeling method to correct for this deviation from pseudo-1st-order conditions. Michoud et al. (2015) found out that the complexity of the reactions inside the CRM reactor causes empirical corrections to yield more reliable results. This is especially due to additional OH formation from peroxy radical photolysis (e.g. Hansen et al., 2017). The deviation from pseudo-1st-order depends on the pyrrole/OH ratio and on the reaction rate constant of the measured trace gas towards OH. Compounds with fast reaction rates (comparable to that of pyrrole) require the largest correction because their concentration inside the reactor decreases at a similar rate as that of pyrrole, leading to an underestimation of their reactivity.

The experimentally derived correction factor is determined by adding certified calibration gases to the CRM system in known amounts, i.e. known total OH reactivities, at varying humidity (i.e. pyrrole/OH ratio). The correction factors "F" for different calibration gases represent the slope of expected vs. observed OH reactivity and are combined in one pyrrole/OH dependent equation (Michoud et al., 2015):

$$F = m \cdot \frac{[pyrrole]}{[OH]} + n \quad (1.22)$$

where F is the correction factor to be applied to raw OH reactivity calculated with the CRM equation, and m and n are empirically derived. This approach is valid for air samples dominated by chemically similar species. In an adapted procedure for changing trace gas mixtures, correction factors for different chemical families are weighted according to the measured composition of the ambient air at the moment of observation (see Chapter 3).

The size of each correction naturally depends on external conditions such as concentrations of OH recycling compounds, humidity (and velocity of its change), or air sample composition. The corrections also impact the uncertainty of the final OH reactivity value. The total uncertainty is propagated from the precision of the PTR-MS signal, the uncertainties of the calibration, of each correction, of the flows and of the reaction rate coefficient (see in detail in Chapter 4). Figure 1.6 depicts the dependency of the total uncertainty on the total OH reactivity for two field measurement

*Note that both NO and NO₂ can react with ozone, influencing the correction when both ozone and NO_x are present at the same time. Experiments for determining a correction for such a combined interference case are described in Appendix A.

campaigns. The difference between both curves at low reactivities is due to using different PTR-MS instruments with different signal precision. For typical OH reactivity ranges, the 1σ uncertainty in CRM is 25–50 %.

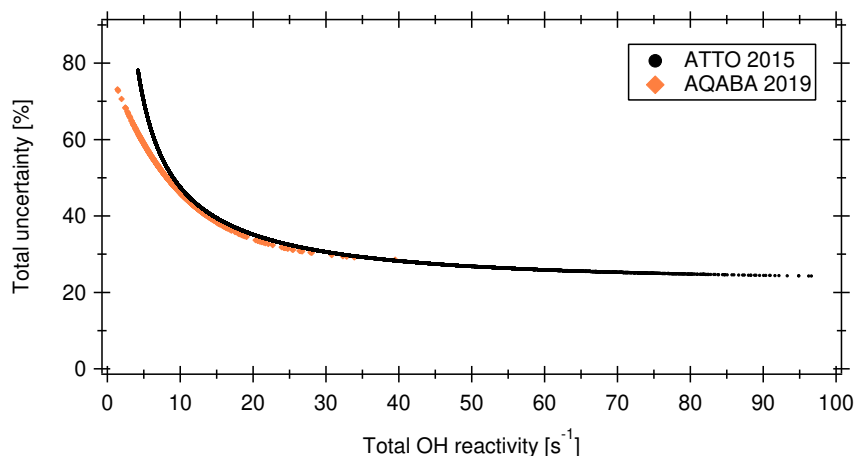


Figure 1.6: Total relative uncertainty of the total OH reactivity measured in November 2015 at the Amazon Tall Tower Observatory site (see Chapter 2) and in July/August 2019 during the AQABA shipborne campaign (see Chapter 3), dependent of the size of the OH reactivity. The difference between both curves at low reactivities is due to the PTR-MS signal precision.

1.2.4 Worldwide observations of total OH reactivity

Since the development of the first techniques for direct OH reactivity observation, ambient measurements have been conducted in many different locations around the world.

Total OH reactivity varies spatially, diurnally, seasonally and vertically. The diel and seasonal variations in OH reactivity can be due to changes in plant metabolism (for biogenic emissions) or in human behavior such as morning rush hour and seasonal heating (for anthropogenic emissions). The spatial variation evident from Fig. 1.7 reflects the global distribution of VOC sources discussed in Sect. 1.1. Biogenic OH reactivity is largest in the tropics, whereas the northern hemisphere is rich in anthropogenic reactive emissions, especially in winter. However, it has to be noted that direct OH reactivity measurements on the southern hemisphere are so far limited to three locations in tropical forests.

Ranges of OH reactivity observed

The graphical overview in Figs. 1.7 and 1.8 shows that forests and megacities generally are environments with largest OH sinks. The highest peak OH reactivities up to $> 200 s^{-1}$ have been observed in the tropical Amazon rainforest canopy (Nölscher et al., 2016) and in Mexico City (Shirley et al., 2006). Extreme values have also been measured in some rural and suburban regions such as the Indo-Gangetic Plain after biomass burning (Kumar et al., 2018) and the densely populated Pearl River Delta in China (Lou et al., 2010). In environments dominated by marine influence, the detected maximum reactivities are much lower (e.g. Ingham et al., 2009; Ramasamy et al., 2016; Sinha et al., 2012; Zannoni et al., 2017 and Chapter 3 in this work). This can be explained by the fact that the sea does not emit large amounts of highly

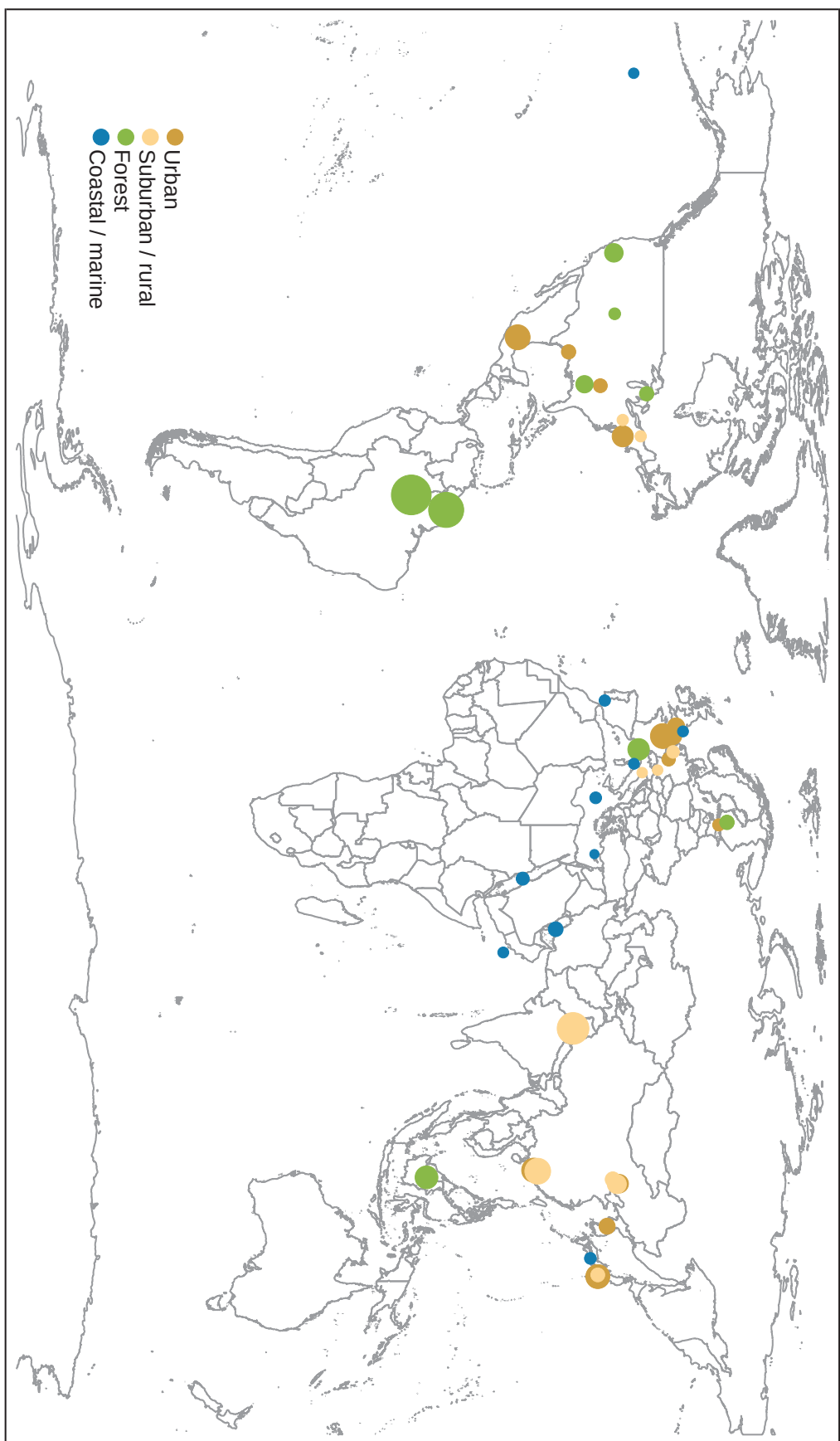


Figure 1.7: Overview of direct measurements of total OH reactivity worldwide. Colors indicate the type of environment, circles are scaled by the average or median OH reactivity observed. References are given in Tab. 1.1 and Tab. 1.2.

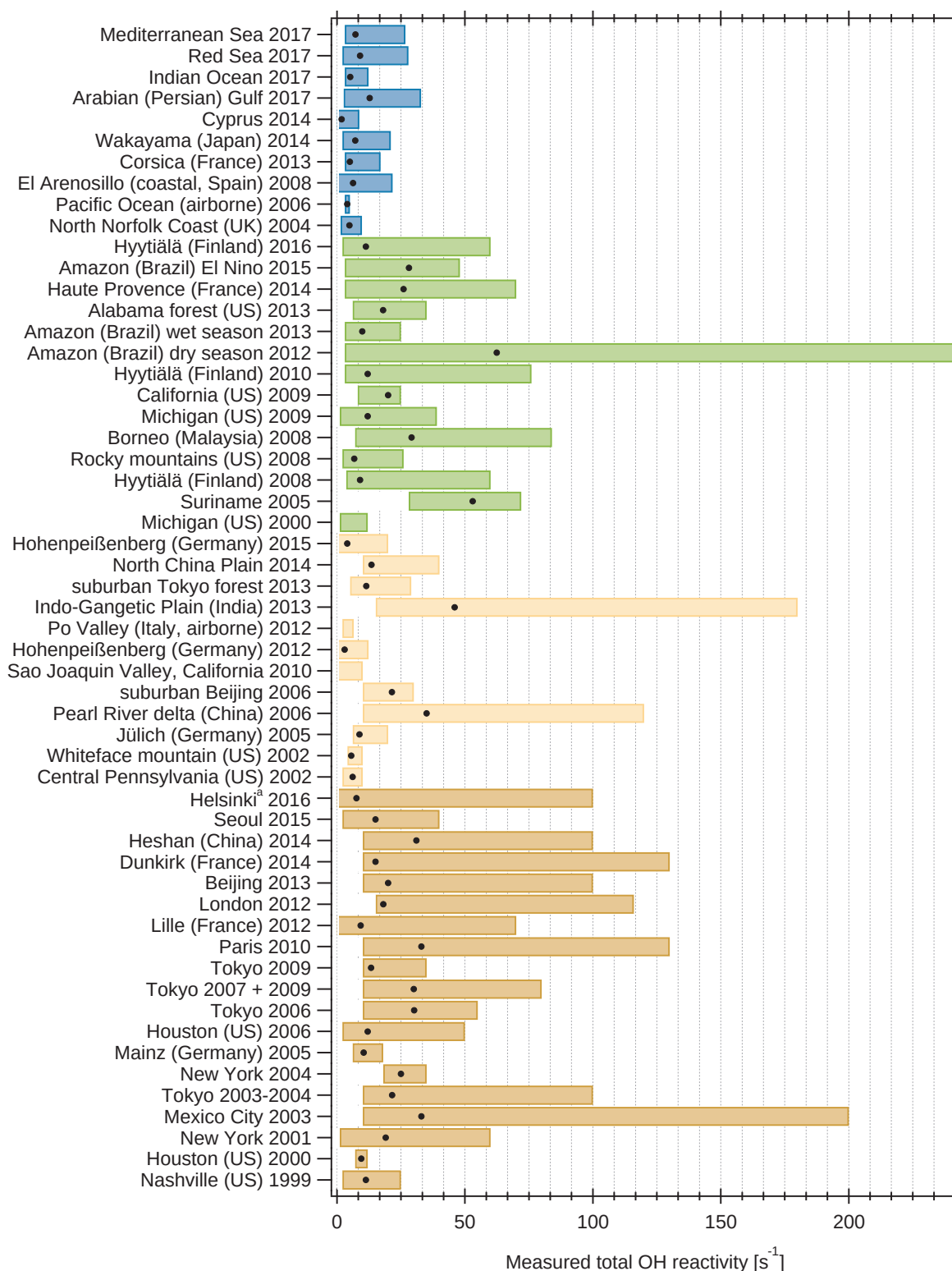


Figure 1.8: Overview of direct measurements of total OH reactivity worldwide grouped by environment (color coding same as in Fig. 1.7). Bars show ranges of observed values, circles the average or median given in the corresponding literature. References are given in Tab. 1.1 and Tab. 1.2. (^a Maxima are influenced by on-site local emissions and therefore not representative for the urban background.)

reactive trace gases, whereas terrestrial plants and human activities such as fossil fuel combustion do. Dominant OH reactants in forests are isoprene (lifetime* (τ) towards OH $\approx$ 1.4 h) and monoterpenes ($\tau \approx$ 23 min [α -terpinene]–2.6 h [α -pinene, camphene]). In cities, the OH sink has often been reported to be dominated by nitrogen oxides ($\tau(\text{NO}_2) \approx$ 14.2 h, $\tau(\text{NO}) \approx$ 14.3 h), carbon monoxide ($\tau \approx$ 40 days) and anthropogenic hydrocarbons (e.g. $\tau(\text{propene}) \approx$ 5.3 h, $\tau(m\text{-xylene}) \approx$ 5.9 h).

Unattributed OH reactivity

Tables 1.1 and 1.2 provide an overview of OH reactivity field measurements worldwide including the unattributed (“missing”) fraction. Unattributed OH reactivity (see Sect. 1.2.1) was observed in the majority of studies, with especially large fractions in biogenic environments (Williams and Brune, 2015; Yang et al., 2016). Up to several tens per second of unattributed OH reactivity were detected in a Michigan forest (Di Carlo et al., 2004; Hansen et al., 2014), in a Finnish boreal forest (Nölscher et al., 2012a) and in the Amazon rainforest (Nölscher et al., 2016). In contrast, some anthropogenic environments such as New York (Ren et al., 2003), Houston (Mao et al., 2010), Seoul (Kim et al., 2016) and the North China Plain (Fuchs et al., 2016) displayed no or low unattributed reactivities. However, significant unattributed fractions were observed in other urban areas such as Paris (Dolgorouky et al., 2012), Tokyo (Yoshino et al., 2012) or Beijing (Yang et al., 2017). Comparing the unattributed fractions between studies is, however, difficult, because the range and chemical detail of OH reactants observed differs.

In some cases, taking into account modeled oxygenated VOCs (OVOCs) closed the gap between measured and calculated OH reactivity (Kaiser et al., 2016; Lou et al., 2010; Whalley et al., 2016). Progress in PTR-MS instrumentation recently led to the possibility of monitoring a wider range of ambient OVOCs by Time-of-Flight (ToF) detectors. An OH reactivity flux experiment with simultaneous PTR-ToF-MS observations in a mixed forest in Michigan showed that 99 % of the upward reactivity flux could be explained by just 18 compounds, while 134 compounds were necessary for explaining 99 % of the downward reactivity flux (Millet et al., 2018). Chapter 3 explores to what extent a wide range of VOCs and especially OVOCs measured by PTR-ToF-MS can explain the total OH reactivity in an environment dominated by anthropogenic air pollution.

The discussion of worldwide field measurements shows that increasing chemical detail of atmospheric observations could reduce unattributed OH reactivity. However, accounting for all relevant OH reactive compounds individually with quantitative measurements was and is currently still often unfeasible. This underlines the value of the total OH reactivity for a complete picture of relevant OH sinks, ozone and secondary organic aerosol production potentials.

*Lifetimes were calculated using $[\text{OH}] = 2 \cdot 10^6 \text{ molecules cm}^{-3}$ and reaction rate constants from IUPAC (2018).

Table 1.1: Overview of total OH reactivity measurements in urban and suburban environments. Measurements using CRM are marked by *.

Site and year	Season	OH reactivity range [s ⁻¹]	OH reactivity average/median [s ⁻¹]	Unattributed OH reactivity	Reference
Nashville (US) 1999	Summer	2–25	11.3	31 %	Kovacs et al., 2003; Martinez et al., 2003
Houston (US) 2000	Summer	7–12	9.5	0 %	Mao et al., 2010
New York 2001	Summer	1–60	19	0 %	Ren et al., 2003
Mexico City 2003	Spring	10–200	33	0 %	Shirley et al., 2006
Tokyo 2003–2004	Year-round	10–100	21.5	0 %	Sadanaga et al., 2004; Yoshino et al., 2006
New York 2004	Winter	18–35	25	50 %	Ren et al., 2006a
Mainz (Germany) 2005*	Summer	6–18	10.4		Sinha et al., 2008
Houston (US) 2006	Summer	2–50	12	0 %	Mao et al., 2010
Tokyo 2006	Summer	10–55	30.12	30 %	Chatani et al., 2009
Tokyo 2007 + 2009	Winter, autumn	10–80	30	15 %	Yoshino et al., 2012
Tokyo 2009	Spring	10–35	13.33	30 %	Kato et al., 2011
Paris 2010*	Winter	10–130	33	50 %	Dolgorouky et al., 2012
Lille (France) 2012*	Autumn	0–70	9.25	0 %	Hansen et al., 2015
London 2012	Summer	15–116	18.1	20 %	Whalley et al., 2016
Beijing 2013*	Summer	10–100	20	21 %	Williams et al., 2016; Yang et al., 2017
Dunkirk (France) 2014*	Summer	10–130	15		Michoud et al., 2015
Heshan (China) 2014*	Autumn	10–100	31	32 %	Yang et al., 2017
Seoul 2015*	Spring	2–40	15	0 %	Kim et al., 2016
Helsinki 2016*	Winter	0–100 ^a	7.6	40 %	This work; Praplan et al., 2017
Central Pennsylvania (US) 2002	Spring	2–10	6.1		Ren et al., 2005
Whiteface mountain (US) 2002	Summer	4–10	5.6	0 %	Ren et al., 2006b
Jülich (Germany) 2005	Summer	6–20	8.8	40 %	Elshorbany et al., 2012
Pearl River delta (China) 2006	Summer	10–120	35	50 %	Lou et al., 2010
suburban Beijing 2006	Summer	10–30	21.45	0 %	Lu et al., 2013; Lu et al., 2010
Sao Joaquin Valley, California (US) 2010	Summer	0–10		0 %	Pusede et al., 2014
Hohenpeißenberg (Germany) 2012*	Summer	0–12.3	3	23 %	Keßel, 2016
Po Valley (airborne, Italy) 2012	Summer	2–6.5		0 %	Kaiser et al., 2015
Indo-Gangetic Plain (India) 2013*	Spring	15–180	46	40 %	Kumar et al., 2018
suburban Tokyo forest 2013	Summer	5–29	11.4	11 %	Ramasamy et al., 2018
North China Plain 2014	Summer	10–40	13.5	0 %	Fuchs et al., 2017b
Hohenpeißenberg (Germany) 2015	Year-round	0–20	4		Muller et al., 2018

^a Maxima are influenced by on-site local emissions and therefore not representative for the urban background.

Table 1.2: Overview of total OH reactivity measurements in forested and marine/coastal environments. Measurements using CRM are marked by *.

Site and year	Season	OH reactivity range [s ⁻¹]	OH reactivity average/median [s ⁻¹]	Unattributed OH reactivity	Reference
Michigan (US) 2000	Summer	1–12		50%	Di Carlo et al., 2004
Suriname 2005*	Spring	28–72	53		Sinha et al., 2008
Hyytiälä (Finland) 2008*	Summer	3.5–60	9	60%	Sinha et al., 2010
Rocky mountains (US) 2008	Summer	2–26	6.7	30%	Nakashima et al., 2014
Borneo (Malaysia) 2008	Summer	7–84	29.1	50%	Edwards et al., 2013
Michigan (US) 2009	Summer	1–39	12	28%	Hansen et al., 2014
California (US) 2009	Summer	8–25	20	20%	Mao et al., 2012
Hyytiälä (Finland) 2010*	Summer	3–76	12	58%	Nölscher et al., 2012a
Amazon (Brazil) 2013*	Dry season ^a	3–241	62.4	up to 79%	Nölscher et al., 2016
Amazon (Brazil) 2013*	Wet Season ^a	3–25	9.9	49%	Nölscher et al., 2016
Alabama forest (US) 2013	Summer	6–35	18	16%	Kaiser et al., 2016
Haute Provence (France) 2014*	Summer	3–70	26	0%	Zannoni et al., 2016
Amazon (Brazil) 2015*	Dry (El Niño) ^b	3–48	28.1		This work; Pfannerstill et al., 2018
Hyytiälä (Finland) 2016*	Spring	2–60	11.3	60%	Praplan et al., 2019
Michigan (US) 2016	Summer	0–40		0–30%	Millet et al., 2018
North Norfolk Coast (UK) 2004	Spring	1–10	4.85	39%	Ingham et al., 2009
Pacific Ocean (airborne) 2006	Spring	3–5	4	30%	Mao et al., 2009
El Arenosillo (coastal, Spain) 2008*	Winter	0–22	6.3		Sinha et al., 2012
Corisca (France) 2013*	Summer	3–17	5	50%	Zannoni et al., 2017
Wakayama (Japan) 2014	Summer	2–21	7.1	22%	Ramasamy et al., 2016
Cyprus 2014*	Summer	0–8.7	1.8	24%	Keßel, 2016
Arabian (Persian) Gulf 2017*	Summer	2.5–33	12.8	28%	This work; Pfannerstill et al., 2019
Indian Ocean 2017*	Summer	3–12	5.2		This work; Pfannerstill et al., 2019
Red Sea 2017*	Summer	2–28	9	50%	This work; Pfannerstill et al., 2019
Mediterranean Sea 2017*	Summer	3–27	7.2	50%	This work; Pfannerstill et al., 2019

^a within canopy^b above canopy

1.3 Research objectives and thesis outline

“The Anthropocene - human dominance of biological, chemical and geological processes on Earth - is already an undeniable reality.”

Paul J. Crutzen (2011)

In the current human-dominated epoch, the Anthropocene, humans are altering atmospheric composition and processes globally on different spatial and temporal scales (e.g. IPCC, 2018; Lewis and Maslin, 2015; Steffen et al., 2007).

Total OH reactivity as a fundamental property of the atmosphere can give insights into the causes and effects of altering atmospheric chemistry in the Anthropocene. This doctoral project encompasses OH reactivity investigations ranging from a phenomenon that will be exacerbated by indirect human influence (drought and heat events in the Amazon forest) to the direct impact of man-made emissions over the Arabian Gulf. Total OH reactivity will be used to examine the amount and properties of unaccounted for emissions, to help understand the causes for photochemical pollution, to identify the trace gases most relevant for local photochemistry, and to give a complete picture of the ambient OH reactant load due to anthropogenic or biogenic emissions.

How biogeochemical feedbacks of the changing climate will influence the globally dominant biogenic VOC emissions and therewith atmospheric OH reactivity is still poorly understood. **Changes in environmental conditions** are likely to implicate terrestrial plants' emissions (Arneth et al., 2010; Denman et al., 2007; Isaksen et al., 2009; Peñuelas, 2003; Peñuelas and Staudt, 2010). **In the tropical Amazon rainforest, periods of drought and heat stress are predicted to occur more frequently in the coming decades due to land use change and an altered ENSO (El Niño Southern Oscillation), so today's observations from such periods give insights of what to expect in the future.** A study in the remote Amazon rainforest during such an El Niño event is part of this thesis. Possible causes and implications of the observed change in the diel cycle of OH reactivity are discussed in **Chapter 2**.

The Anthropocene also means that human activity is **altering the air composition regionally and locally** and causing air pollution. **A hotspot of photochemical pollution is the region around the Arabian Peninsula** (Lelieveld et al., 2009). In order to better understand the causes for the extreme concentrations of air pollutants observed there, total OH reactivity was measured while traveling around the **Arabian Peninsula** in the first shipborne total OH reactivity measurements. In a new approach, a wide range of ≈ 120 compounds, including unidentified VOCs and OVOCs observed by PTR-ToF-MS, was used to calculate speciated reactivity. OVOCs were identified as the dominant contributor to OH reactivity in the region. The study in **Chapter 3** investigates how emissions from ship traffic and oil/gas production cause conditions that favor ozone pollution.

Understanding the changing atmospheric chemistry in the Anthropocene, but also the processes in a pristine atmosphere, relies on accurate measurements with a substantial global coverage. Especially observations of VOCs are still comparably scarce worldwide due to the complexity of the equipment necessary for their observation. Therefore, reactive organics are a source of uncertainty in predicting regional air

quality (Zhu et al., 2019) and in global atmospheric models (e.g. Intergovernmental Panel on Climate Change, 2014). Robust measurements of total OH reactivity would, if they became a standard in atmospheric monitoring stations, help to reduce this uncertainty by providing a sum of the reactive trace gas load. The second half of this thesis therefore focuses on the CRM measurement technique, its interferences and applicability for long-term observations, and robustness of the data compared between different measurement methods.

To date, **field observations of total OH reactivity**, especially in biogenic environments, **have been limited to short-term campaigns** (Sect. 1.2.4). Due to the temporal variability of sources and sinks of reactive trace gases, these only provide snapshots of local atmospheric photochemistry. For constraining atmospheric chemistry models by a thorough understanding of the seasonal cycle, of inter-annual variability, of the impact of weather events or of anthropogenic climatic changes, long-term measurements would be of great value. As a first step **towards the long-term autonomous deployment of a CRM instrument** at the Finnish boreal forest field station in Hyytiälä, **a new CRM-PID was characterized through laboratory and field experiments at the Finnish Meteorological Institute in Helsinki**. This collaboration study led by Arnaud Praplan is discussed in **Chapter 4**.

In the 15 years following the first publication of a technique for OH reactivity measurement, three more methods had been developed and deployed in a variety of environments and locations (Sect. 1.2.2 and 1.2.4), but **a comprehensive inter-comparison had never been conducted** (Williams and Brune, 2015). In order to evaluate the validity of past results and possible room for methodological improvement, a large intercomparison was performed in 2015 and 2016 at the atmospheric simulation chamber SAPHIR in Jülich. As a part of this dissertation project, **the performance of the MPIC (Max Planck Institute for Chemistry) CRM instrument was compared there to eight other instruments**. A sensitivity towards ozone was discovered in the CRM reactor. The intercomparison results are shown in **Chapter 5** and complemented by experiments to improve CRM accuracy in **Appendix A**. Implications and future perspectives for the CRM technique are discussed in **Chapter 6**.

Chapter 2

Total OH reactivity changes over the Amazon rainforest during an El Niño event

(published in *Frontiers in Forests and Global Change*, 2018.)



Chapter 3

Shipborne measurements of total OH reactivity around the Arabian Peninsula and its role in ozone chemistry

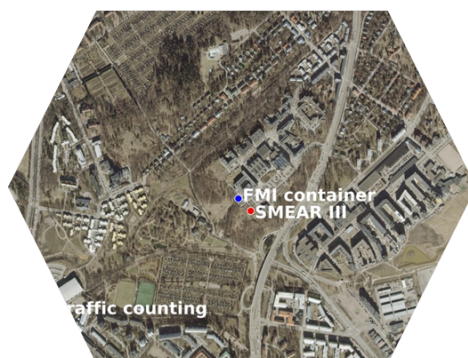
(published in *Atmospheric Chemistry and Physics*, 2019.)



Chapter 4

OH reactivity of the urban air in Helsinki, Finland, during winter

(published in *Atmospheric Environment*, 2017.)



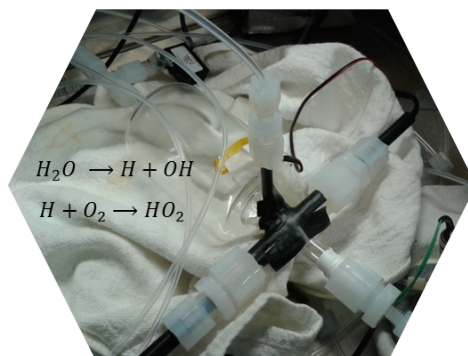
Chapter 5

Comparison of OH reactivity measurements in the atmospheric simulation chamber SAPHIR

(published in *Atmospheric Measurement Techniques*, 2017.)



Chapter 6

Conclusions and future perspectives for the CRM method and atmospheric OH reactivity observations

Total OH reactivity changes over the Amazon rainforest during an El Niño event

This chapter has been published as:

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Contribution to this publication by Eva Y. Pfannerstill: *Performed the data analysis and prepared the manuscript.*

Abstract. The 2015/16 El Niño event caused unprecedented drought and warming in the Amazon basin. How tropical forests react to such extreme events in terms of volatile organic compound (VOC) emissions is of interest as the frequency of these events is predicted to increase through climate change. The diverse VOCs emitted can be significant for plants' carbon budgets, influence ozone and particle production, and through their reactivity impact OH concentrations. Total OH reactivity is a directly measureable quantity that gives the reaction frequency of OH radicals with all reactive species in the atmosphere in s^{-1} . Here we present a comparison of the OH reactivity diel cycle from November 2015, i.e. extreme drought and elevated temperatures associated with strong El Niño conditions, with November 2012, a "normal" El Niño Southern Oscillation (ENSO)-neutral period. Interestingly, the diel maximum of OH reactivity during the El Niño event occurred at sunset instead of, under normal conditions, early afternoon. The absolute total diel OH reactivity, however, did not change significantly. Daytime OH reactivity averages were $24.3 \pm 14.5 \text{ s}^{-1}$ in 2012 and $24.6 \pm 11.9 \text{ s}^{-1}$ in 2015, respectively. Our findings suggest that a combination of stronger turbulent transport above the canopy with stress-related monoterpene and, possibly, other biogenic volatile organic compound (BVOC) emissions were responsible for this increased reactivity at sunset.

2.1 Introduction

Amazonia contains more than half of the world's tropical forests (Morley, 2000), 25 % of the Earth's biodiversity (Dirzo and Raven, 2003) and nearly 15 % of terrestrial biomass (Bar-On et al., 2018; Houghton et al., 2001). As such the Amazon rainforest is an ecosystem of global relevance for water, energy and carbon cycles (Aragão et al., 2018; Malhi, 2002; Werth, 2002). Its biosphere-atmosphere interface is of utmost significance for a complete understanding of global biogeochemical cycles.

How the Amazon biosphere and the overlying atmosphere will react to future climate change is therefore an important question. Most near- and long-term IPCC models predict warming, combined with decreasing precipitation and soil moisture in Amazonia (Intergovernmental Panel on Climate Change, 2014). Drought and increasingly elevated temperatures are already being observed (Aragão et al., 2018; Erfanian et al., 2017; Feldpausch et al., 2016; Jiménez-Muñoz et al., 2016; Li et al., 2008; Marengo and Espinoza, 2016; Marengo et al., 2011; Yang et al., 2018) and are predicted to occur more often there in the future. Tropical forests are vulnerable to climate change variables such as precipitation decrease and warming. These can lead to increased tree mortality and reduced net primary productivity, with the result that the forest is no longer a sink, but a source of atmospheric carbon (Brienen et al., 2015; Feldpausch et al., 2016; McDowell et al., 2018; Metcalfe et al., 2010; van der Laan-Luijkx et al., 2015). The frequency of El Niño events is predicted to increase (Cai et al., 2015; Timmermann et al., 1999), as well as anthropogenic land use change (i.e. forest loss), which exacerbates water deficits and elevated temperatures in Amazonia (Alkama and Cescatti, 2016; Baidya Roy, 2002; Swann et al., 2015; Zemp et al., 2017; Zeng et al., 1996).

A highly relevant factor in atmospheric chemistry, which is expected to alter in response to climate change (Monson et al., 2007), is the emission of biogenic volatile organic compounds (BVOCs) by plants. Tropical forests represent the main source for BVOCs on Earth (Guenther et al., 2012). These relatively short-lived (minutes to days) atmospheric species are important as they can influence local tropospheric ozone and particle formation. Some plant BVOCs, e.g. isoprene and monoterpenes, are thought to act as antioxidants against stress-induced reactive oxygen species or help plants cope with abiotic stress by changing membrane properties (Jardine et al., 2013; Karl et al., 2010; Sharkey and Monson, 2017; Sharkey et al., 2008; Vickers et al., 2009). Once released to the atmosphere, the BVOCs mainly react with OH radicals formed from the ozone photoproduct O^1D and water. This oxidation pathway has important implications for secondary organic aerosol formation and, in turn, for cloud formation and climate (Ehn et al., 2014; Palm et al., 2018; Pöschl et al., 2010); as well as for the modulation of greenhouse gas and pollutant concentrations (e.g. methane and CO; Arneth et al., 2010; Peñuelas and Staudt, 2010). For carbon cycle closure, BVOCs represent a challenge: without stress, 1-2 % of net primary production by land plants is emitted as monoterpenes and isoprene (Harrison et al., 2013; Kesselmeier et al., 2002; Sharkey and Loreto, 1993). These numbers may be regarded as small related to net primary production (NPP) and gross primary production (GPP), but the amount of carbon lost as VOC emissions can be highly significant relative to net ecosystem productivity (Kesselmeier et al., 2002). Furthermore, if multiple abiotic stress factors such as heat, drought or high irradiance are applied,

up to 10 % (Peñuelas, 2003) or even in extreme cases 67 % (Sharkey and Loreto, 1993) of plant carbon can be allocated to BVOCs.

Studies of BVOCs in tropical forests tend to be, for technical reasons, limited to a modest number of abundant compounds such as isoprenoids and some oxygenated species (e.g. Jardine et al., 2015; Kesselmeier et al., 2000; Kuhn et al., 2004; Kuhn et al., 2007; Rinne et al., 2002; Rizzo et al., 2010; Rottenberger et al., 2004; Yáñez-Serrano et al., 2015; Yáñez-Serrano et al., 2018). This is despite the fact that plants are known to release more than 30 000 different VOCs (e.g. Harley, 2013). A measure for the combined effect of all VOCs and other OH reactive species in ambient air, i.e. the total OH sink, is termed the total OH reactivity. Total OH reactivity in Amazonia is thought to be dominated by isoprene and other reactive BVOCs (Nölscher et al., 2016) that are emitted as a function of temperature and light (e.g. Rinne et al., 2002). These emissions are higher in the dry season than in the wet season. However, especially in the dry season a significant part of OH reactivity remains unexplained by individually measured trace gases, the so-called “missing reactivity” (Nölscher et al., 2016; Williams et al., 2016).

Here we compare OH reactivity measurements at a central Amazonian site under two contrasting regimes which are due to the influence of El Niño Southern Oscillation (ENSO): 1) ENSO-neutral conditions (November 2012) and 2) strong El Niño conditions with record-breaking precipitation deficit and heat (November 2015). The 2015/16 drought and warming event is unprecedented in records since 1900 and is attributed to an unusually strong El Niño period (Erfanian et al., 2017; Jiménez-Muñoz et al., 2016; Paek et al., 2017; Varotsos et al., 2016; Wang and Hendon, 2017; Yang et al., 2018). Satellite data of 2015/16 show a regional land surface temperature anomaly of up to +4° C for October through December 2015 in the Amazon basin (Jiménez-Muñoz et al., 2016) and that 43 % of the Amazon biome encountered a significant negative maximum climatological water deficit (Aragão et al., 2018). Due to these extreme conditions, stress-related plant emissions may occur. Therefore, by extension we may hypothesize that compared to ENSO-neutral conditions, El Niño conditions would lead to increased total OH reactivity as a result of elevated, stress-induced emissions. In this study we examine the OH reactivity behavior in data collected in these two contrasting regimes, both in absolute terms and as a function of time of the day.

2.2 Materials and Methods

2.2.1 Sampling Site

The Amazonian Tall Tower Observatory (ATTO) site (Andreae et al., 2015) is located in a dense, non-flooded *terra firme* forest 150 km northeast of Manaus, Brazil, at 120 m above sea level (Fig. 2.1). The main wind direction at the site, as in the whole trade wind influenced region, is northeast (MacGregor and Nieuwolt, 1998; Pöhlker et al., 2019; Fig. 2.2). This means that it is mainly influenced by air masses that have passed over several hundred km of undisturbed old-grown rainforest (Supplementary Fig. 1).

The walk-up tower (Instant UpRight Ltd, Dublin, Ireland) is located at $S 02^{\circ} 08' 38.6''$, $W 58^{\circ} 59' 59.9''$ (height above ground level: 80 m). It has been in operation since 2012, and is equipped with instrumentation for continuous measurements such as meteorology, micrometeorology, greenhouse gases, phenology, inorganic trace gases and aerosol particles. During intensive observation periods, these are complemented by, amongst others, VOC and total OH reactivity measurements. The maximum canopy top height in the footprint area of the tower is approximately 35 m and more than 400 tree species have been identified there (Andreae et al., 2015). The average tree height did not change significantly over time because this forest consists of trees in all stages of life and the timespan between the two measurement periods was relatively short in comparison with the lifetime of a tree. The zero-plane displacement height ($0.9h$, where h is canopy height) is 31.5 m. Suppl. Fig. 2 and 3 show the footprint and the origin of up to 80 % of the flux for this displacement height.

2.2.2 Measurement periods

The intensive measurement campaign in 2015 was set at the end of the dry season (June–October). During this season, cumulative precipitation generally does not exceed 120 mm per month (Restrepo-Coupe et al., 2013). Sampling took place continuously from November 11 until November 23, 2015. This period fell into the extreme 2015/16 El Niño event (Erfanian et al., 2017; Jiménez-Muñoz et al., 2016; Wang and Hendon, 2017; Yang et al., 2018). There was no rainfall during the measurement period – the last rain event before the campaign took place on November 9, the next one on November 27, 2015.

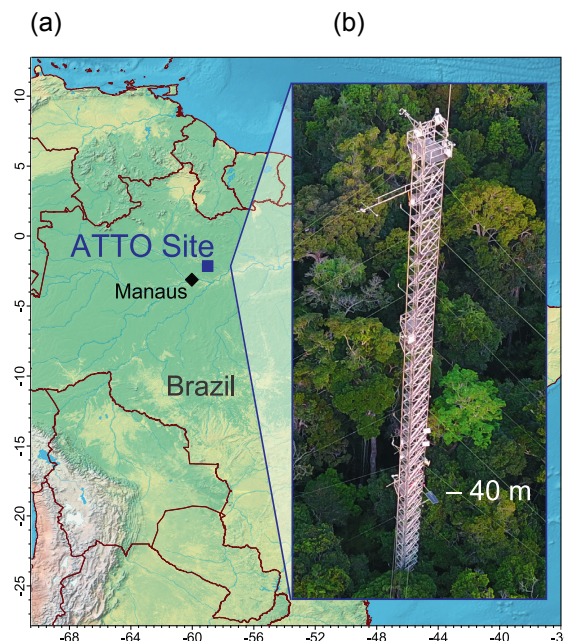


Figure 2.1: (a) Location of the ATTO site. (b) 80 m walk-up tower with inlet at 41 m height above ground level.

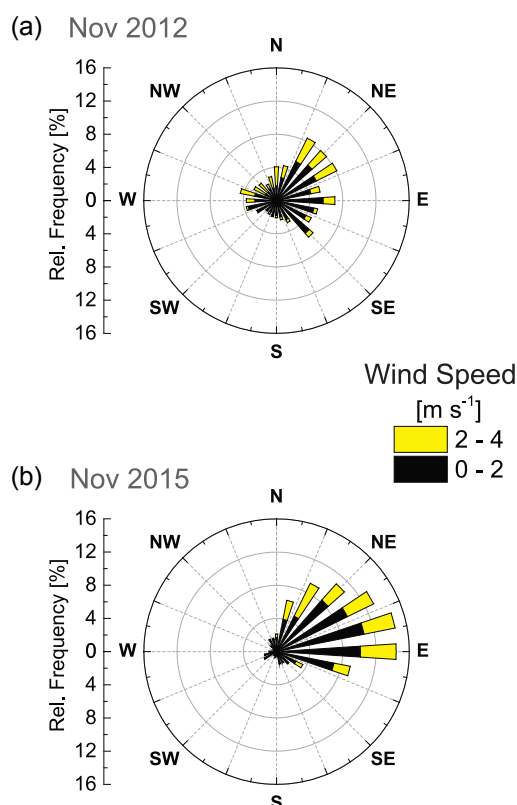


Figure 2.2: Frequency distribution of wind directions and wind speed in m s^{-1} measured (a) at 38 m above ground level from November 01–28, 2012 and (b) at 41 m above ground level from November 11–23, 2015.

The data used to compare this period with an ENSO-neutral November were collected in 2012 (10 full days between November 1 and November 28). The sampling details for this campaign are described elsewhere (Nölscher et al., 2016; Yáñez-Serrano et al., 2015). During the 2012 campaign, inlets were situated at several heights on the 80 m walk-up tower, however, for this comparison we only considered OH reactivity and VOC data measured at the 38 m inlet, which was closest to the 41 m inlets used in 2015. Ozone, NO₂, NO, CO, and CH₄ were monitored at 38 m during both campaigns. The vertical distance from the 38 m inlet to the tallest trees directly adjacent to the tower was 10 m (Fig. 1 in Chor et al., 2017).

2.2.3 OH reactivity and trace gas measurements

During the two campaigns, total OH reactivity was determined using the Comparative Reactivity Method (CRM, Sinha et al., 2008). It is based on the competitive reaction between pyrrole (Westfalen AG, Münster, Germany) and reactive compounds from ambient air inside a glass reactor. OH radicals are created by flushing humidified nitrogen (6.0 grade, Westfalen AG, Münster, Germany) over a Hg/Ar UV lamp (LOT Quantum Design, Darmstadt, Germany). The different modes used in CRM – C1 (dry pyrrole + UV light), C2 (OH + pyrrole), and C3 level (ambient air + pyrrole + OH) – are described in detail in Sinha et al. (2008). In our study, the C3 level was measured for 48 min starting at the full hour and the C2 level for 12 minutes at the end of the hour. The C1 level was determined at least every two days, and calibrations with a pyrrole gas standard (Westfalen AG, Münster, Germany) were performed every 3–6 days. Changes in pyrrole mixing ratio were monitored by a Quadrupole Proton Transfer Reaction-Mass Spectrometer (PTRMS, Ionicon Analytik, Innsbruck, Austria (Lindinger and Jordan, 1998)) at $m/z = 68$ (dwell time: 5 s). Measurement intervals were 7 s. The PTRMS was operated at 50 °C drift temperature, 2.2 mbar drift pressure, 600 V drift voltage and 127 Td. In parallel, another Quadrupole PTRMS, calibrated regularly with a multicomponent pressurized gas VOC standard (Apel-Riemer Environmental Inc., Colorado, USA), was deployed to monitor two important contributors to OH reactivity (Nölscher et al., 2016): Isoprene (detected as m/z 69) and the sum of isoprene oxidation products (m/z 71, methyl vinyl ketone (MVK), methacrolein (MACR) and isoprene hydroperoxide (ISOPOOH)). Their mixing ratios were measured with fast response (1 Hz) in 2015. Eleven more masses were monitored additionally in 2012 (see Nölscher et al., 2016; Yáñez-Serrano et al., 2015).

2.2.4 Sampling

A heated and insulated polytetrafluoroethylene (PTFE) inlet tube (1/2" = 1.27 cm outer diameter), topped with a routinely changed PTFE filter (pore size: 5 μ m) to avoid contamination by insects or particles, was positioned at ca. 41 m height above ground level on the tower. Air samples were continuously drawn at a flow rate of ≈ 30 slpm into an air-conditioned laboratory container located below the tower. In order to avoid underpressure in the CRM reactor, the sampled air passed through a chemically inert pump with a Teflon membrane (Neuberger KNF, Freiburg, Germany) at ca. 500 sccm before entering the CRM instrument. The inlet residence time determined by spiking with methanol was 19 s.

2.2.5 Flux calculations

Isoprene was measured with the above described PTRMS at a time resolution of 1 s. It was sampled from a separate 3/8" inlet at 41 m above ground level at a flow rate of about 10 L min⁻¹. The delay time of the PTRMS signal was corrected by maximizing the covariance between the water cluster signal of the PTRMS with the signal of an open path water analyzer (Li-COR 7500, LI-COR Inc., Lincoln, USA). A CSAT3 sonic anemometer (Campbell Scientific Inc., Logan, USA), situated at a distance of 0.5 m to the isoprene inlet, was used for high frequency three-dimensional measurement of the wind speed. The software package EddyPro (LI-COR Inc., Lincoln, USA) was applied to calculate eddy covariance fluxes of CO₂, water and isoprene by correlating fluctuations of the vertical wind vector to the fluctuations of the CO₂, water and isoprene concentrations. The method of Vickers and Mahrt (1997) was employed for de-spiking and raw data statistical screening. Half-hourly averaged fluxes were flagged according to the data quality control method of Mauder and Foken (2004). Only data with highest quality (flags 0 and 1) was kept for further analyses. High frequency losses for sampling frequencies between 0.1 and 0.8 Hz have been found to be below 10 % (Guenther and Hills, 1998; Holst et al., 2010; Jensen et al., 2018; Spirig et al., 2005). We calculated footprints according to the two-dimensional model of Kljun et al. (2015) for a geographic domain of 2 x 2 km centered at the tower. We used the Tovi Footprint Analysis Toolbox (LI-COR Inc., Lincoln, USA) to calculate half-hourly footprints and aggregate them for the measurement period.

2.2.6 Total OH reactivity data analysis

The PTRMS signal at $m/z = 68$ (protonated mass of pyrrole) was used for calculating pyrrole mixing ratios. Pyrrole PTRMS data were corrected for high O₂⁺ concentration in the ion source of up to 12 %, which ionized isoprene as $m/z = 68$. This artefact caused by ambient isoprene (slightly higher signal on $m/z = 68$) was corrected for using the isoprene mixing ratios collected by the VOC-PTRMS measuring from a parallel inlet at the same height, and an experimentally derived yield of isoprene after the reactions in the CRM reactor have taken place. This correction was below the total uncertainty of the measurements (on average 0.28 ± 0.18 (standard deviation) ppbv of pyrrole, which corresponds to an OH reactivity of ca. 1.6 s⁻¹).

CRM data analysis was conducted following the general procedures described in Keßel (2016). During C2 (background) measurements, ambient air passed through a catalytic converter that removes all VOCs. Humidity can differ between C2 level and C3 level (ambient air), especially as the C2 level is measured only once per hour and ambient humidity is subject to change in the meantime. This difference has to be accounted for because the amount of OH radicals generated in the reactor depends on humidity. C2 data therefore were corrected using a relationship derived from an empirical test as recommended in Michoud et al. (2015). The C2 correction applied to match C3 level humidity amounted on average 0.92 ± 0.31 ppbv of pyrrole, which equals ca. 5.3 s⁻¹ of OH reactivity.

The CRM method is sensitive to NO and NO₂ due to OH recycling caused by HO₂, which is formed in the reactor simultaneously with OH (Michoud et al., 2015; Sinha et al., 2008). However, NO and NO₂ mixing ratios at the ATTO site were at all times below 3 ppbv, which is the threshold over which a significant effect is visible in the

CRM instrument (maximum observed NO: 0.91 ppbv; maximum NO₂: 1.38 ppbv). Therefore, no interference from NO_x was expected.

An ozone interference for CRM was discovered recently (Fuchs et al., 2017a). The interference for this instrument was characterized using an ozone generator (Dynamic Gas Calibrator 146C, Thermo Environmental Instruments LLC, Franklin, USA). The resulting correction was ca. 0.018 ppbv of pyrrole per ppbv of ozone, which corresponds to ca. 0.1 s⁻¹ per ppbv of ozone. This correction increased OH reactivity values by up to 1 %.

The calculation of total OH reactivity based on three modes (C1, C2, and C3 levels) assumes pseudo 1st order conditions (i. e. [pyrrole] >> [OH]). As the experiments are conducted at pyrrole/OH ratios of 1.2 to 2 in order to provide detectable differences between the CRM modes, a correction needs to be applied. A chemical model (Facsimile) was used to derive a relationship between true total reactivity and calculated reactivity from the CRM equation. This correction reduced the OH reactivity value by maximum 6 %.

Finally, a dilution factor of 1.28 was applied to account for the humidified nitrogen mixed with the ambient air in the reactor.

The detection limit (LOD) was 4.2 s⁻¹ (derived from 2 σ standard deviation on C2 levels). Accuracy of the measurements was ca. 30 %, with a precision of 10-20 % depending on the quantity of reactivity (for total uncertainty, dependent on the amount of OH reactivity: see Supplementary Figure 4).

Total OH reactivity expected from individually measured compounds is the sum of the OH reactivities of the respective compounds:

$$R_{total} = \sum k_{X+OH} [X] \quad (2.1)$$

Contributions of measured trace gases (X, where [X] is their respective concentration in molecules cm⁻³) to total OH reactivity (R_{total} in s⁻¹) were calculated using the reaction rate constants (k_{X+OH} in cm³ molecule⁻¹ s⁻¹) of trace gases (X) with the OH radical as shown in Supplementary Table 1 for November 2015. For the purpose of this calculation, it is assumed that the different inlets of trace gas measurements and OH reactivity were co-located. The difference between measured total OH reactivity and the sum of individual trace gas contributions to OH reactivity is termed “unexplained” or “missing” OH reactivity.

All data analysis was conducted using IGOR Pro 6.37.

2.2.7 Canopy stomatal conductance calculation

Stomatal conductance is generally estimated using an approach described by Ball (1987). It is derived from the ratio of measured water flux and estimated release capacity based on the water vapor gradient between leaf and atmosphere at ambient temperatures measured inside the canopy (assuming a water vapor saturation of 100 % inside the leaf. We note that this assumption has been recently challenged for conifer leaves, where humidity was below 100 % (Cernusak et al., 2018). As a general rough approximation, we considered the whole canopy as a single large leaf and relative humidity inside the canopy (26 m) as the driving force of the water vapor gradient.

2.2.8 Analysis of turbulent transport

Turbulence drives the transport of reactive species out of the canopy from below and from the boundary layer aloft to the height at which OH reactivity is measured. Therefore, it is useful to assess the strength of turbulent transport and whether it was different between the two years.

The Richardson number is an indicator for atmospheric stability and the occurrence of turbulence. It expresses the ratio of buoyant consumption versus mechanical (shear) production of turbulence (Stull, 1988). The gradient Richardson number (Ri_g) was calculated from average diel wind and temperature data for both observation periods. Observations at various measurement heights were interpolated with a logarithmic function to obtain continuous gradients (measurement heights above ground level were in 2012: 4, 36, 46, 81 m for wind data and 0.4, 1.5, 4.4, 12, 26, 36, 55, 73 m for temperature data; in 2015: 14, 22, 40, 55, 81 m for wind data and 0.51, 1.67, 4.4, 26, 36, 40, 73 m for temperature data). Ri_g was then calculated for each hour of the day in 1 m height resolution from 20 m up to 80 m using the following equation (e.g. Stull, 1988):

$$Ri_g = \frac{\frac{g}{\theta_v} \frac{\partial \theta_v}{\partial z}}{\left(\frac{\partial u}{\partial z}\right)^2 + \left(\frac{\partial v}{\partial z}\right)^2} \quad (2.2)$$

where g is the acceleration due to gravity (9.81 m s^{-2}), θ_v is the virtual potential temperature (K), z the height above ground level (m), and u and v the wind vectors (m s^{-1}) in the x and y direction, respectively.

A second variable of interest is the atmospheric boundary layer (ABL) height, since this determines the depth over which emitted species will be mixed. To assess the potential impact of ABL dynamics, the MXL/MESSy model (Janssen and Pozzer, 2015) was used to investigate two case study days (November 22, 2015 and November 10, 2012). The MXL model has been shown before to reproduce tropical boundary layer dynamics well in comparison with a turbulence resolving large eddy simulation (Vilà-Guerau de Arellano et al., 2011) and in comparison with ABL height as observed by Lidar (Janssen et al., 2013). Observations of surface sensible and latent heat fluxes, potential temperature and specific moisture were used to constrain the simulated boundary layer development. Additionally, ABL height observations were available for 2015. For both years, a subsidence rate of $3 \cdot 10^{-5} \text{ s}^{-1}$ was applied to account for large-scale downward vertical motions.

2.3 Results and discussion

2.3.1 OH reactivity during El Niño compared to an ENSO-neutral period

A comparison of diel (24 hour) temperature and humidity cycles between a November under strong El Niño influence (2015) and an ENSO-neutral November (2012) is shown in Fig. 2.3. The El Niño period was hotter and less humid than a “usual” dry season. Maximum temperatures of the day (from 1 min diel medians of the 2015 measurement period) reached up to 34.4°C , compared to 32.2°C in 2012. The lowest median relative humidity of the day (from 1 min medians) during the 2015

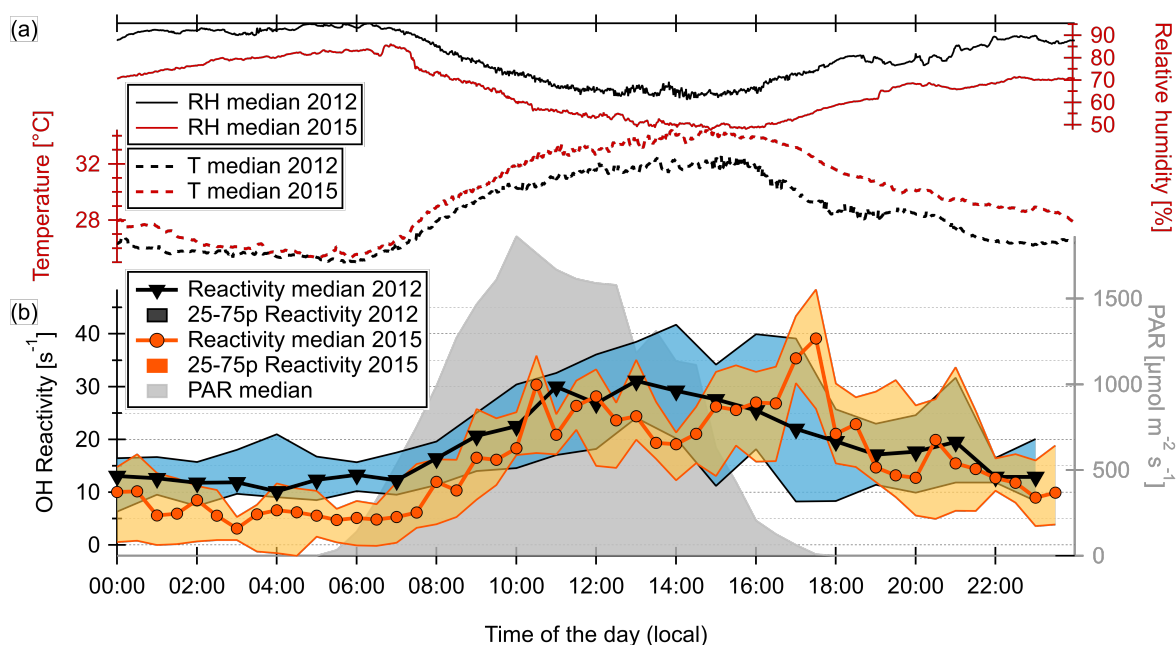


Figure 2.3: (a) Median diel cycles of relative humidity and temperature for measurement periods in November 2012 and November 2015. (b) Diel medians of OH reactivity for Nov 2012 (hourly) and Nov 2015 (half-hourly), and photosynthetic active radiation (PAR) for Nov 2015 measured at 41 m height above ground level. The shaded areas depict 25th to 75th percentiles of OH reactivity.

measurement period was 47.8 % (2012: 62.4 %). This corresponds to a difference in average absolute humidity of 17 % (21.4 g m⁻³ in 2012, 18.3 g m⁻³ in 2015). The El-Niño-attributed extreme drought was also reflected in soil water content, which was reduced by 20–25 % with $0.149 \pm 0.003 \text{ m}^3 \text{ m}^{-3}$ (average $\pm$ standard deviation for November 2015) compared to $0.184 \pm 0.008 \text{ m}^3 \text{ m}^{-3}$ in ENSO-neutral November 2014 (used here because of data unavailability for 2012). The unusually dry and hot conditions at the ATTO site reflect general observations of the Amazon basin and the whole of South America for the 2015/16 El Niño (Erfanian et al., 2017; Jiménez-Muñoz et al., 2016; Yang et al., 2018).

Diel cycles of OH reactivity measured above the forest canopy (at 41 m height above ground level) were compared between November 2012 and November 2015 (Fig. 2.3 (b)). Photosynthetic active radiation (PAR) measurements show that sunrise and sunset occurred at ca. 5:30 and 18:00 LT (local time, i.e. UTC-4), respectively. For most of the day, the OH reactivity pattern in the respective measurement periods was very similar. Nighttime OH reactivity was low, often close to the detection limit of 4.2 s⁻¹. Due to the larger uncertainty of low reactivity values (see Supplementary Fig. 4), nighttime and early morning differences between the 2012 and 2015 diel cycles can be considered as insignificant. Both cycles showed a maximum at noon of on average $27.0 \pm 14.2 \text{ s}^{-1}$ (2015) and $36.4 \pm 22.1 \text{ s}^{-1}$ (2012) with very similar respective medians of 28.1 s⁻¹ (2015) and 26.8 s⁻¹ (2012). A striking difference, however, was that the averages and medians of 13 days of OH reactivity in 2015 showed a second, and higher, maximum around the time of sunset ($35.2 \pm 14.5 \text{ s}^{-1}$, compared to $27.4 \pm 18.8 \text{ s}^{-1}$ in 2012 / medians: 36.5 s⁻¹ (2015) and 22.0 s⁻¹ in 2012 at 17:00 LT). A less distinct sunset increase is also indicated in the 75th percentile of the 2012 data, but for that year the median was decreasing as one would expect when night falls

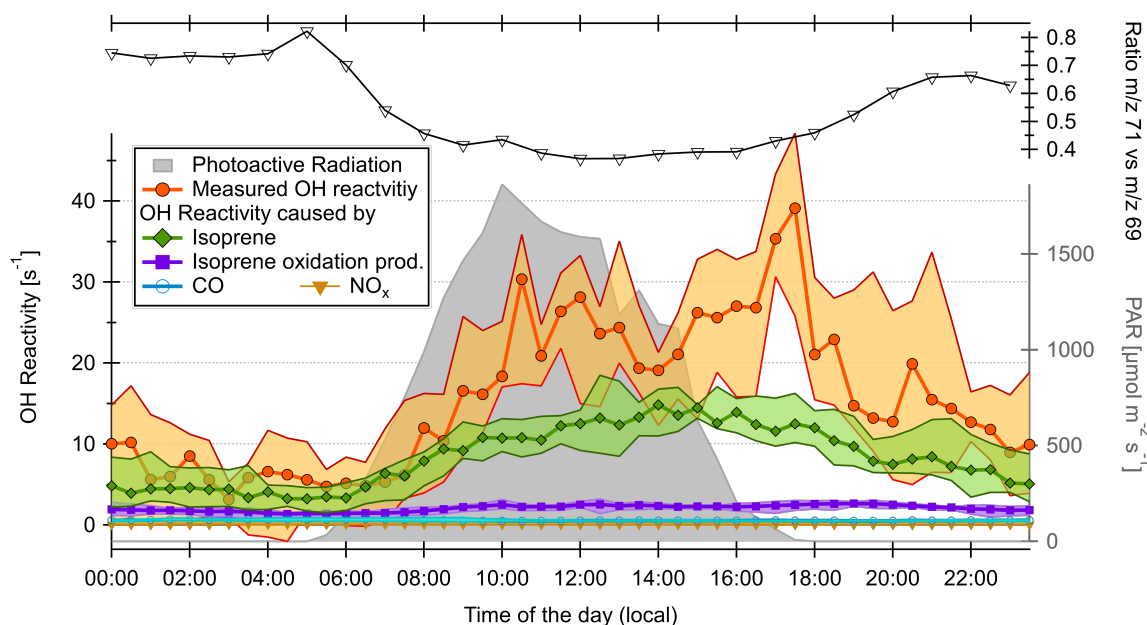


Figure 2.4: Diel half-hourly medians over 13 days of measurements in November 2015 for calculated OH reactivity of isoprene, isoprene oxidation products, NO_x and CO, diel medians of measured OH reactivity; and hourly medians of the isoprene oxidation product vs. isoprene ratio. Filled areas represent the 25th–75th percentiles of data. Not depicted: contributions of ozone (max. 0.05 s⁻¹), and methane (max. 0.22 s⁻¹). Photosynthetic active radiation (PAR) is displayed on the right axis (half-hourly medians).

and photosynthetic activity of the plants declines. In contrast to the diel pattern, the absolute daytime OH reactivity did not differ significantly between both observation periods: Average OH reactivity values above the LOD of 10 days between 6:00 and 19:00 LT were $24.3 \pm 14.5 \text{ s}^{-1}$ in 2012, compared to $24.6 \pm 11.9 \text{ s}^{-1}$ in 2015. The hour from 18:00 till 19:00 was included here into “daytime” values, because the evening OH reactivity maximum under El Niño influence sometimes remained until 18:30.

Only a few VOC species were measured in 2015 because the campaign was focused on fast response measurements of isoprene. Therefore, total OH reactivity can only be compared with the reactivity of isoprene, the sum of three isoprene oxidation products (MVK/MACR/ISOPOOH, $m/z = 71$), NO_x, and CO (Fig. 2.4), methane, and ozone (not displayed due to insignificant contribution to OH reactivity, see Supplementary Table 1). Isoprene and isoprene oxidation products have been reported to be the main known contributors to OH reactivity at the ATTO site, however with average unexplained fractions of 49 % in the wet season and 79 % in the dry season (Nölscher et al., 2016). In 2015, isoprene levels were similar as reported previously by Nölscher et al. (2016, for 2012) and Yáñez-Serrano et al. (2015). Although NO_x did not contribute significant amounts of OH reactivity at any time (maximum: 0.48 s^{-1}), a higher number of forest fires during the El Niño influenced period compared to other dry seasons (Aragão et al., 2018) was visible in NO mixing ratios. Indeed they were four times as high as in an ENSO neutral November (here: 2013 due to data unavailability in 2012) with an average of $0.061 \pm 0.068 \text{ ppbv}$ in November 2015 and of $0.014 \pm 0.078 \text{ ppbv}$ in November 2013. Long-term measurements of NO_x at the site until 2015 never exceeded 2 ppb, with median values consistently below 250 ppt (Wolff, 2015). The high NO_x values observed in November 2015 with

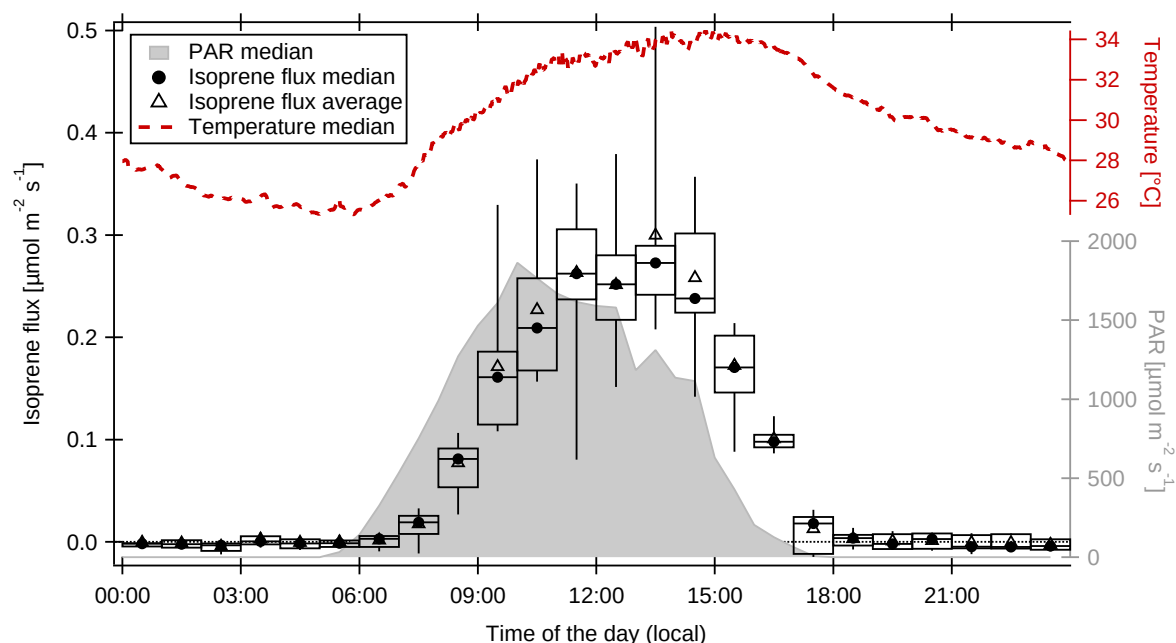


Figure 2.5: Diel hourly averages and medians of isoprene fluxes measured at 41 m above ground level at the ATTO site between November 11 and 23, 2015. Boxes and whiskers represent the 25th–75th and 5th–95th percentiles, respectively. The diel medians of photosynthetic active radiation (PAR) and ambient temperature measured at the same height are displayed on the right axes.

peak values of 2.1 ppb demonstrate the exceptional conditions caused by the strong El Niño event.

The total OH reactivity time series (Suppl. Fig. 5) shows that except for two days within the measurement period, the daily reactivity maximum in 2015 was observed during or shortly after sunset. The two days where this effect was not visible were each preceded by a day with ambient relative humidity above 95 %. During the rest of the El Niño influenced observation period, relative humidity always remained below 95 %, which indicates that the evening OH reactivity maximum may be related to dry conditions. From the data collected by the VOC-PTRMS running in parallel, it is possible to calculate the theoretical OH reactivity contributed to measured total OH reactivity by isoprene and its oxidation products (Fig. 2.4). Isoprene accounted for most of the OH reactivity during most of the day (e.g. 78 % on average at 14:00 LT), but on average only for 33 % during the unusual increase at sunset (17:00 LT). Isoprene oxidation products accounted for up to 20 % (19:30 LT), CO for up to 11 % (5:00 LT) of OH reactivity (Fig. 2.4). The unexplained (“missing”) fraction of total OH reactivity was largest at 17:30 LT (60 % on average). The isoprene flux (Fig. 2.5) followed photosynthetic active radiation and temperature, as expected. However, it persisted, albeit weakly, until 18:30 LT. As plants continued to emit isoprene, other biogenic emissions might as well have continued during sunset and contributed to unexplained OH reactivity.

The isoprene oxidation product-to-isoprene ratio is generally higher in the dry season than in the wet season, but in November 2015 (ca. 0.4 at 12–15:00 LT, Fig. 2.4) it was higher than reported for the dry seasons in 2013 (Yáñez-Serrano et al., 2015) or in 2001 (Kuhn et al., 2007), with values below 0.4 in both cases. This means that the even drier conditions during the strong El Niño period could have caused

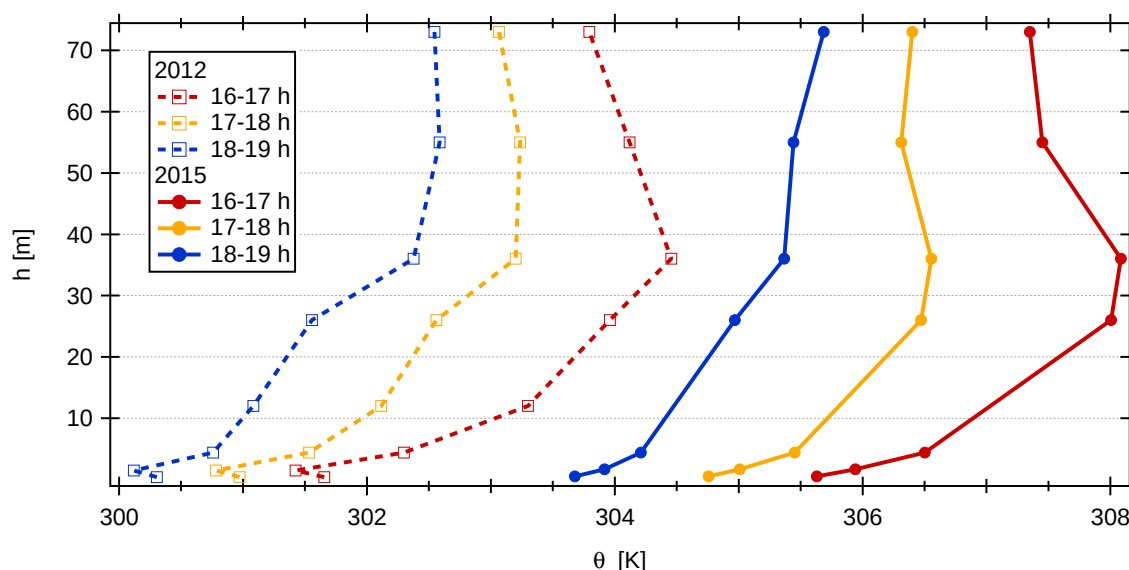


Figure 2.6: Vertical potential temperature profiles between forest floor and 73 m height above ground level for November 2012 and November 2015. Three different profiles represent temporal variation for the evening hours (local time).

a higher oxidative efficiency than during average dry seasons. Part of the unexplained evening reactivity might stem from elevated values of oxidized VOCs other than MVK/ methacrolein/ ISOPOOH.

2.3.2 Possible influence of turbulent transport

Another potential reason for the shift of the diel OH reactivity maximum could be a change in turbulent transport of reactive species from the canopy below or from the boundary layer above the point of observation. Especially below the canopy, soil and underwood emissions could contain highly reactive species (Nölscher et al., 2016). Indeed it has been recently reported that strong emissions of sesquiterpenes from the forest floor occur under drier conditions (Bourtsoukidis et al., 2018).

To assess the stability of the canopy and surface layer, the potential temperature profiles of November 2012 and 2015 were compared (Fig. 2.6). Overall, the structure of both profiles is similar; with the El Niño influenced profile shifted to higher temperatures and with less pronounced gradients. However, in 2012 an inversion is present during the daytime hours at a height of 1.5 m, which caps a stably stratified layer just above the forest floor. These stable conditions close to the ground surface suggest that emissions of reactive species from the soil may not have been transported upwards through and out of the canopy. Such thermal stratification of the lower canopy has been observed in Amazonian forests before and could be related to absorption of radiation by the upper canopy (Andreae et al., 2015; Gerken et al., 2017; Kruijt et al., 2000; Santana et al., 2018). In 2015, net radiation measured at the ATTO site was on average $\approx 100 \text{ W m}^{-2}$ higher than in 2012, which may have facilitated penetration of radiation further into the canopy and hence the break-up of the inversion (Fig. 2.6). In addition, wind shear in the canopy was higher in 2015 than in 2012 (Suppl. Fig. 6), which could also have contributed to the generation of turbulence and transport away from the forest floor (Santana et al., 2018). As a result, a larger

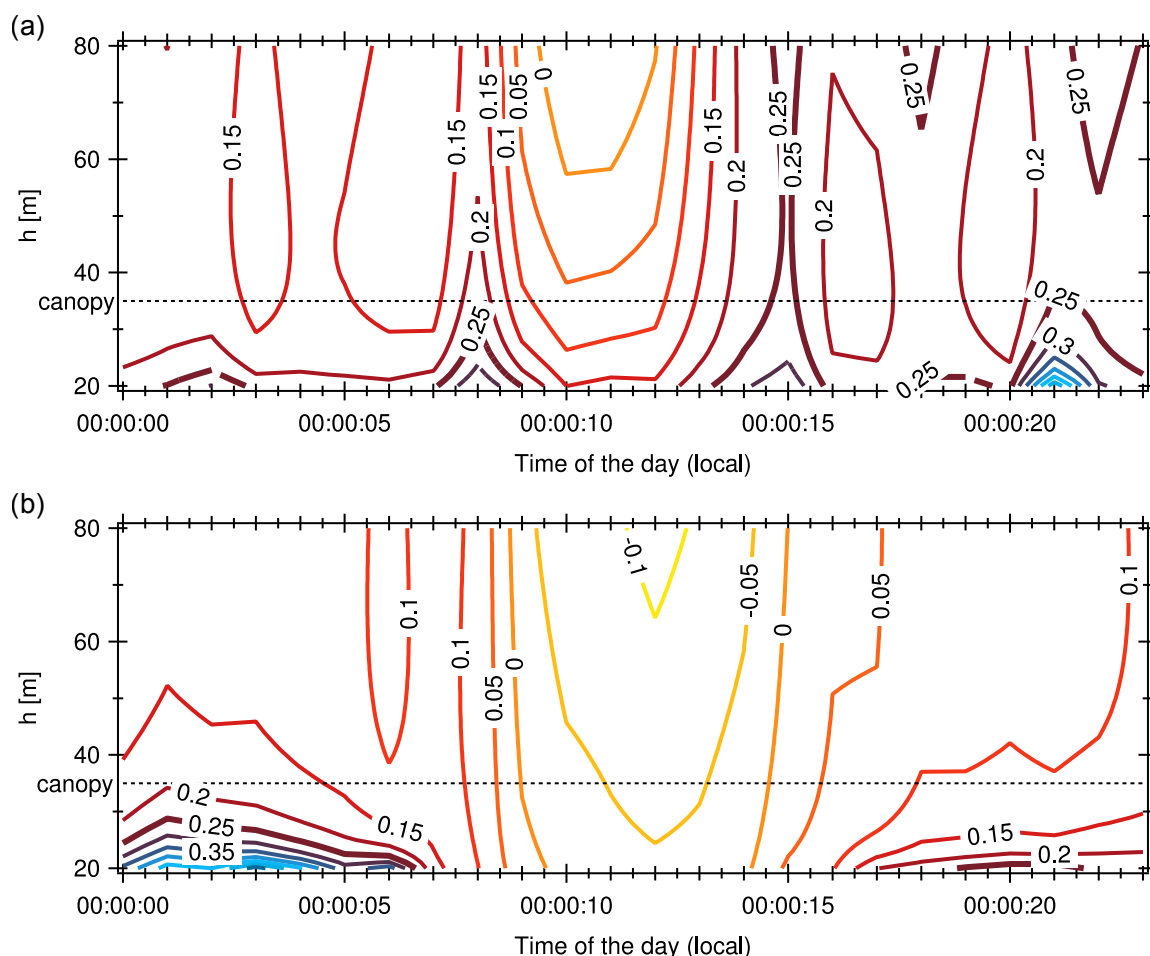


Figure 2.7: Diel patterns of gradient Richardson numbers from 20 m to 80 m height above ground level for (A) November 2012 and (B) November 2015. The critical Richardson number (0.25) is indicated with a thicker line. The dashed line represents canopy top (35 m).

part of unexplained daytime OH reactivity during the El Niño event might stem from soil emissions than in 2012.

Average diel gradient Richardson number patterns derived from meteorological measurements are displayed for November 2015 and November 2012 in Fig. 2.7. It is visible that turbulent conditions above and inside the canopy ($Ri_g < 0.25$) persisted longer in the evening in 2015. Between 17:00 and 18:00 LT, the conditions for vertical transport were far less favorable in 2012 than in 2015, when canopy emissions were likely transported up to 41 m. Consequently, the observed sunset increase in OH reactivity might be related to this turbulent transport. However, the peak OH reactivity being not reflected in isoprene mixing ratios, additional change in biogenic emissions has to be considered.

For a closer investigation of the boundary layer dynamics, the MXL/MESSy boundary layer model was run for two case study days (November 22, 2015 and November 10, 2012, Supplementary Fig. 7 and 8; note that the boundary layer model is not suitable for representing the nocturnal boundary layer and therefore the simulations end at 17:00). As shown in Supplementary Fig. 8 in comparison with observations, MXL captures the diurnal variability of the atmospheric boundary layer (ABL) for the 2015 case well until about 14:00 LT. After 14:00 LT, other factors like cloud formation

(which are not included in the model) could have impacted boundary layer depth. ABL height observations were not available for 2012. What can be inferred, however, is that the lower surface forcing (sensible heat flux) in 2012 led to a lower boundary layer in 2012, assuming that other forcings (e.g. subsidence) were equal to the 2015 case. The shape of the modelled daytime boundary layer development did not differ much between 2012 and 2015, with ABL height peaking around 14:30 LT for both years. The simulated maximum ABL height is about 200 m higher in 2015 than in 2012, because of higher sensible heat fluxes. This means that reactive species which are emitted from the canopy during daytime were mixed over a deeper layer under the 2015 conditions and more diluted by entrainment of cleaner air from aloft, which should in principle cause lower reactivities. However, this did not lead to significant differences in overall daytime reactivity between the two years, possibly because higher emissions balanced the higher dilution.

2.3.3 Possible influence of plants' emission behavior

Stomatal or non-stomatal BVOC release?

Persisting isoprene emission fluxes until after 18:00 LT (Fig. 2.5) indicate the possibility of continuing BVOC emissions as a reason for the evening OH reactivity maximum under El Niño conditions. Plant volatiles can be released from the leaf tissue either under stomatal control or without. The pathway depends on localization and physicochemical nature of the VOC species (Harley, 2013; Niinemets et al., 2004). In order to explore a possible drought stress related difference in plants' emission behavior as a reason for the shift of diel OH reactivity maxima between an El Niño and an ENSO-neutral November, canopy stomatal conductance was derived from water fluxes, air temperature and humidity measured in November 2015. As expected, canopy stomatal conductance increased at sunrise (between 5:00 and 6:00 LT), associated with BVOC release reflected in increasing OH reactivity (Fig. 2.8). When temperatures had increased to a level that water loss via the stomata would become unfavorably large, conductance decreased (around 10:00 LT) and did not increase again until the next morning. This diel cycle shows the same pattern as in studies of stomatal conductance of tropical trees such as Dolman et al. (1991) and Granier et al. (1992), even though the approach applied here is more indirect. Diel medians of canopy stomatal conductance did not increase significantly at 17:00–17:30 LT, when OH reactivity was in its maximum. Santos et al. (2018) showed that drought during the 2015 El Niño decreased average stomatal conductance in an Amazon forest. Therefore, the release of unmeasured compounds responsible for the OH reactivity increase most likely was not affected by plants' stomata.

For BVOCs that are not stored in specialized storage compartments of the leaf, release from plants independent of stomatal control has been reported especially for isoprene (Fall and Monson, 1992) and monoterpenes (Loreto et al., 1996). Niinemets and Reichstein (2002) found that β -ocimene and limonene emissions were unaffected by stomatal closure (in contrast to oxygenated monoterpenes). A general overview has been reported by Niinemets et al. (2004). In the absence of stomatal opening during the evening hours, such an emission mechanism independent of stomatal conductance could be responsible for the OH reactivity maximum seen at sunset under extremely dry conditions at the ATTO site.

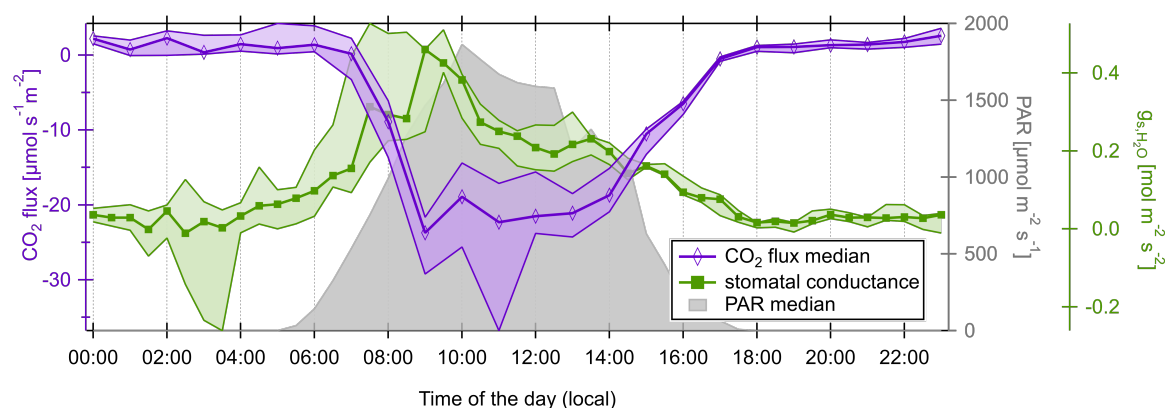


Figure 2.8: Diel half-hourly medians and 25th–75th percentiles (shaded areas) of canopy stomatal conductance at 26 m (inside canopy), and of CO₂ flux at 41 m height above ground level. The diel cycle of photosynthetic active radiation is displayed as grey shades.

As isoprene was among the measured species and can only to a small extent explain total OH reactivity, one group of compounds that is likely to be at least partly responsible is monoterpenes. Monoterpenes were not monitored during the observation period described here, but one month prior to the El Niño influenced campaign (see following section). The decrease of ambient temperature at the end of the day started ca. 1 h later in 2015 than in 2012 (Fig. 2.3). This means that the build-up of temperature-related VOCs such as monoterpenes might have lasted longer than usual. OH radical formation is dependent on sunlight. Therefore, during the sunset hour, the most important sink of BVOCs was decreasing rapidly and additionally released BVOCs were more likely to accumulate in the atmosphere. As discussed in section 2.3.2, these emissions were more efficiently transported out of the canopy up to the point of observation than in 2012.

Monoterpene emissions

VOC data acquired at the ATTO site in October 2015, one month before our campaign, show 1) higher monoterpene emissions than in other dry seasons (Yáñez-Serrano et al., 2018) and 2) a second monoterpene maximum at sunset (Fig. 2.9). October 2015 was already influenced by El Niño, but it was less dry and hot than November. Average temperatures were 0.6 °C lower, average RH was 5.7 % higher. In the monoterpene time series (Supplementary Figure 9), a tendency towards higher monoterpene emissions is visible on drier and warmer days. Biogenic monoterpene emissions are well known to be promoted by elevated temperatures (e.g. Guenther et al., 1993). At high temperatures, monoterpene emissions can be uncoupled from net primary production (Jardine et al., 2017). Based on these observations, we speculate that it is very likely that monoterpene emissions during the exceptionally warm conditions in November 2015 were even higher than in October 2015. Using the emission factors for evergreen tropical broadleaf plants trees from Guenther et al. (2012) and the G93 equation for monoterpene emissions from Guenther et al. (1993), we estimate that the temperature increase for 17:00 LT of ca. 2.5 °C in November 2015 compared to October 2015 could have caused ca. 28 % higher monoterpene emissions.

In November 2015 at the ATTO site, maximum leaf surface temperatures at the top of the canopy reached up to 42.6 °C (11:00 LT). In an ENSO-neutral November (due to

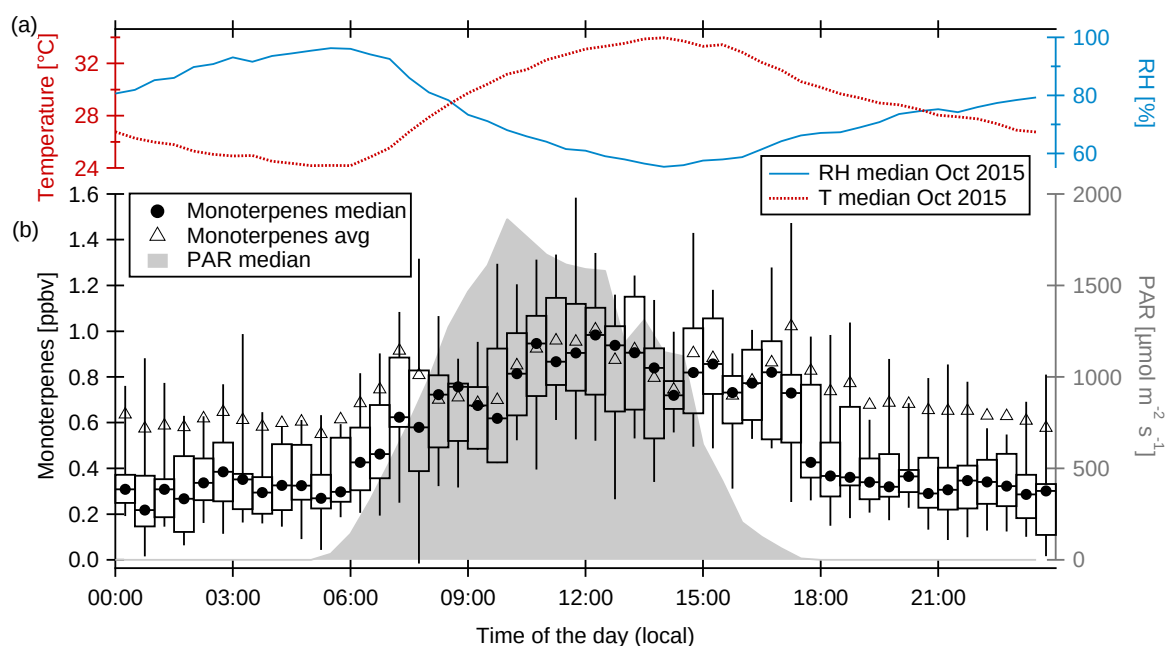


Figure 2.9: (a) Diel cycles of temperature and relative humidity measured at 41 m above ground level in October 2015. (b) Diel cycle of ambient monoterpene mixing ratios measured at 38 m above ground level during 12 days in October 2015 showing half-hourly monoterpene medians (circles) and averages (triangles). Boxes and whiskers represent the 25th–75th and 5th–95th percentiles, respectively. The diel cycle of photosynthetic active radiation (PAR) is displayed on the right axis.

data availability here November 2014), the maximum was 4.0 °C lower and average leaf temperatures at 17:00 LT were 3.9 °C lower than in 2015. Interestingly, Jardine et al. (2017) reported a dependence of monoterpene speciation in the Amazon region on leaf temperature. They found that extreme heat in 2015/16 triggered a shift of plant emissions towards more reactive monoterpenes such as β -ocimene, which is ≈ 100 times more reactive towards OH than the usually predominant α -pinene. Estimating a 28 % increase of monoterpene mixing ratios at 17:00 LT, an OH reactivity of up to 7.8 s^{-1} if dominated by β -ocimene (4.8 s^{-1} when assuming a speciation as observed by Jardine et al., 2017) could be explained by monoterpenes, which is 22 % of total OH reactivity and more than one third of the unexplained (“missing”) fraction.

Among other purposes, monoterpenes are thought to serve plants in stress relief, e.g. as antioxidants against elevated levels of cell-damaging reactive oxygen species and ozone (Loreto et al., 2004). Ozone levels at the ATTO site were on average 69 % higher in November 2015 (16.7 ± 6.6 ppbv) than in November 2012 (9.9 ± 4.3 ppbv), with respective maxima of 40.6 ppbv in 2015 and of 20.5 ppbv in 2012. This difference can be attributed to a larger number of and more closely located forest fires (Aragão et al., 2018, and represented in elevated NO_x values (see Sect. 2.3.1)). The ozone maximum occurred between 15:00 and 18:00 LT (Fig. 2.10). It might have induced an oxidant stress reaction in plants which is reflected in higher monoterpene emissions. Moreover, due to the low OH concentration normally present at dusk being further suppressed by high OH reactivity, and the higher ozone levels at the same time, enhanced ozone-terpene reactions at the end of the day will lead to more efficient SOA formation. Reactions of the predominant terpene at the site (α -pinene)

with ozone produce more particles than with OH (Bonn and Moorgat, 2002; Griffin et al., 1999; Jokinen et al., 2015). SOA formation is additionally furthered by a high VOC/NO_x ratio (Donahue et al., 2005; Presto et al., 2005) as it is observed in the tropical forest. A fraction of the SOA will become cloud condensation nuclei (CCN). We therefore tentatively speculate this may represent a possible cloud formation feedback.

In addition to the temperature and ozone effects, drought stress has been reported to enhance monoterpene emissions in several different plant species (Blanch et al., 2009; Llusà et al., 2008; Ormeno et al., 2007; Šimpraga et al., 2011). However, in some other studies drought had the opposite effect (e.g. Bourtsoukidis et al., 2014; Llusia et al., 2016; Lüpke et al., 2016; Saunier et al., 2017). Some species even show a trade-off between isoprene and monoterpenes: isoprene emissions can be reduced in favor of monoterpene emissions (Harrison et al., 2013).

Not much is known about the effect of combined multiple stress factors on plants' VOC emission behavior, although this is what usually occurs in nature (e.g. in this study a combination of water deficit, heat, and 69 % higher ozone levels.) However, Holopainen and Gershenzon (2010) suggest an additive effect of multiple abiotic stresses on BVOC emissions. We therefore conclude that the largely unexplained OH reactivity maximum observed during the sunset hours in 2015 could to some extent be explained by higher and more reactive monoterpene emissions from vegetation due to a combination of factors: Higher temperatures that decreased later in the course of the day, water deficit and ozone stress, combined with more efficient transport.

The 66 % increase of OH reactivity seen at 17:00 LT in 2015 compared to 2012 (+ 14.5 s⁻¹) would equal, depending on the compounds, an equivalent of several ppbv of unmeasured VOCs (e.g. ca. 2 ppbv of β -ocimene). 2 ppbv is within the variability of the ozone diel cycle (Fig. 2.10), meaning that, based on ozone mixing ratios, a release of monoterpenes or other compounds that react quickly with ozone cannot be ruled out.

Other stress-induced BVOC emissions

Assuming non-stomatal release and build-up of monoterpenes as a potential cause of the high OH reactivity at sunset, stress factors may have induced the release of other reactive BVOCs alongside with monoterpenes. Water deficit stress is known to alter plants' mesophyll chemistry for maintaining osmotic potential (Ruehr et al., 2009) and can modify their BVOC composition and emission behavior. Drought stress is able to induce new emissions (Niinemets, 2010). For example, Šimpraga et al. (2011) found a burst of an unidentified green-leaf volatile associated with acute water deficit in beech trees.

Apart from triggering monoterpene emissions (see above), ozone can induce the release of additional BVOCs. For example, Bison et al. (2018) observed sesquiterpene emissions, which had not been there without ozone stress, after the Brazilian tropical tree species *Croton floribundus* was exposed to high ozone levels. Ozone-driven sesquiterpene emissions have been observed in other species as well (e.g. Bourtsoukidis et al., 2012).

O'Connell et al. (2018) report that drought had a more severe influence on biogeochemical cycles in tropical forest soils than previously thought, in particular concentrations of inorganic phosphorous (which usually is a limiting factor in tropical

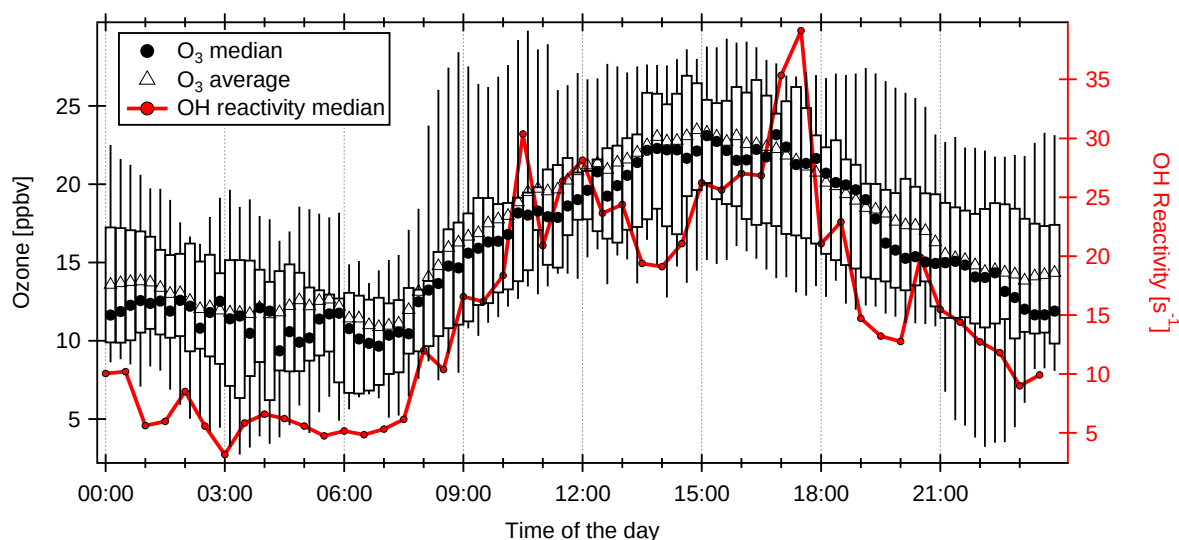


Figure 2.10: (a) Quarter-hourly diel cycle of Ozone measured at 38 m height above ground level in November 2015 with medians (circles) and averages (triangles). Boxes and whiskers represent the 25th–75th and 5th–95th percentiles, respectively. The half-hourly median diel cycle of OH reactivity is displayed on the right axis.

forest net primary productivity) were decreased, and organic phosphorous concentrations increased. Drought-impacted soil chemistry (e.g. changed nutrient availability) could therefore strongly influence plants. Nutrient availability might also affect VOC emission from soils, which may be highly relevant considering a recent report about significant sesquiterpene release from soil (Bourtsoukidis et al., 2018).

The 2015 OH reactivity maximum occurred during the light-dark transition of sunset. Several studies have shown VOC bursts of isoprene, acetaldehyde and/or (stress related) green-leaf volatiles after light-dark transitions (Brilli et al., 2011; Graus et al., 2004; Hayward et al., 2004; Jardine et al., 2012; Jud et al., 2016; Karl et al., 2002). These so-called “post-illumination bursts” are thought to be associated with fast changes in intracellular pH in fast light-to-dark-transitions (Brilli et al., 2011), a “pyruvate overflow mechanism” (Hayward et al., 2004; Karl et al., 2002), or a “pyruvate dehydrogenase bypass pathway” (Jardine et al., 2012). However, Jud et al. (2016) reported that acute drought stress lead to a disappearance of the “post-illumination bursts”. Only when recovering from stress, green leaf volatiles were enhanced after the light-to-dark transition. Moreover, these bursts have only been observed under laboratory conditions. In a forest, illumination changes gradually and differently for every single leaf.

Green-leaf volatiles (GLVs) and sesquiterpenes are highly reactive towards the OH radical. If drought and/or ozone stress induced their release from vegetation alongside with monoterpenes, they might explain part of the unexplained OH reactivity. Courtois et al. (2009) observed 264 stress-related volatile organic compounds emitted by tropical trees, amongst which there were 137 different sesquiterpenes and 13 GLVs. Applying an average of known literature reaction rate coefficients of sesquiterpenes and GLVs with OH ($k_{X+OH} = 9.71 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), an average of 40 pptv of each of the 137 sesquiterpenes and 13 GLVs would be sufficient to explain the 14.5 s^{-1} increase in total OH reactivity seen at 17:00 LT in 2015 compared to 2012.

2.4 Summary and conclusions

2.4.1 Influence of extreme drought and high temperature conditions on the diel cycle of OH reactivity

The diel cycle of total OH reactivity in November 2015 exhibits two maxima - one around noon, and a second, higher one, in the sunset phase of the day, which is only by 40 % explained by the measured VOC species. This is in contrast to the diel cycle in November 2012, where only one maximum occurred around noon. The absolute amount of OH reactivity over the course of the day did not differ significantly between both observation periods, contradicting our initial hypothesis that drought stress would increase total OH reactivity.

The difference in diel behavior is attributed to extreme warming and drought linked to the 2015/16 El Niño event, reflected in lower soil and ambient humidities, and a higher number of regional forest fires. In the evening hours, less stable conditions inside and above the canopy favored air transport to 41 m (observation height). Additionally, we conclude that a combination of factors lead to higher, probably non-stomatal, emissions of unmeasured BVOCs during the El Niño period which, transported above the canopy by turbulence, resulted in a sunset maximum in OH reactivity. The key factors identified are:

- (a) The temperature decrease at the end of the day began 1 h later in November 2015, which suggests that temperature-related BVOCs such as monoterpenes were still released during the sunset hour, while their most important sink (OH radicals) was already decreasing.
- (b) Temperature levels were generally elevated in comparison to other dry seasons, causing above-normal emissions of monoterpenes and, potentially, other BVOCs.
- (c) Monoterpene speciation in the emissions was probably shifted towards more reactive species, such as β -ocimene, due to the high temperatures.
- (d) Drought stress might have induced additional emissions of monoterpenes and/or other BVOCs associated with maintaining osmotic pressure and/or antioxidant purposes in the evening hours.
- (e) A higher number of forest fires prompted elevated ozone levels (+ 69 %) especially in the afternoon/evening, with possible oxidant stress implications for plants. Monoterpenes, sesquiterpenes and/or green-leaf volatiles may have been released to mitigate this stress.

2.4.2 Implications for an Amazon rainforest subject to future global change

Under stress such as elevated temperatures and water deficit, up to 10–67 % of net primary production by land plants is thought to be allocated to BVOCs (Peñuelas, 2003; Sharkey and Loreto, 1993). This poses a challenge to carbon cycle closure. The observations presented in this study have implications for future Amazon rainforest carbon balance and air chemistry, because it is expected that the frequency of strong El Niño events will increase due to climate change (Cai et al., 2015; Timmermann et al., 1999), and the expanding anthropogenic deforestation exacerbates precipitation deficits and warming in the Amazon region (Alkama and Cescatti, 2016; Baidya Roy,

2002; Swann et al., 2015; Zemp et al., 2017; Zeng et al., 1996). Therefore, it can be expected that warming and drought events like the one in 2015/16 will occur more often in the Amazon region (Marengo and Espinoza, 2016). Such periods of continuous elevated stress levels (oxidative, thermal, drought) generally result in a shift of the Amazon ecosystem from sink to source of atmospheric carbon (Brienen et al., 2015; Feldpausch et al., 2016; Metcalfe et al., 2010; van der Laan-Luijkx et al., 2015) – one of the reasons being elevated emissions of stress-mitigating BVOCs.

With total OH reactivity observations, we show that, although the total sum of day-time OH reactivity was not altered, the diel cycle and amount of VOC mixing ratios as well as the diel cycle of the size of the OH sink did change in a rainforest under drought and heat stress. This change in the timing of the release of ambient OH reactivity can potentially impact atmospheric chemistry above the Amazon rainforest with subsequent implications for, amongst others, atmospheric oxidation capacity, photochemistry, and SOA formation. The increase of OH reactivity above the canopy at the end of the day would tend to favor terpene-ozone over terpene-OH reactions. This is because OH radical concentrations decrease with fading sunlight. Terpene-ozone reactions are more efficient in SOA production, and therefore potentially elevated CCN formation occurred at the time of nocturnal boundary layer formation. Our findings show that under El Niño conditions, total daytime OH reactivity was equivalent to ENSO-neutral conditions. However, as CO₂ uptake by the forest is reduced under drought, heat and oxidative stress, the fraction of carbon uptaken that is released as VOCs has potentially increased. The effect of drought and warming needs more investigation in order to understand how diel rainforest carbon cycles and air chemistry will be modified under future climate change.

Plants emit more than 30 000 VOCs (Harley, 2013), and most studies of tropical forest VOCs have so far only focused on few of them. Often, compounds of very low concentration can be chemically highly important due to their high reactivity (Yáñez-Serrano et al., 2018). For a complete understanding of rainforest atmospheric chemistry and to close the gap of unidentified (“missing”) OH reactivity (Nölscher et al., 2016), more VOCs should be taken into account in future studies.

Conflict of Interest. The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Author Contributions. AN, AY, EB, SK and JW performed CRM and VOC measurements. SW, AT, MS, DW and JL contributed inorganic trace gas/greenhouse gas measurements and part of the micrometeorological data. AT calculated flux data. MOS and AA were responsible for meteorological measurements and data. RJ designed the meteorological model and contributed to meteorological data analysis. CD analyzed the boundary layer height observations. JK contributed the canopy stomatal conductance approach. EP performed the data analysis and wrote the first draft of the manuscript. All authors contributed to manuscript writing and revision, read and approved the submitted version.

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Data Availability Statement. The raw data supporting the conclusions of this manuscript will be made available by the authors, without undue reservation, to any qualified researcher. The OH reactivity dataset is available on www.attodata.org.

Supplementary Material. The Supplementary Material for this article can be found online at: www.frontiersin.org/articles/10.3389/ffgc.2018.00012/full#supplementary-material.

Shipborne measurements of total OH reactivity around the Arabian Peninsula and its role in ozone chemistry

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Contribution to this publication by Eva Y. Pfannerstill: Conducted the OH reactivity measurements during the first half of the campaign, performed the data analysis and prepared the manuscript.

Abstract. The Arabian Peninsula is characterized by high and increasing levels of photochemical air pollution. Strong solar irradiation, high temperatures and large anthropogenic emissions of reactive trace gases result in intense photochemical activity, especially during the summer months. However, air chemistry measurements in the region are scarce. In order to assess regional pollution sources and oxidation rates, the first ship-based direct measurements of total OH reactivity were performed in summer 2017 from a vessel travelling around the peninsula during the AQABA (Air Quality and Climate Change in the Arabian Basin) campaign. Total OH reactivity is the total loss frequency of OH radicals due to all reactive compounds present in air and defines the local lifetime of OH, the most important oxidant in the troposphere. During the AQABA campaign, the total OH reactivity ranged from below the detection limit (5.4 s^{-1}) over the north-western Indian Ocean (Arabian Sea) to a maximum of $32.8 \pm 9.6 \text{ s}^{-1}$ over the Arabian Gulf (also known as Persian Gulf) when air originated from large petroleum extraction/processing facilities in Iraq and Kuwait. In the polluted marine regions, OH reactivity was broadly comparable to highly populated urban centers in intensity and composition. The permanent influence of heavy maritime traffic over the seaways of the Red Sea, Gulf of Aden and Gulf of Oman resulted in median OH sinks of $7.9\text{--}8.5 \text{ s}^{-1}$. Due to the rapid oxidation of direct volatile organic compound (VOC) emissions, oxygenated volatile organic compounds (OVOCs) were observed to be the main contributor to OH reactivity around the Arabian Peninsula (9–35 % by region). Over the Arabian Gulf, alkanes and alkenes from the petroleum extraction and processing industry were an important OH sink with $\approx 9\%$ of total OH reactivity each, whereas NO_x and aromatic hydrocarbons ($\approx 10\%$ each) played a larger role in the Suez Canal, which is influenced more by ship traffic and urban emissions. We investigated the number and identity of chemical species necessary to explain the total OH sink. Taking into account ≈ 100 individually measured chemical species, the observed total OH reactivity can typically be accounted for within the measurement uncertainty (50 %), with 10 dominant trace gases accounting for 20–39 % of regional total OH reactivity. The chemical regimes causing the intense ozone pollution around the Arabian Peninsula were investigated using total OH reactivity measurements. Ozone vs. OH reactivity relationships were found to be a useful tool for differentiating between ozone titration in fresh emissions and photochemically aged air masses. Our results show that the ratio of NO_x - and VOC-attributed OH reactivity was favorable for ozone formation almost all around the Arabian Peninsula, which is due to NO_x and VOCs from ship exhausts and, often, oil/gas production. Therewith, total OH reactivity measurements help to elucidate the chemical processes underlying the extreme tropospheric ozone concentrations observed in summer over the Arabian Basin.

3.1 Introduction

The Arabian Peninsula is a hotspot of global change. It is already subject to extremes of heat and drought, which are predicted to intensify (Chenoweth et al., 2011; Cook et al., 2016; Donat et al., 2014; Lelieveld et al., 2012; Lelieveld et al., 2016a; Tanarhte et al., 2012; Terink et al., 2013; Wasimi, 2010; Zhang et al., 2005), and to photochemical air pollution (Abdelkader et al., 2015; Farahat, 2016; Lelieveld et al., 2009; Smoydzin et al., 2012). The Middle East accommodates densely populated urban centers with a total of 350 million people, and is a hub of fossil fuel extraction and processing with more than half of the world's known oil and gas reserves (Khatib, 2014). Moreover, the waters surrounding the Arabian Peninsula are key routes of global trade and bottlenecks for marine traffic, another source of air pollution (Boersma et al., 2015; Endresen, 2003; Eyring, 2005; Mertens et al., 2018) that is expected to increase in the future (Eyring et al., 2007).

Photochemistry in the region is thought to be particularly active due to a combination of factors: large anthropogenic emissions of reactive hydrocarbons and NO_x ($= \text{NO} + \text{NO}_2$) from the petroleum industry, shipping and energy-intensive urban areas; with high levels of solar irradiation and hence photolysis rates; and high temperature, which disfavors NO_x reservoirs such as PAN and N_2O_5 . The main regional photochemical oxidation process is initiated by ozone photolysis to $\text{O}(^1\text{D})$, which reacts with water vapor to form hydroxyl radicals (OH). The OH radicals react with volatile organic compounds (VOCs) to yield peroxy radicals that can convert NO to NO_2 , leading to ozone formation (Haagen-Smit, 1952; Ren et al., 2013; Sillman, 1999). The abundance of precursors and intense photochemistry make conditions in the Arabian Basin very favorable for photochemical ozone production, leading to extremely high ozone mixing ratios up to 200 ppb (Krotkov et al., 2016; Lelieveld et al., 2009; Smoydzin et al., 2012). Ozone formation was reported to be enhanced even 300 km downwind of a hydrocarbon processing facility at the coast of the Arabian Gulf (Moradzadeh et al., 2019). In addition, VOC oxidation by OH and ozone can generate secondary organic aerosol (Grosjean and Seinfeld, 1989; Kroll and Seinfeld, 2008) with implications for human health (Lelieveld et al., 2015) and regional radiative budgets (Ezhova et al., 2018).

Despite being an air pollution hotspot, very few observational atmospheric data exist from the Arabian Basin, and studies of VOCs in the region are scarce and mostly urban (Barletta et al., 2017; Doskey et al., 1999; Khalil et al., 2016; Matysik et al., 2010; Salameh et al., 2014; Salameh et al., 2016; Simpson et al., 2014). In order to chemically map the region, a comprehensive suite of atmospheric measurements was performed from a ship sailing around the Arabian Peninsula in summer 2017 during the AQABA (Air Quality and Climate Change in the Arabian Basin) cruise.

The number of known VOCs in air has been estimated to be between 10^4 and 10^5 species (Goldstein and Galbally, 2007), and it is assumed that many more remain unknown. Accounting for all of these chemical compounds individually with quantitative measurements is currently unfeasible. Instead, the combined load of OH reactive species (mainly VOCs and CO) in ambient air, termed the total OH reactivity, can be measured directly. Total OH reactivity denotes the total sink, or loss frequency, of the OH radical. When compared to the OH reactivity calculated from all individually measured compounds (termed the speciated OH reactivity), total OH reactivity can be used to infer the occurrence of VOCs that were not measured (termed the

unattributed or “missing” OH reactivity). Moreover, total OH reactivity is necessary for a quantitative understanding of ozone production and can help estimating its sensitivity to VOCs and NO_x (Kirchner et al., 2001; Pusede et al., 2014; Sinha et al., 2010; Yang et al., 2017). The OH sink also affects the atmospheric residence time of methane and therewith its global budget, which still poses a challenge in models (Zhao et al., 2019).

With VOC and NO_x emissions from ship exhausts (Boersma et al., 2015; Endresen, 2003; Huang et al., 2018) and VOCs from oil and gas operations (Buzcu and Fraser, 2006; Gilman et al., 2013; Gilman et al., 2009; Milazzo et al., 2017; Schade and Roest, 2016), the air around the Arabian Peninsula is expected to contain significant levels of pollution. In Saudi Arabian cities, OH reactivity has been reported to range from 14 to 42 s⁻¹ (from the sum of individual measurements), dominated by alkenes (Barletta et al., 2017). Downwind of oil and gas production in Colorado, OH reactivity of VOCs was dominated by alkanes (60 %), followed by OVOCs (27 %) and alkenes (8 %; Gilman et al., 2013). The largest OH sink among the VOCs in the exhaust plume of a ship operating at full speed are alkenes (42 %), followed by aromatics (40 %), OVOCs (12 %) and alkanes (5 %; estimated using emission factors from Huang et al. (2018)).

Unattributed OH reactivity in locations dominated by anthropogenic VOCs has been measured to be as low as zero in Lille, France (Hansen et al., 2015) or New York, U.S. (Ren et al., 2006a), to 10–54 % in Paris, France (Dolgorouky et al., 2012) and 10–80 % in Tokyo, Japan (Yoshino et al., 2006). However, comparing unattributed OH reactivity between different studies is difficult, because it depends on the air mass and coverage of inorganic trace gases and VOCs measured in each campaign. In this work, we apply an approach that aims to use comprehensive trace gas information gathered by various instruments, even compounds with unidentified chemical structure measured by PTR–ToF–MS, for calculation of speciated OH reactivity. Therewith, we identify the trace gases representing the major OH sinks and try to obtain closure on apportioning OH reactivity.

This study provides an overview of total OH reactivity around the Arabian Peninsula and investigates its sources in the different environments along the route of the campaign. Total OH reactivity is applied for assessing the regional oxidation chemistry and the underlying reasons for the extreme ozone concentrations observed in summer over the Arabian Basin. By combining OH reactivity and ozone measurements, we aim to investigate ozone production processes and to identify differentiated chemical regimes. We demonstrate the utility of in-situ OH reactivity measurements to characterize the role of anthropogenic emissions in modifying the chemical composition of the air.

3.2 Materials and methods

3.2.1 AQABA Campaign

The Air Quality and Climate Change in the Arabian Basin (AQABA) measurements took place on-board the vessel *Kommandor Iona* from June 25 till September 3, 2017. The first leg began in La-Seyne-sur-mer (near Toulon, France), continued via the Mediterranean, the Suez Canal, the Red Sea, the Indian Ocean, the Gulf of Oman

and the Arabian Gulf to Kuwait. On the second leg, the vessel returned via the same route (Fig. 3.1a/b). The ship was equipped with a weather station and four laboratory containers with instrumentation for in-situ and offline monitoring of a large suite of (trace) gases, particles and radicals.

3.2.2 Sampling

Air sampling was performed from a high-flow ($10 \text{ m}^3 \text{ min}^{-1}$) cylindrical stainless steel inlet (sampling height: 5.5 m above deck, diameter: 0.2 m), situated between the containers on the front deck of the ship. This position ensured that inlets were ahead of any contamination sources from the vessel itself when pointed into the wind. Air was drawn from the center of the high-flow inlet and sub-sampled at a rate of approximately 5 slpm (standard L min^{-1} , first leg) and 3 slpm (second leg) into an air conditioned laboratory container using a FEP (fluorinated ethylene propylene) inlet tube ($1/2'' = 1.27 \text{ cm}$ o.d., length ca. 10 m), heated to 50–60 °C. A PTFE (polytetrafluoroethylene) filter, changed weekly (and additionally after intense particle contamination events such as dust storms), prevented contamination of the sub-sampling line by particles or sea spray. This inlet system was used for monitoring both VOCs and total OH reactivity simultaneously. We assume that the length of the inlet prevented some of the larger, extremely low volatile VOCs from reaching the instruments (see Sect. 3.3.3). The combined inlet residence time in FEP tubing and reactor for the OH reactivity instrument was determined as $\approx 15 \text{ s}$ during the first leg and $\approx 25 \text{ s}$ during the second leg by spiking with acetone.

3.2.3 OH reactivity and trace gas measurements

Total OH reactivity was measured using the Comparative Reactivity Method (CRM, Sinha et al., 2008), which proved to be robust enough to run nearly continuously for 10 weeks on a ship, often in rough conditions due to high waves. The method has been applied in many regions of the world (Yang et al., 2016) and has recently been compared to other methods (Fuchs et al., 2017a). The CRM is based on a competitive reaction between reactive compounds from ambient air and a reagent, pyrrole (Westfalen AG, Münster, Germany), inside a glass reactor. OH radicals are produced in the reactor by flushing humidified nitrogen (6.0 grade, Westfalen AG, Münster, Germany) over a Hg/Ar UV lamp (LOT Quantum Design, Darmstadt, Germany). CRM uses three different modes: C1 (pyrrole + OH scavenger + UV light, at $\approx$ ambient humidity), C2 (OH + pyrrole, ambient humidity), and C3 (ambient air + pyrrole + OH). For more details of the method see Sinha et al. (2008) and Michoud et al. (2015).

The system was operated at a pyrrole/OH ratio of 1.9 ± 0.1 (average $\pm$ standard deviation). Because this ratio deviates from pseudo-first order conditions, as is typical for CRM, a correction needed to be applied (see Sect. 3.2.4). Sampling air was continuously drawn into the system and the instrument was switched between C3 (measured for 22–24 minutes) and C2 (measured for 6–8 min) modes. The longer C2 measurements were used when ambient humidity was unstable. C1 was determined every 5–7 days (average $\pm$ standard deviation over the whole campaign: $60.71 \pm 1.18 \text{ ppb}$ of pyrrole). Changes in pyrrole mixing ratio were monitored by a Proton Transfer Reaction-Quadrupole Mass Spectrometer (PTR-QMS, Ionicon Analytik, Innsbruck, Austria (Lindinger and Jordan, 1998) at $m/z = 68$ (dwell time: 5 s).

The PTR–QMS was calibrated every week. It was operated at 60 °C drift temperature, 2.2 mbar drift pressure and 600 V drift voltage ($E/N = 137$ Td). In parallel, a PTR–Time of Flight (ToF)–MS was deployed to monitor VOCs and OVOCs (m/z up to 280), and a gas chromatograph with flame ionization detector (GC–FID) to monitor non-methane hydrocarbons (NMHCs; 20 compounds). Average detection limits for the different NMHCs ranged from 1–25 ppt. The NMHC and methane measurements are described in detail elsewhere (Bourtsoukidis et al., 2019). The PTR-ToF-MS was deployed at 60 °C drift temperature, 2.2 mbar drift pressure and 600 V drift voltage ($E/N = 137$ Td). 1,3,5-trichlorobenzene was fed continuously into the sample stream for mass scale calibration. The time resolution of the measurement was 1 min and background measurements were performed every 3 h for 10 min. The PTR-ToF-MS was calibrated with a multicomponent pressurized gas VOC standard (Apel-Riemer Environmental Inc., Colorado, USA). Mass resolution (full width at half maximum) at 96 amu ranged between ≈ 3500 and ≈ 4500 . Average detection limits for the compounds measured by PTR-ToF-MS ranged from 1–107 ppt. A full list of the trace gases measured by GC-FID and PTR-ToF-MS can be found in Table S1.

Formaldehyde (HCHO) and inorganic trace gases (NO , NO_2 , O_3 , SO_2) were measured sampling from the same chimney (the instruments used are specified in Table S1). Based on SO_2 , NO_x and ethene measurements, a filter was applied to exclude sampling periods that were influenced by the vessel's own exhaust.

3.2.4 Total OH reactivity data analysis

CRM data analysis was conducted following the general procedures described in Keßel (2016) and Pfannerstill et al. (2018).

Humidity in C2 (background) measurements can differ from that of C3 (ambient) measurements because C2 was measured only twice per hour. As the amount of OH radicals generated in the CRM reactor depends on humidity, C2 data were corrected for these C2/C3 humidity differences by applying an empirical relationship of the pyrrole signal vs. the PTR–MS water cluster signal as described in Michoud et al. (2015). The C2 correction applied to match C3 humidity decreased pyrrole levels by on average 0.05 ± 0.04 ppb, corresponding to an OH reactivity of $\approx 0.3 \text{ s}^{-1}$. NO , NO_2 and ozone cause interferences in CRM due to OH recycling induced by HO_2 , which is formed in the reactor simultaneously with OH (Fuchs et al., 2017a; Michoud et al., 2015; Sinha et al., 2008). Ozone, NO and NO_2 interferences were quantified in the laboratory (details of the experiments can be found in Sect. S1). NO_2 loss and conversion to NO in the mass flow controller during tests was monitored by an NO/NO_2 analyzer (Two-channel-chemiluminescence detector). The combined NO , NO_2 and ozone corrections amounted to a median of $\approx 24\%$ of total OH reactivity or an average of 0.36 ± 0.19 ppb of pyrrole over the whole campaign, which equals $\approx 1.9 \text{ s}^{-1}$, with a maximum absolute correction of 1.39 ppb ($7.4 \text{ s}^{-1} / 27\%$ of total OH reactivity) under the influence of closely located ship emissions (high NO_x). A frequency distribution of the corrected fraction of total OH reactivity is displayed in Fig. S1.

The calculation of total OH reactivity with the CRM equation (see Sinha et al., 2008) assumes pseudo-1st-order conditions inside the reactor, which can, however, not be met while preserving a reasonable sensitivity (C3–C2 difference). The correction for deviation from pseudo-1st-order conditions inside the reactor was derived from empirical test gas measurements adapted from the approach in Michoud et al. (2015).

The deviation from pseudo-1st-order depends on the pyrrole/OH ratio and on the reaction rate constant of the measured trace gas towards OH. Trace gases with fast reaction rates (comparable to that of pyrrole) require the largest correction because their concentration inside the reactor decreases at a similar rate as that of pyrrole, leading to an underestimation of their reactivity. Such gases, namely alkenes, were sometimes present during AQABA (e.g. a C_5H_8 -alkene which was not isoprene). This is why we did not use an average correction factor for all gas mixes as in Michoud et al. (2015), but applied a correction where the composition of the air mass is taken into account. Test gases used were toluene (for aromatics correction), isoprene and propene (for alkenes correction), propane and cyclohexane (correction for other species). These test gases are representative of the relevant trace gases and ranges of reaction rate coefficients observed during AQABA. In test experiments, these trace gases were added to the CRM system in known amounts, i.e. known total OH reactivities, at pyrrole/OH ratios representative for the campaign. The correction factors resulting from comparing the observed reactivity with the expected reactivity were weighted according to the measured composition of the ambient air at the moment of observation:

$$F = a X_{aromatic} + b X_{alkenes} + c (1 - X_{aromatic} - X_{alkenes}) \quad (3.1)$$

where F is the total correction factor and the weighted compound-class-specific correction factors are $a = 1.22$, $b = 2.89$ and $c = 1.44$. X is the speciated OH reactivity fraction (in s^{-1}) of the respective class of compounds (aromatics, alkenes). This correction increased OH reactivity by a factor of 1.4 to 2.5 (average $\pm$ standard deviation: $F = 1.5 \pm 0.1$, median = 1.5).

The dilution of ambient air with humidified nitrogen was accounted for with a dilution factor of 1.34.

The 5 min detection limit (LOD) was $5.4 s^{-1}$, derived from the 2σ standard deviation of clean air measurements in the Arabian Sea. Total uncertainty (1σ) of the measurements was $\approx 50\%$ (median and average), with a precision of 10–76 % over 5 min depending on the quantity of reactivity.

3.2.5 Calculated OH reactivity from individually measured compounds (speciated OH reactivity)

The speciated OH reactivity is the sum of the OH reactivities attributed to individual (measured) trace gases:

$$R = \sum k_{M+OH} [M] \quad (3.2)$$

Contributions of trace gases (M , where $[M]$ is their respective concentration in molec cm^{-3}) to OH reactivity (R in s^{-1}) are calculated using the reaction rate constants (k_{M+OH} in $\text{cm}^3 \text{ molecule}^{-1} s^{-1}$) of the respective trace gases (M) with the OH radical. The difference between measured total OH reactivity and the sum of individual trace gas contributions to OH reactivity is termed “unattributed” or “missing” OH reactivity. The trace gases taken into account here for calculating speciated OH reactivity and their reaction rate constants used are listed in Table S1. Out of a total of 120 chemical species that were considered for the calculation of speciated reactivity, 42 chemical species (specified in Table S1), including many of the known important contributors to OH reactivity, were calibrated with gas standards and therefore have low uncertainties in their concentrations as well as in their reaction rate coefficients (5–15 %).

A further 78 exact masses (specified in Table S1) monitored by PTR–ToF–MS were attributed to molecular formulae, and their concentrations derived using a theoretical approach (Lindinger and Jordan, 1998), which has an uncertainty of ca. 50 %. In cases where several trace gases could be responsible for the measured mass, an average of the known reaction rate coefficients with OH was used for calculating the speciated OH reactivity. In the few cases where rate coefficients were unknown in literature, the rate coefficient of a trace gas with comparable functional groups was applied (see Table S1). The uncertainty of the reaction rate coefficients k_{M+OH} is estimated to be 100 % due to the occasional large differences in rate coefficients between possible structures. The uncertainty of the resulting speciated (i.e. calculated) OH reactivity depends on the fraction of gas-standard calibrated compounds in the ambient air at any given point of time and varies between 10 % and 92 %, with an average and median of 45 % over the whole campaign. In accordance with the time resolution of the GC-FID, which monitored compounds with a significant share of OH reactivity, speciated OH reactivity was calculated in 50 min time resolution.

3.2.6 Air mass back trajectories

To investigate the origin of air masses encountered, back trajectories were derived using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPPLIT, version 4, 2014). This model is a hybrid between a Lagrangian and an Eulerian model for tracing small imaginary air parcels forward or back in time (Draxler and Hess, 1998). Back trajectories were calculated based on a start height of 200 m above sea level, going 216 h back in time on an hourly grid beginning at the ship position.

3.3 Results and discussion

3.3.1 Overview of total OH reactivity around the Arabian Peninsula

The air masses encountered during the AQABA campaign were delineated according to the geographical region (Fig. 3.1a/b). A notable difference between leg 1 and leg 2 was the general wind direction over the Arabian Gulf, which changed from north-west (from Iraq/Kuwait) to northeast (from Iran). The range of observed total OH reactivities over the whole campaign was from below the detection limit over the Arabian Sea (north-west Indian Ocean) up to $303.6 \pm 83.9 \text{ s}^{-1}$ during fuelling/bunkering of the ship at the port of Fujairah (United Arab Emirates), due to fresh fuel emissions. The largest fraction of attributed OH reactivity was provided by OVOCs in almost all AQABA regions (9–35 %), which is comparable to previous studies in the oil impacted region of Houston, where between 11 % and 24 % of the OH sink was due to OVOCs (Mao et al., 2010). There were notable regional differences in both the total OH reactivity and the contributing trace gases, which will be discussed hereafter. An overview is displayed in Table 3.1, which divides the reactivity into different chemical families. A list of chemical species attributed to each chemical family is available in Table S1.

The measured sulfur-containing VOCs (SVOCs) and halogenated VOCs (HalVOCs) played virtually no role for OH reactivity in any of the AQABA regions (Table 3.1).

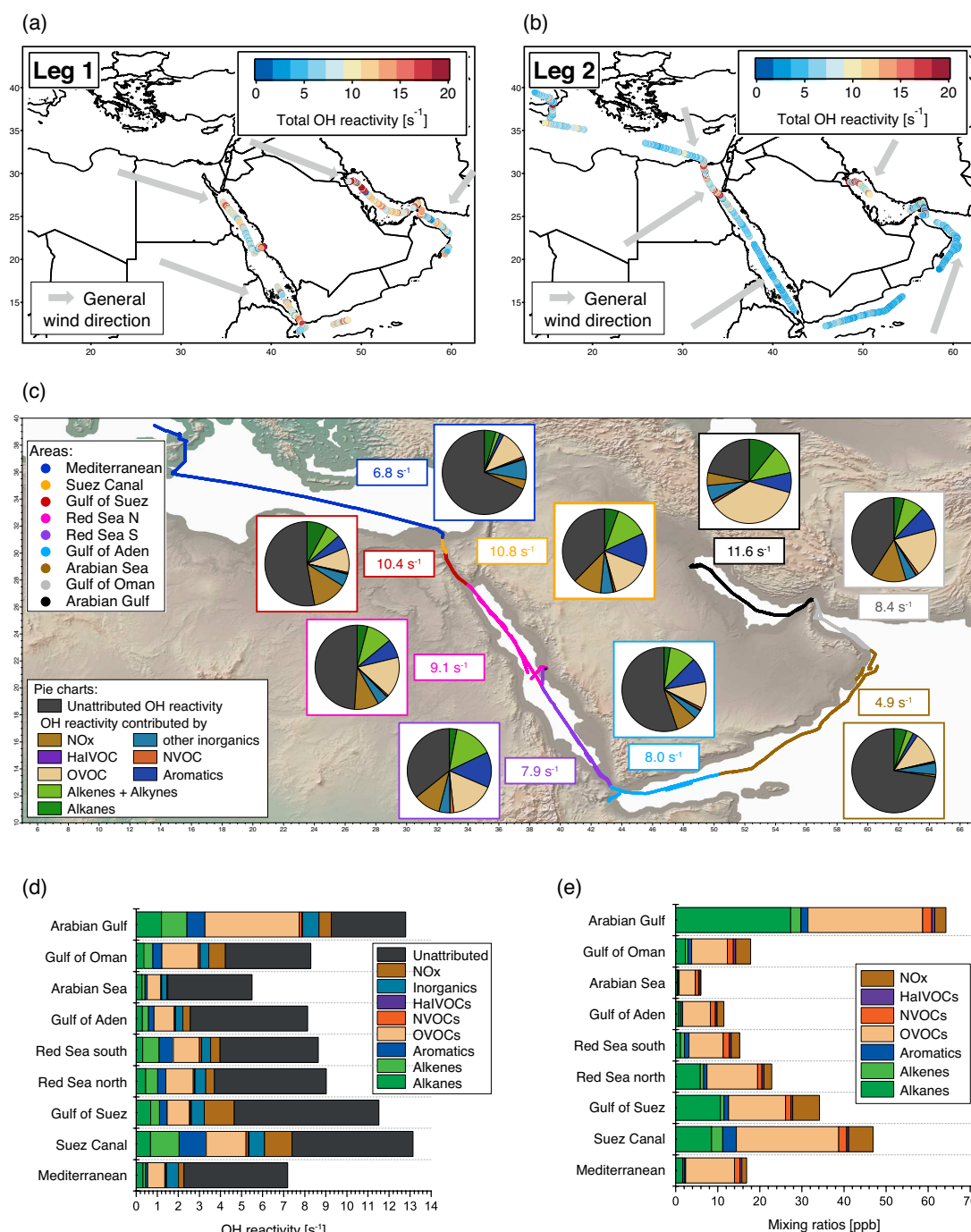


Figure 3.1: Overview of total OH reactivity around the Arabian Peninsula during the AQABA campaign. OH reactivity during (a) leg 1 (July 5–July 31, 2017) and (b) leg 2 (August 3–August 31, 2017). The maximum in the color scales is set to 20 s^{-1} for better visibility of differences, although there are a few datapoints above this value. Arrows depict general wind directions for the respective regions. (c) Total OH reactivity medians by region, and pie charts showing the contribution of compound classes for datapoints where speciated OH reactivity $\geq \text{LOD}$ (exception: pie charts of Mediterranean and Arabian Seas show average of all datapoints, due to low number of points above LOD). (d) Average OH reactivity and speciation by region for all datapoints, including those where speciated OH reactivity was below the LOD. Error bars show the total uncertainty of the measurement. (e) Average mixing ratio of VOCs/trace gases in ppb by compound class and region (except for the class of inorganic compounds other than NO_x). The individual compounds included in each class are listed in Table S1. Port calls and bunkering are excluded from all averages.

The OH reactivity of the monitored NVOs (nitrogen-containing VOCs) was also very minor with not more than 1 % of total OH reactivity over the whole campaign.

Strongly polluted regions: Arabian Gulf, Gulf of Suez and Suez Canal

Compounds with short lifetimes are generally more relevant for total OH reactivity than long-lived species (see also Sect. 3.3.3). Since emissions from oil and gas production and cities contain high mixing ratios of reactive alkenes, the Arabian Gulf, the Gulf of Suez and the Suez Canal, where such sources abound, showed the highest average OH reactivities (Fig. 3.1c/d). In these regions, obvious nearby emission sources were cities, industrial complexes, and especially oil/gas production/processing (Fig. 3.2). The large alkane mixing ratios associated with oil and gas production (Fig. 3.1e; Bourtsoukidis et al., 2019) were not reflected in an equally large share of total OH reactivity due to the slow reaction rate coefficient of alkanes with the OH radical (Fig. 3.1d). The average total OH reactivity ($\pm$ standard deviation) was $12.9 \pm 6.2 \text{ s}^{-1}$ (median: 11.2 s^{-1}) over the Arabian Gulf, $13.2 \pm 6.9 \text{ s}^{-1}$ (median: 10.8 s^{-1}) over the Suez Canal and $11.6 \pm 4.2 \text{ s}^{-1}$ (median: 10.4 s^{-1}) over the Gulf of Suez. There were short periods with higher total OH reactivities ($\pm$ total uncertainties) up to $32.8 \pm 9.6 \text{ s}^{-1}$ over the Arabian Gulf and $26.6 \pm 8.2 \text{ s}^{-1}$ over the Suez Canal (see Sect. 3.3.2). These ranges are comparable to OH reactivities reported from some urban areas, e.g. Beijing, China (Williams et al., 2016), Houston, Texas (Mao et al., 2010), New York City (Ren et al., 2006a), and to OH reactivities calculated from ship-based VOC observations in the fossil fuel production impacted Houston/Galveston Bay (Gilman et al., 2009). The AQABA observations are, however, more than three times as high as VOC-attributed OH reactivity calculated from observations downwind of gas and oil production in south Texas (Schade and Roest, 2016) and twice as high as at the Boulder Atmospheric Observatory when impacted by gas wells (Swarthout et al., 2013).

The largest percentage of attributed OH reactivity over the Arabian Gulf was provided by OVOCs (35 % of total, in contrast to 14 % observed over the Houston/Galveston Bay (Gilman et al., 2009)). This was surprising, as the Gulf region was expected to be similarly dominated by direct hydrocarbon emissions from the fossil fuel industry as the Houston/Galveston Bay. Although the alkanes and OVOCs had broadly equivalent mixing ratios over the Arabian Gulf (Fig. 3.1e), the former have generally lower OH reactivity. Conditions in the Gulf region during summer favor rapid photooxidation of hydrocarbon emissions to OVOCs, due to high temperatures (on average 34.5°C), high humidity (up to 92 % RH) and strong irradiation.

Description for Table 3.1. “ $\geq$ LOD” signifies the use of exclusively those datapoints where speciated OH reactivity is equal to or above the LOD. Percentages of contribution to total OH reactivity by group were calculated from all datapoints in 50 min time resolution. The chemical species attributed to each group are listed in Table S1. For an explanation of unattributed or speciated OH reactivity and “theoretical approach” species refer to Sect. 3.2.5. The 10 most important species are the species with largest average OH reactivity over the respective region. The ratios of C_3 or C_5 carbonyls vs. their precursor or toluene vs. benzene are indicators for air mass age. *Note that the detection limit was 5.4 s^{-1} . (Medit. = Mediterranean.)

Table 3.1: Overview of measured and speciated OH reactivity by region. Further description see opposite page.

	Medit. Sea	Suez Canal	Gulf of Suez	Red Sea north	Red Sea south	Gulf of Aden	Arabian Sea	Gulf of Oman	Arabian Gulf
Aromatic hydrocarbons	1 %	10 %	3 %	4 %	8 %	3 %	2 %	5 %	7 %
Alkanes	4 %	5 %	6 %	5 %	4 %	4 %	5 %	4 %	9 %
Alkenes	2 %	10 %	4 %	6 %	9 %	4 %	3 %	5 %	9 %
OVOCs	11 %	14 %	9 %	14 %	14 %	12 %	12 %	21 %	35 %
NVOCs	1 %	1 %	0 %	1 %	1 %	1 %	1 %	1 %	1 %
SVOCs	0 %	0 %	0 %	0 %	0 %	0 %	1 %	1 %	0 %
Halogenated VOCs	0 %	0 %	0 %	0 %	0 %	0 %	0 %	0 %	0 %
Inorganics	8 %	6 %	5 %	6 %	5 %	4 %	4 %	5 %	6 %
NO _x	4 %	10 %	12 %	5 %	5 %	4 %	1 %	9 %	5 %
Unattributed OH reactivity fraction (all datapoints) $\pm 1 \sigma$ total uncertainty	68 $\pm$ 52 %	44 $\pm$ 43 %	59 $\pm$ 44 %	59 $\pm$ 50 %	54 $\pm$ 54 %	68 $\pm$ 51 %	72 $\pm$ 57 %	49 $\pm$ 55 %	27 $\pm$ 55 %
Unattributed OH reactivity fraction $\geq$ LOD $\pm 1 \sigma$ total uncertainty	none	37 $\pm$ 35 %	53 $\pm$ 34 %	49 $\pm$ 39 %	35 $\pm$ 55 %	55 $\pm$ 38 %	none	41 $\pm$ 52 %	22 $\pm$ 56 %
Fraction of species with concentrations derived from theoretical approach	28 %	28 %	22 %	38 %	51 %	46 %	42 %	46 %	46 %
Speciated (calculated) OH reactivity, averages $\pm$ standard deviation [s⁻¹]	2.3 $\pm$ 1.2	7.4 $\pm$ 5.8	4.7 $\pm$ 2.2	3.7 $\pm$ 1.7	4.0 $\pm$ 2.1	2.6 $\pm$ 1.1	1.5 $\pm$ 0.2	4.3 $\pm$ 1.2	9.3 $\pm$ 5.6
Speciated (calculated) OH reactivity, medians, 25th–75th percentile [s⁻¹]	2 1.9–2.2	5.4 2.7–13.4	4.3 3.0–5.9	3.3 2.5–4.5	3.7 2.2–5.5	2.4 2.0–2.9	1.5 1.4–1.7	4 3.2–5.2	7.6 5.2–11.9
Measured OH reactivity, averages $\pm$ standard deviation [s⁻¹]	7.2 $\pm$ 2.9	13.2 $\pm$ 6.9	11.6 $\pm$ 4.2	9.1 $\pm$ 3.3	8.7 $\pm$ 4.2	8.2 $\pm$ 3.1	5.6* $\pm$ 2.0	8.3 $\pm$ 3.6	12.9 $\pm$ 6.2
Measured OH reactivity [s⁻¹], medians, 25th–75th percentile	6.8 5.8–7.8	10.8 7.4–18.8	10.4 8.2–15.0	8.5 7.0–10.5	7.9 5.7–10.9	8 5.9–10.1	4.9* 4.1–6.5	8.4 5.9–10.5	11.2 8.9–15.2
OH reactivity of 10 most important species (sum) [s⁻¹]	1.7	3.8	3.1	2.1	2.2	1.7	1.1	3.3	4.9
Fraction of total OH reactivity contributed by 10 most important species	24 %	29 %	27 %	23 %	25 %	21 %	20 %	39 %	38 %
C3 carbonyls / propane [ppb ppb⁻¹], medians	8.6	3.4	2.6	1.9	9.4	6.8	none	2.4	0.9
C5 carbonyls / pentanes [ppb ppb⁻¹], medians	3.0	1.7	1.1	1.3	1.9	2.4	3.8	1.2	2.8
Toluene / benzene [ppb ppb⁻¹], medians	0.24	0.88	0.8	0.39	0.78	0.33	0.18	0.79	0.47

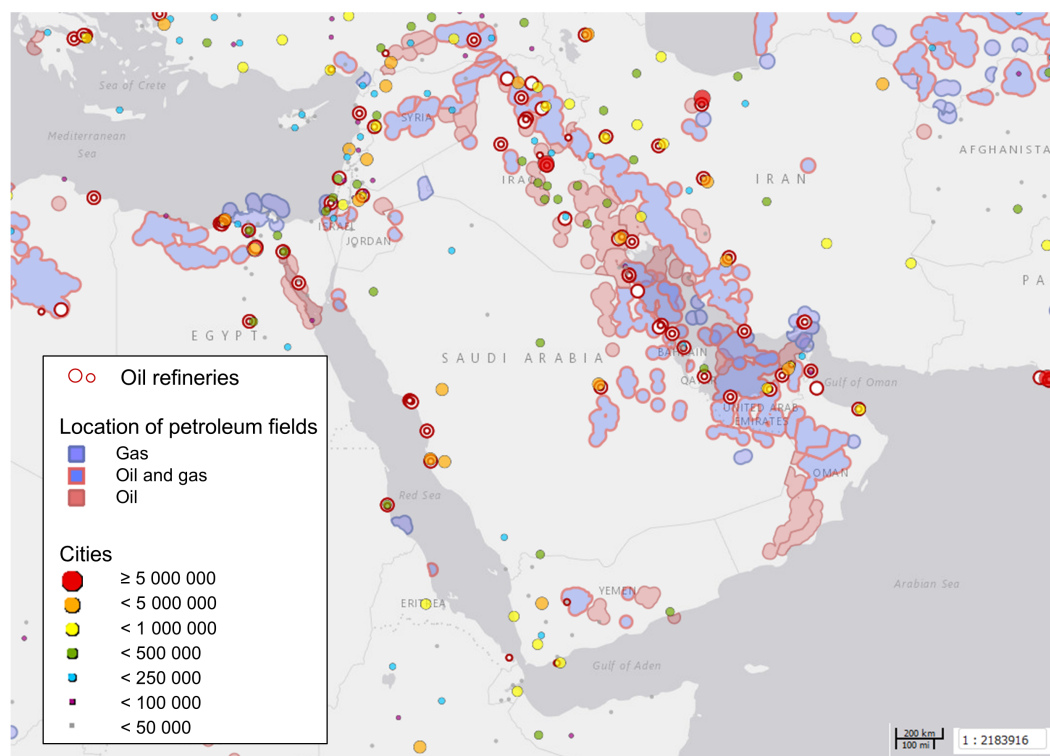


Figure 3.2: Oil refineries, petroleum fields and cities in the Arabian Basin. City markers are scaled with the number of inhabitants as denoted in the legend. Source: Harvard WorldMap Project (<https://worldmap.harvard.edu/maps/6718/dJT>).

It should also be noted that as the ship passed through the Arabian Gulf, it was only exposed to primary emissions for relatively short periods of time, when located directly downwind of the sources. The more oxidized regional background air was sampled for longer periods. Furthermore, a bias towards OVOCs in the assessment of speciated OH reactivity is also possible in this study, because they were well covered by PTR–ToF–MS measurements, while longer-chain or branched alkenes and alkanes, which are components of oil and other fuels (D’Auria et al., 2009; Gueneron et al., 2015) were in the AQABA measurements limited to C₂–C₈ compounds. Nonetheless, considering the whole campaign, the Arabian Gulf was the region with the highest OH reactivity from alkanes (on average $\approx 1.2 \text{ s}^{-1}$ or $\approx 9\%$ of total OH reactivity). An important influence of oil and gas production on total OH reactivity in the Arabian Gulf is therefore evident in our data.

Petroleum extraction facilities and refineries are located at both shores of the Gulf of Suez and Canal, (Fig. 3.2), and wind from both east and west lead to a relatively large contribution of alkanes (5–6%; Fig. 3.1d/e).

By virtue of their double bond, alkenes are more reactive towards OH than alkanes. Indeed, in Saudi Arabian cities, OH reactivity of alkenes has been reported to be twice as high as the reactivity of alkanes, despite higher abundance of the latter (Barletta et al., 2017). Similarly, over the Arabian Gulf, the AQABA campaign results show an equivalent average share of OH reactivity from alkenes and alkanes (both $\approx 1.2 \text{ s}^{-1}$, which equals $\approx 9\%$), despite an ≈ 11 times larger average mixing ratio of alkanes. Certainly a fraction of highly reactive alkenes emitted on land will have already been oxidized before the emission impacted air mass reached the point of observation on the ship. Alkene-attributed OH reactivity was slightly higher in the

Suez Canal (1.4 s^{-1} vs. 1.2 s^{-1}), where the distance to emission sources is generally shorter due to the narrowness of the canal. Additionally, and probably more importantly, alkenes are only minor components in fossil fuel emissions generally. They are emitted from vehicle exhausts (a possible source near the Suez Canal) due to incomplete combustion (Koppmann, 2007). Alkanes, on the other hand, can be so abundant in emissions from oil and gas production that they dominate OH reactivity, as was observed in Colorado, where 60 % of OH reactivity calculated from VOC measurements (not total OH reactivity) was due to alkanes and only 8 % from alkenes (Gilman et al., 2013). In another study at the same site, alkanes contributed 26 %, alkenes 3 %, and aromatics 2 % of total OH reactivity (Swarthout et al., 2013). In contrast to that, alkenes (41 %) dominated over alkanes (23 %) in the OH reactivity calculated from VOC observations over the Houston/Galveston Bay (Gilman et al., 2009).

Aromatics are important components of fossil fuels besides alkanes and alkenes (Koppmann, 2007). In Egyptian cities, ambient VOC mixing ratios from traffic have been reported to be dominated by aromatics (Matysik et al., 2010), whereas in Saudi Arabian cities, alkanes were more abundant (Barletta et al., 2017). Consistent with these findings, we observed higher average speciated OH reactivity from aromatics (1.3 s^{-1}) in the Suez Canal (influenced by air from Cairo, roads next to the Canal, a refinery, and a power plant) compared to the Arabian Gulf (0.9 s^{-1} , influenced by oil/gas industry emissions and partly by urban air from Saudi Arabia, Iraq and Kuwait).

A strong influence of maritime traffic in the narrow and highly frequented Suez Canal and Gulf is evident from the large NO_x contribution to total OH reactivity (≈ 10 and ≈ 12 %, respectively). Here, other vessels and their exhaust plumes passed by closely during waiting periods (before entering the Suez Canal in the northern Gulf of Suez and inside the Canal).

The Arabian Gulf and Suez Canal will be discussed in more detail in case studies in Sect. 3.3.2.

Seaways influenced by maritime traffic: Red Sea, Gulf of Aden and Gulf of Oman

The Red Sea, the Gulf of Aden, and the Gulf of Oman displayed similar total OH reactivities with medians of $7.9\text{--}8.5 \text{ s}^{-1}$ during the AQABA campaign (northern Red Sea: median 8.5 s^{-1} / mean $\pm$ standard deviation $9.1 \pm 3.3 \text{ s}^{-1}$, southern Red Sea: 7.9 s^{-1} / $8.7 \pm 4.2 \text{ s}^{-1}$, Gulf of Aden: 8.0 s^{-1} / $8.2 \pm 3.1 \text{ s}^{-1}$, Gulf of Oman: 8.4 s^{-1} / $8.4 \pm 3.1 \text{ s}^{-1}$, also see Table 3.1 and Fig. 3.1c/d). These values are comparable to urban observations in the lower range, such as in Helsinki, Finland (Praplan et al., 2017), or Mainz, Germany (Sinha et al., 2008).

The OH reactivity over the Red Sea, Gulf of Aden and Gulf of Oman can largely be attributed to the influence of maritime transport in these busy, relatively constricted seaways. Refineries at the eastern shore of the northern Red Sea (Fig. 3.2) are not thought to have influenced our measurements due to prevailing wind from north-west and west.

Among the three regions, the Gulf of Aden was the one with the lowest average total OH reactivity. Likely, this is due to its location in the transition zone to the open north-western Indian Ocean (see Fig. 3.1c). Here, air masses were less influenced by pollution than over the Red Sea or Gulf of Oman, as the AQABA cruise took place during northern hemisphere summer, when the ITCZ is over India and comparably clean air is drawn north over the north-western Indian Ocean (Ajith Joseph et al., 2018). In accordance with this finding, Bourtsoukidis et al. (2019) showed by

lifetime-variability regression of alkanes that the Gulf of Aden was the area with the most remote character during AQABA.

In ship exhausts, the highest emission factors (apart from CO_2) have been found for NO_x (Endresen, 2003; Eyring, 2005; Huang et al., 2018). Large ship engines emit an average of 76 kg of NO_x per ton of fuel combusted (Eyring, 2005). This is reflected in the OH reactivity share of NO_x , which was in these relatively narrow seaway regions in the range of 4–9 % (Table 3.1). OVOCs accounted for 12–21 % of total OH reactivity there, alkenes 4–9 %, inorganics (dominated by SO_2 and CO) 4–6 %, aromatics 3–8 % and alkanes 4–5 %. All those classes of compounds can stem from fuel combustion in ships (Endresen, 2003; Eyring, 2005; Huang et al., 2018; Xiao et al., 2018), which emit an average of 43 kg of SO_x , 4.7 kg of CO and 7 kg of hydrocarbons per ton of fuel combusted (Eyring, 2005).

The C_3 carbonyls ($\text{C}_3\text{H}_6\text{O}$) vs. propane (C_3H_8), C_5 oxidation products ($\text{C}_5\text{H}_{10}\text{O}$) vs. pentanes (C_5H_{12}) and toluene vs. benzene ratios (Table 3.1) were used here as indicators of the oxidation state (and, thereby, the extent of photochemical ageing) of the air. We note that this approach is based on two assumptions: 1) that production of the carbonyls by oxidation dominates over direct emission, although some direct combustion emissions cannot be excluded, and 2) that the only carbonyl precursor is the corresponding C_3 or C_5 compound without significant fragmentation of larger VOCs. The toluene vs. benzene relationship is based on the assumption of simultaneous emission of both compounds. Notably, a distinct difference between northern (less oxidized, $[\text{C}_3\text{H}_6\text{O}]/[\text{C}_3\text{H}_8] \approx 1.9$ and $[\text{C}_5\text{H}_{10}\text{O}]/[\text{C}_5\text{H}_{12}] \approx 1.3$) and southern Red Sea (oxidized, $[\text{C}_3\text{H}_6\text{O}]/[\text{C}_3\text{H}_8] \approx 9.4$ and $[\text{C}_5\text{H}_{10}\text{O}]/[\text{C}_5\text{H}_{12}] \approx 1.9$) was observed. Although it did not result in large differences in total OH reactivity values (median of 7.9 s^{-1} in the photochemically aged air masses in the south Red Sea and 8.5 s^{-1} in the north Red Sea), it reflects the origin of air masses: urban centers in northeast Africa for the north Red Sea, and the less populated and more distant Sudan and Chad for the south Red Sea.

Cleaner regions: Mediterranean and Arabian Sea

Over the more open seas, notably the Mediterranean and Arabian Sea (north-western Indian Ocean), the air was aged, cleaner, and less reactive to OH. Here, total OH reactivities were mostly close to the detection limit of 5.4 s^{-1} . The median over the Mediterranean was 6.8 s^{-1} (average $\pm$ standard deviation: $7.2 \pm 2.9 \text{ s}^{-1}$), which compares to the lower limits of observations from rural areas such as Whiteface Mountain (Ren et al., 2006b), Norfolk, UK (Ingham et al., 2009), Central Pennsylvania (Ren et al., 2005) or Arenosillo at the Spanish coast (Sinha et al., 2012), and more remote locations such as the Rocky Mountains (Nakashima et al., 2014). Total OH reactivity measured over the Arabian Sea during AQABA was with a median of 4.9 s^{-1} (average $\pm$ standard deviation: $5.6 \pm 2.0 \text{ s}^{-1}$) below the detection limit of 5.4 s^{-1} . The marine OH reactivity calculated from trace gas measurements over the central Gulf of Mexico was 1.01 s^{-1} (Gilman et al., 2009), a value which was slightly exceeded in our observations over the open Arabian Sea with a speciated OH reactivity of $1.5 \pm 0.2 \text{ s}^{-1}$.

Larger OH reactivity occurred over the Mediterranean Sea during short episodes of polluted air from the mainland in the Strait of Messina (between Sicily and Italy), visible in Fig. 3.1b. In the Strait of Messina and surroundings, total OH reactivity amounted to between $6.7 \pm 3.6 \text{ s}^{-1}$ and $26.7 \pm 8.2 \text{ s}^{-1}$ for 5 h, whereas before and

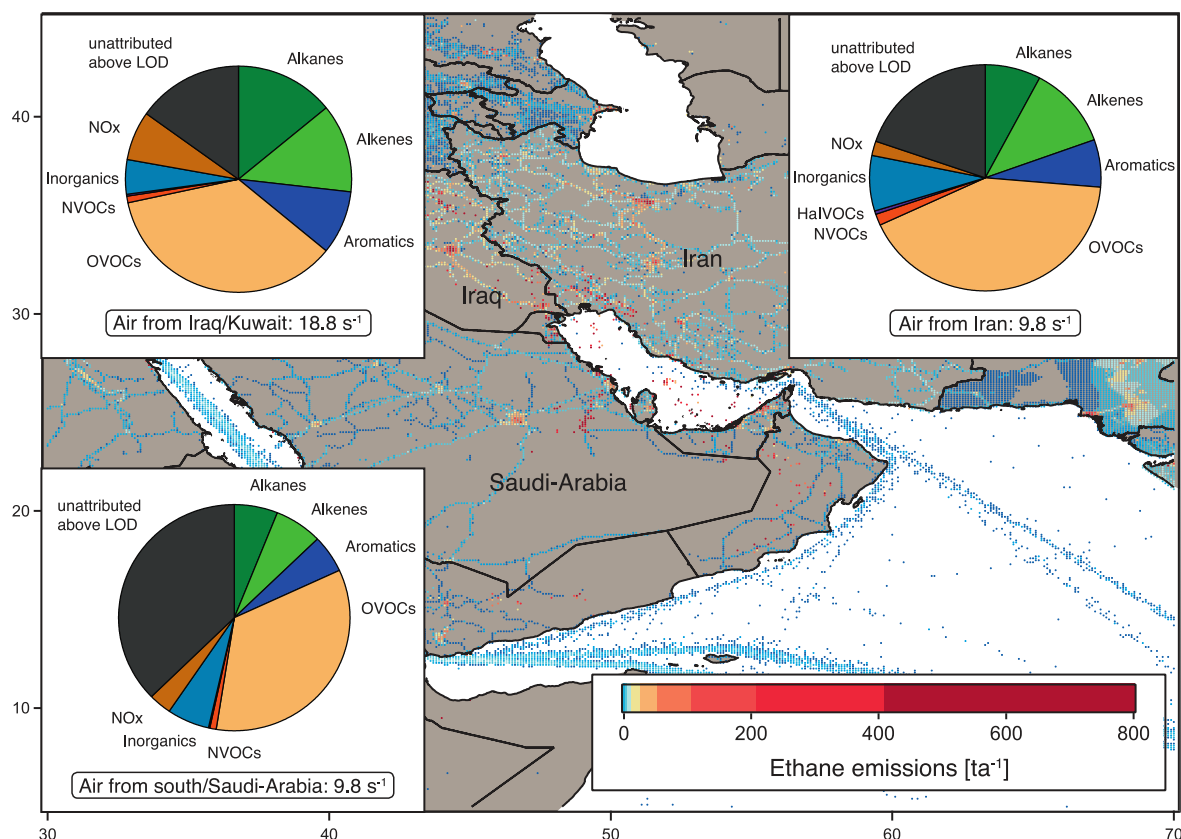


Figure 3.3: OH reactivity composition and average $\pm$ standard deviation in the Arabian Gulf, separated by origin of the measured air masses: from Iraq/Kuwait, from Iran from southern Arabian Gulf/Saudi Arabia. Background: Ethane emissions map using data from the EDGAR database (<http://edgar.jrc.ec.europa.eu>, for 2012) as an indicator for the distribution of petroleum extraction and other anthropogenic sources.

after, it was close to the detection limit. OVOCs were with $\approx 11\text{--}12\%$ of total OH reactivity the largest group of identified OH sinks in both the Mediterranean and Arabian Sea. Over the Mediterranean, the influence of shipping emissions was larger than over the Arabian Sea, evident from NO_x-attributed OH reactivity, which was on average 0.26 s⁻¹ or $\approx 4\%$ of the total in the Mediterranean in contrast to 0.05 s⁻¹ or $\approx 1\%$ of the total in the Arabian Sea. Johansson et al. (2017) found that ship traffic over the Arabian Sea causes 3% of the global NO_x emissions from maritime transport, which explains why even here the conditions were not completely pristine.

3.3.2 Case studies

Arabian Gulf

Figure 3.1 shows the average OH reactivity composition for the Arabian Gulf. However, the air measured over the Arabian Gulf originated partly from Kuwait/Iraq, partly from Iran and partly from the south. The composition of total OH reactivity between the different regions of origin displayed distinct differences, and can therefore be divided according to origin of the measured air masses, shown in Fig. 3.3. Notably, the air from Iraq and/or Kuwait showed obvious influence from oil extraction industries with large fractions of alkanes, alkenes and aromatics (Fig. 3.3). Here, emission sources were closest to the point of observation, which was reflected in

highest total OH reactivity (median: 18.8 s^{-1} , average $\pm$ standard deviation: $18.7 \pm 7.9 \text{ s}^{-1}$) and low C_3 carbonyls/propane and high toluene/benzene ratio medians of 0.3 and 0.8, respectively. In contrast, OH reactivity in the air originating from Iran was lower (median: 9.8 s^{-1} , average $\pm$ standard deviation: $10.8 \pm 3.4 \text{ s}^{-1}$), with a slightly higher C_3 carbonyls/propane and a lower toluene/benzene ratio (both 0.4). The OH reactivity here was similar to that found in air from the south (Saudi Arabia) with a median of 9.8 s^{-1} and a mean of $9.7 \pm 3.3 \text{ s}^{-1}$, however, the C_3 carbonyls/propane ratio of 2.0 points to more oxidized air masses. The high OH reactivity in air originating from Kuwait and Iraq can be attributed to emissions from petrochemical extraction and processing industries that would explain the large contribution of alkanes, alkenes and aromatics. Apart from two notable exceptions, the distribution of OH reactivity did not differ significantly between air from Iran and the south. In air from Iran, the alkene fraction was larger than in air from the south, probably due to closer and different emission sources (gas extraction at the Iranian coast), which would also explain the lower C_3 carbonyls/propane ratio. The NO_x fraction was larger in air from south, most likely for reasons of ship traffic influence.

Figure 3.4 (a) depicts a time series of measurements along the ship track from entering the Arabian Gulf to Kuwait and back. The upper part of the graph shows indicators of the photochemical age of the air mass. The $[\text{C}_3\text{H}_6\text{O}]/[\text{C}_3\text{H}_8]$ ratio decreases and the toluene/benzene ratio increases when getting closer to Kuwait, meaning that the research vessel was approaching the emission sources (refineries, oil platforms). Both these indicators show opposite patterns, as expected. The $[\text{C}_5\text{H}_{10}\text{O}]/[\text{C}_5\text{H}_{12}]$ ratio follows the $[\text{C}_3\text{H}_6\text{O}]/[\text{C}_3\text{H}_8]$ ratio except for an increase towards Kuwait, which shows that the fresh emissions observed here were richer in propane than in pentanes, and indicates a mix of fresh emissions with aged air masses. This observation will be discussed in more detail in Sect. 3.3.4. Changes in relative humidity indicate the varying influence of dry desert air and more humid air masses.

The following five case studies (orange numbered labels in Fig. 3.4 with corresponding air mass back trajectories) will go into more detail regarding the origin of OH reactivity (reported with $\pm 1 \sigma$ total uncertainty) in the Arabian Gulf:

1) At the entrance to the Arabian Gulf after passing the Strait of Hormuz, total OH reactivity was comparably low ($8.0 \pm 4.0 \text{ s}^{-1}$). Sampled air had traversed the open Indian Ocean, but passed over the Musandam Peninsula, where urban areas probably contributed some OH reactivity. OVOCs dominated ($36 \pm 20\%$ of OH reactivity), with an insignificant unattributed fraction of $38 \pm 76\%$.

2) At this location in the northern part of the Arabian Gulf, ca. 100 km from the coast of Saudi Arabia, total OH reactivity amounted to $22.1 \pm 7.2 \text{ s}^{-1}$, mainly due to OVOCs ($57 \pm 29\%$), with large fractions of alkanes ($10 \pm 1\%$), alkenes ($16 \pm 8\%$) and aromatics ($10 \pm 5\%$). The back trajectories originate from eastern Iraq, with the urban areas of Amara and Basra. The large fraction of OVOCs is an indicator for chemically aged air. The aromatics, alkenes and alkanes probably were emitted from offshore oil/gas extraction platforms (Fig. 3.4b) and mixed with the oxidized air contaminants coming from larger distance. Within the uncertainty of the measurement, there is no unattributed OH reactivity at this location; with values of $19.4 \pm 9.9 \text{ s}^{-1}$ for the speciated OH reactivity and $22.1 \pm 7.2 \text{ s}^{-1}$ for the measured total OH reactivity.

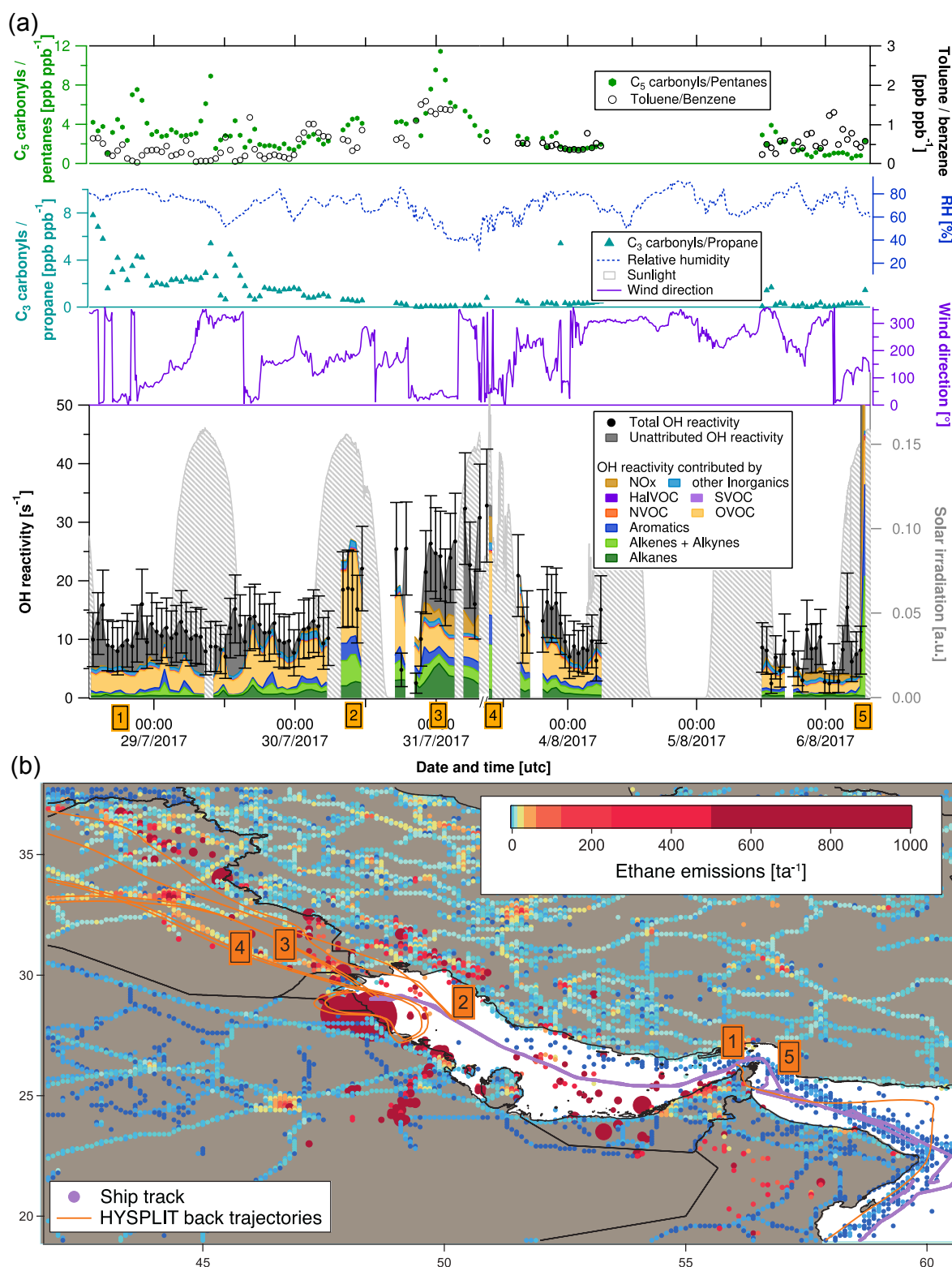


Figure 3.4: (a) C_3 carbonyls/propane ratio, C_5 carbonyls/pentanes ratio and toluene/benzene ratio, relative humidity, solar irradiation, wind direction, speciated and measured OH reactivity in the Arabian Gulf. Error bars of total OH reactivity display the 1σ total uncertainty of the measurement. (b) Ship track of the campaign in the Arabian Gulf with HYSPLIT air mass back trajectories and numbered labels of case study points. Ethane emissions from the EDGAR database (<http://edgar.jrc.ec.europa.eu>, for 2012) as an indicator for petroleum extraction/processing and other anthropogenic sources are shown on a logarithmic colour scale. Emissions out of scale ($> 1000 \text{ t a}^{-1}$) are shown with larger circles.

3) Approximately 30 km from the coast of Kuwait, the back trajectories indicate that the sampled air masses travelled over the Rumaila oil field in Basra (Iraq). Consequently, the total OH reactivity of $26.4 \pm 8.1 \text{ s}^{-1}$ was mainly due to alkanes from oil extraction ($24 \pm 2 \%$). In contrast to the previous case study, significant unattributed OH reactivity was observed here ($40 \pm 37 \%$), which might be due to components of oil such as higher than C_8 and/or branched hydrocarbons that were not measured on board the *Kommandor Iona*.

4) Just after departure from the port of Kuwait, the highest observed OH reactivity ($32.8 \pm 9.6 \text{ s}^{-1}$) of the campaign was measured (except for refueling). HYSPLIT back trajectories show that it likely originated from large pollution sources at the coast: refineries (Saudi Aramco refinery and industrial area with storage tanks in Khafji, Saudi Arabia) and oil fields (Wafra oil field in Kuwait; oil platforms at the sea). Notably, alkenes ($23 \pm 14 \%$) were a much larger OH sink here than alkanes ($5 \pm 0.5 \%$), and the unattributed OH reactivity was zero within the uncertainty.

5) The largest OH reactivity measured during the whole campaign was $303.6 \pm 83.9 \text{ s}^{-1}$ during refueling of the vessel in front of the port of Fujairah (United Arab Emirates). A back trajectory would not be relevant here, as these are direct diesel fuel evaporation emissions, mainly composed of alkenes ($27 \pm 18 \%$ of speciated OH reactivity) and aromatics ($21 \pm 10 \%$), mixed with NO_x ($39 \pm 4 \%$) from the bunker ship's own fuel combustion. Wu et al. (2015) measured total OH reactivity from gasoline evaporation with the CRM method. In their study, alkenes contributed 40 % of measured OH reactivity, and they found an unattributed OH reactivity fraction of 43 %. In our study, a larger percentage ($75 \pm 42 \%$) of total OH reactivity remains unexplained in the fuel evaporation measurement, which is most likely due to the fact that less of the higher and branched hydrocarbons were measured.

Suez Canal

The Suez Canal transit on August 24, 2017, was among the episodes of highest total OH reactivities during the whole campaign and will therefore be discussed in more detail here. In August 2017, 49 ships transited the Canal per day (Suez Canal Authority, 2018). It is one of the world's most heavily used shipping lanes and there are no regulations concerning the fuel used or emission limitations. The Suez Canal is 193 km long and at the water surface 313 m wide (Suez Canal Authority, 2017). Given its narrowness, other vessels and their exhausts, as well as urban areas or streets were relatively close to the *Kommandor Iona* while it was traveling along the Canal. Consequently, variations in OH reactivity can mainly be attributed to local emissions. Therefore, back trajectories are usually not helpful for explaining OH reactivity over the Suez Canal.

Four case studies (orange numbered labels in Fig. 3.5) will elucidate the origin of OH reactivity (reported with $\pm 1\sigma$ total uncertainty) measured over the Suez Canal:

1) This 4 h period of higher OH reactivity ($15.2 \pm 5.8 \text{ s}^{-1}$ to $19.1 \pm 6.6 \text{ s}^{-1}$) occurred during a waiting period at the southern entrance to the Suez Canal, in the port area of Suez City. Interestingly, OH reactivity was dominated by alkanes here ($\approx 10\text{--}15 \%$). This can be explained by the wind coming from north where directly at the shore a petrol storage area is located (Nasr Petroleum Company, Suez, Egypt). The toluene/benzene ratio was between 1 and 3, indicating fuel combustion emis-

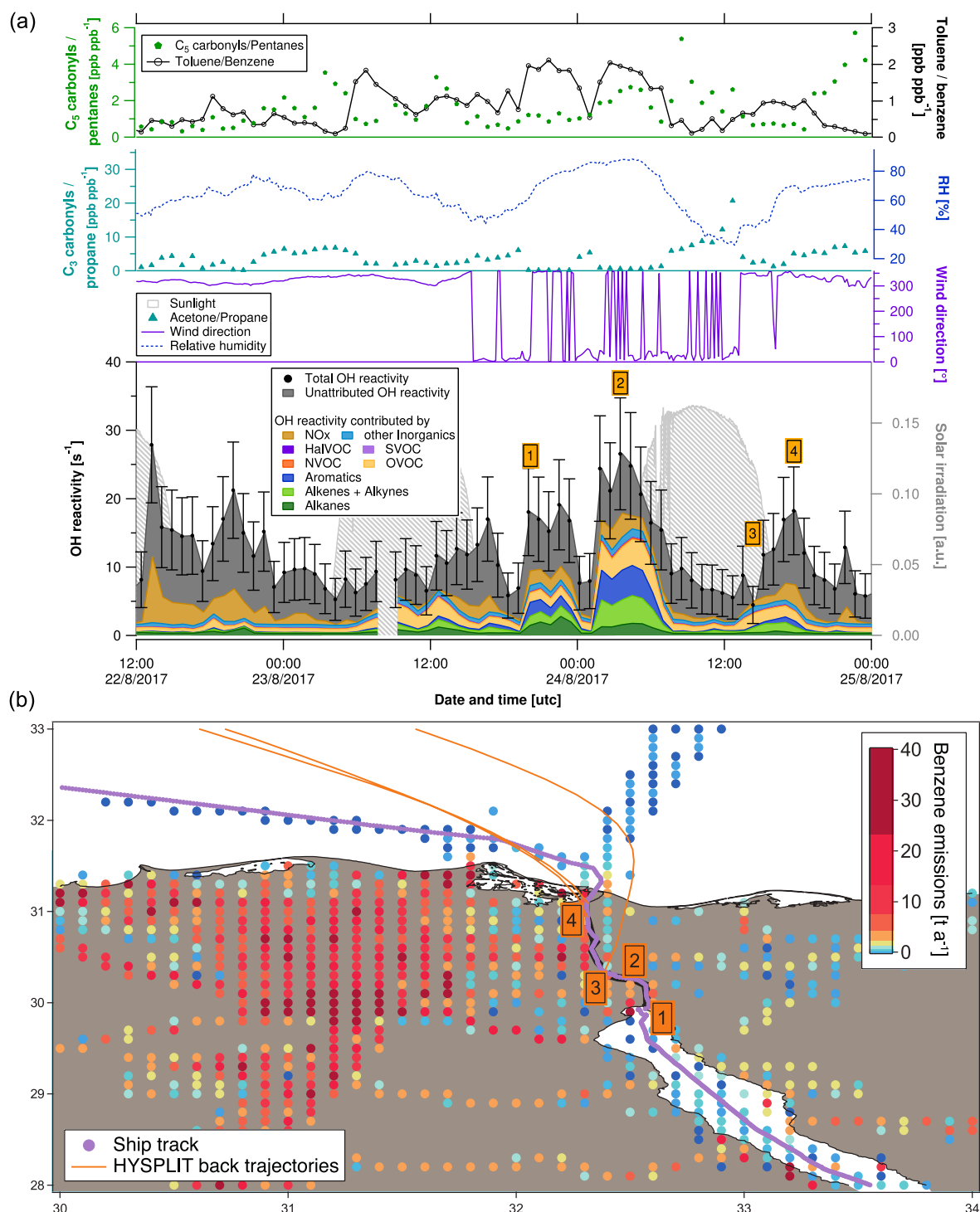


Figure 3.5: (a) C_3 carbonyls/propane ratio, C_5 carbonyls/pentanes ratio and toluene/benzene ratio, relative humidity, solar irradiation, wind direction, speciated and measured OH reactivity in the Suez Canal. Error bars of total OH reactivity display the total uncertainty of the measurement. (b) Ship track of the cruise in the Suez Canal with HYSPLIT air mass back trajectories and numbered labels of case study points. Benzene emissions as an indicator for anthropogenic sources from the EDGAR database (<http://edgar.jrc.ec.europa.eu>, for 2012) are shown on a logarithmic colour scale.

sions as a source in Suez City and/or from ships, rather than biomass burning which tends to be richer in benzene.

2) The Great Bitter Lake is part of the Suez Canal and is used by ships as a “passing lane”. During the 4 h waiting time in the lake, the highest OH reactivity of the transit was observed ($20.6 \pm 6.9 \text{ s}^{-1}$ to $26.6 \pm 8.2 \text{ s}^{-1}$). Alkenes, aromatics and OVOCs contributed almost equally to this value ($\approx 16\%$, $\approx 17\%$, and $\approx 17\%$, respectively). Especially the large amount of aromatics is notable. With $7 \pm 1\%$ contribution, alkanes were less relevant here than in the Suez City port (case study 1). A visible source of nearby emissions at the northern lakeshore (with northerly winds) was a power plant running on natural gas and/or heavy fuel oil (Abu Sultan Power Station, Ismailia, Egypt; Global Energy Observatory (2015)). Its emissions may have been mixed with those from the lakeshore settlements and from bypassing cargo ships, with a toluene/benzene ratio between 1 and 3, characteristic for fuel combustion emissions.

3) This point of observation was low in OH reactivity ($5.5 \pm 3.2 \text{ s}^{-1}$) as well as in relative humidity (29.2%). Combined with the back trajectory, this indicates that the air mass sampled here had passed over the Sinai Desert. In this location, the C_3 carbonyls/propane ratio was 20.7, indicating a photochemically aged air mass. For comparison, the ratio was never above 10 anywhere else in the area, and in case studies 1 and 2 even between 0 and 1. Similarly, the C_5 carbonyls/pentanes ratio was elevated (2.6) and the toluene/benzene ratio was low (0.5).

4) The wind direction at case study point 4 was north/north-west. Total OH reactivity was in a 4 h peak of $11.8 \pm 5.0 \text{ s}^{-1}$ to $18.2 \pm 6.4 \text{ s}^{-1}$. Ca. 15% of it was caused by NO_x and $\approx 9\%$ by alkenes. The toluene/benzene ratio was ≈ 1 , which indicates a fuel combustion source. There is a highway located west of this northern part of the Canal (Ismailia–Port Said Road), but given the wind direction, exhaust plumes of other vessels sailing in front of the research ship were probably relevant for the OH reactivity as well as traffic on land.

3.3.3 How many and which chemical species contribute to total OH reactivity around the Arabian Peninsula?

Many studies of ambient total OH reactivity show significant unattributed or “missing” OH reactivity (Yang et al., 2016). Care must be taken in interpreting this missing fraction as it depends on which individual compounds are taken into account, although forest studies have tended to show greater missing reactivity fractions than urban (Williams and Brune, 2015). Using a total of 120 chemical species (listed in Table S1), we calculated the speciated OH reactivity in 50 min time resolution for the whole AQABA campaign. For the datapoints with speciated OH reactivity above the CRM detection limit, the unattributed fraction of total OH reactivity is plotted against the number of compounds taken into account in Fig. 3.6. Only datapoints above the detection limit were chosen in order to exclude seemingly unattributed OH reactivity which is actually due to the detection limit (unattributed fractions for all datapoints are shown along with those for above the LOD in Table 3.1). The graph shows that when up to ca. 100 species are considered, the unattributed OH reactivity fraction decreases. The remaining compounds collectively contribute only minor additional OH reactivity (less than 0.012 s^{-1}). Total OH reactivity is best explained by measured

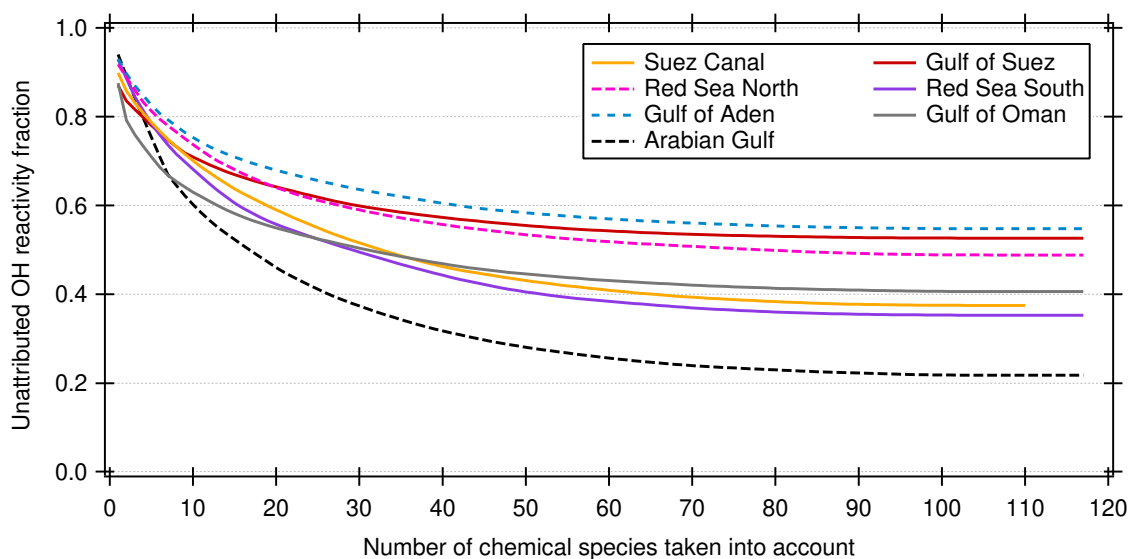


Figure 3.6: Unattributed OH reactivity fraction as a function of the number of compounds/chemical species taken into account for calculating speciated OH reactivity. The chemical species are taken into account with decreasing average OH reactivity. Only datapoints where the summed speciated OH reactivity is larger than or equal to the detection limit (LOD) of the CRM measurement are considered here. The Mediterranean and Arabian Sea are not shown because of insignificant number of datapoints above the LOD.

trace gases in the Arabian Gulf ($22 \pm 56\%$ unattributed), in the Suez Canal and southern Red Sea ($37 \pm 34\%$ and $35 \pm 55\%$ unattributed, respectively). The largest unattributed OH reactivity was found in the Gulf of Aden ($55 \pm 38\%$). Other regions with significant unattributed fractions were the northern Red Sea ($49 \pm 39\%$) and the Gulf of Suez ($53 \pm 35\%$). The unattributed reactivity fraction does not correlate with the indicators used for estimating the air mass age.

Figure 3.7 shows the average OH reactivity of VOCs by molecular mass (NO_x and other inorganic compounds are not considered in this graph) and color-coded for groups of compounds for the Arabian Gulf and the Suez Canal. Higher-mass aromatics play a larger role in the Suez Canal while the same OVOCs are important in both regions. Generally, less VOCs in the higher mass ranges were measured, which is likely due to larger molecules being partially lost in the ca. 10 m long, 50°C inlet line. This means that some less volatile components of total OH reactivity might have been missed in this setup. As the same inlet was used for VOC and OH reactivity measurements, however, this does not impact the unattributed reactivity fraction.

The 10 chemical species which contributed most to OH reactivity in each region traversed during the AQABA campaign are displayed in Fig. 3.8. Generally, in no regional average was one single compound responsible for an OH reactivity of more than 1.4 s^{-1} . This reflects the previous discussion highlighting the necessity of considering a large number of species to get a complete picture of total OH reactivity. The concentrations of some of the compounds among the 10 most relevant ones were derived with the theoretical approach (see Sect. 3.2.5) and therefore have larger uncertainties. However, their potential importance underlines that a focus on the 14 compounds calibrated with a typical PTR–MS gas standard would not be sufficient for a comprehensive understanding of OH reactivity. Overall, the contribution of the

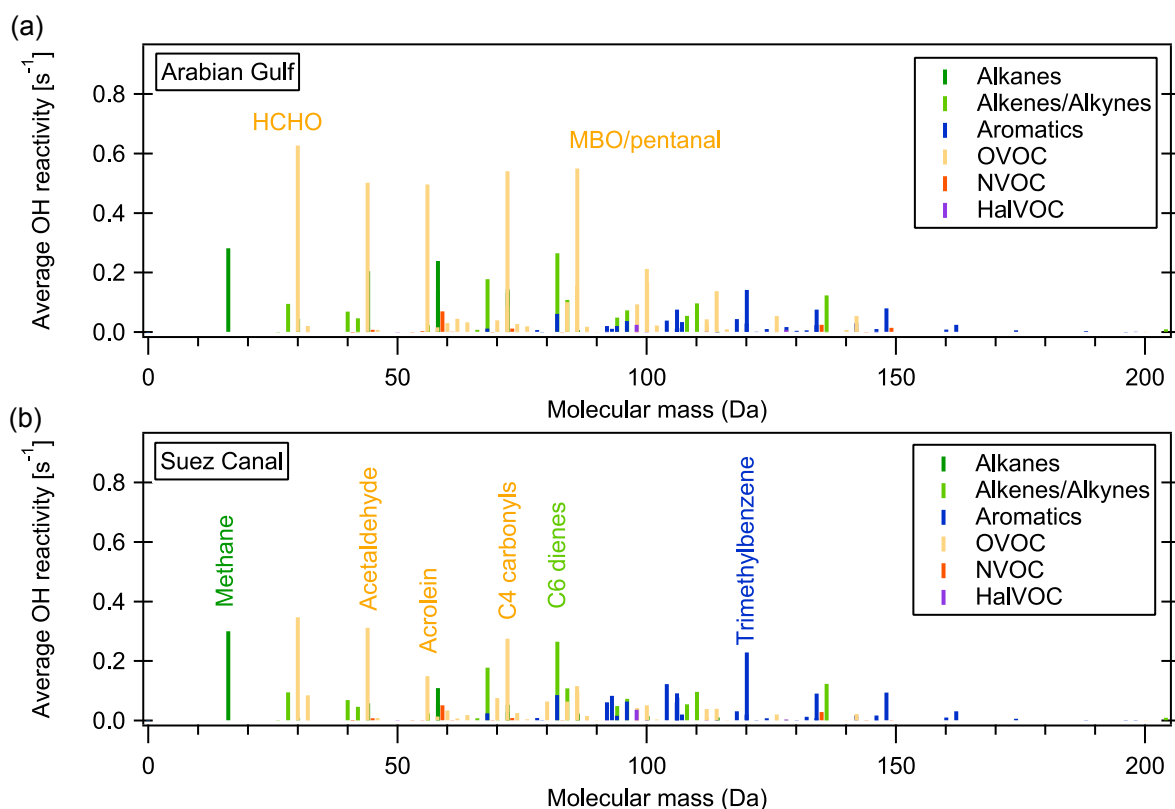


Figure 3.7: Average OH reactivity of VOCs by molecular mass in the Suez Canal and Arabian Gulf. Colors show the compound class.

78 species derived by the theoretical approach amounts to between 22 % (Gulf of Suez) and 51 % (southern Red Sea) of speciated OH reactivity (see Table 3.1). The highest percentage contribution to total OH reactivity by the 10 most important compounds was seen in the Gulf of Oman (39 ± 20 %) and the Arabian Gulf (38 ± 20 %), amongst which were the four theoretically calibrated exact masses of acrolein, MBO/pentanal, C₄ carbonyls and C₆ dienes.

The importance of the seaways around the Arabian Peninsula for maritime transport is reflected in the large contribution of NO₂ and CO (associated with fuel combustion), which are among the three highest contributors to OH reactivity in most of the regions and among the top 10 in all of them. Oxygenated species such as aldehydes and ketones were important OH sinks in all the areas, in particular formaldehyde, acetaldehyde and, to a lesser extent, the C₄ and C₅ carbonyls. Directly emitted hydrocarbons were among the 10 most important OH reactivity contributors only in areas closer to emission sources: e.g. n-butane and propane in the Gulf of Suez, or unsaturated hydrocarbons such as C₆ dienes, C₅ dienes (without isoprene) and ethene in the Suez Canal. The importance of oxygenates in the air composition during AQABA reflects the fast photooxidation of direct emissions during this summertime campaign (also see Sect. 3.3.1). In winter, the directly emitted hydrocarbons would have longer lifetimes and therefore gain importance in the OH reactivity budget at the expense of oxygenates.

In the Arabian Sea, which was the area with the lowest total OH reactivities (3.1, Table 3.1), the global background OH reactivity from methane was a major OH sink. Dimethyl sulfide (DMS), a biogenic molecule emitted by algae which has been ob-

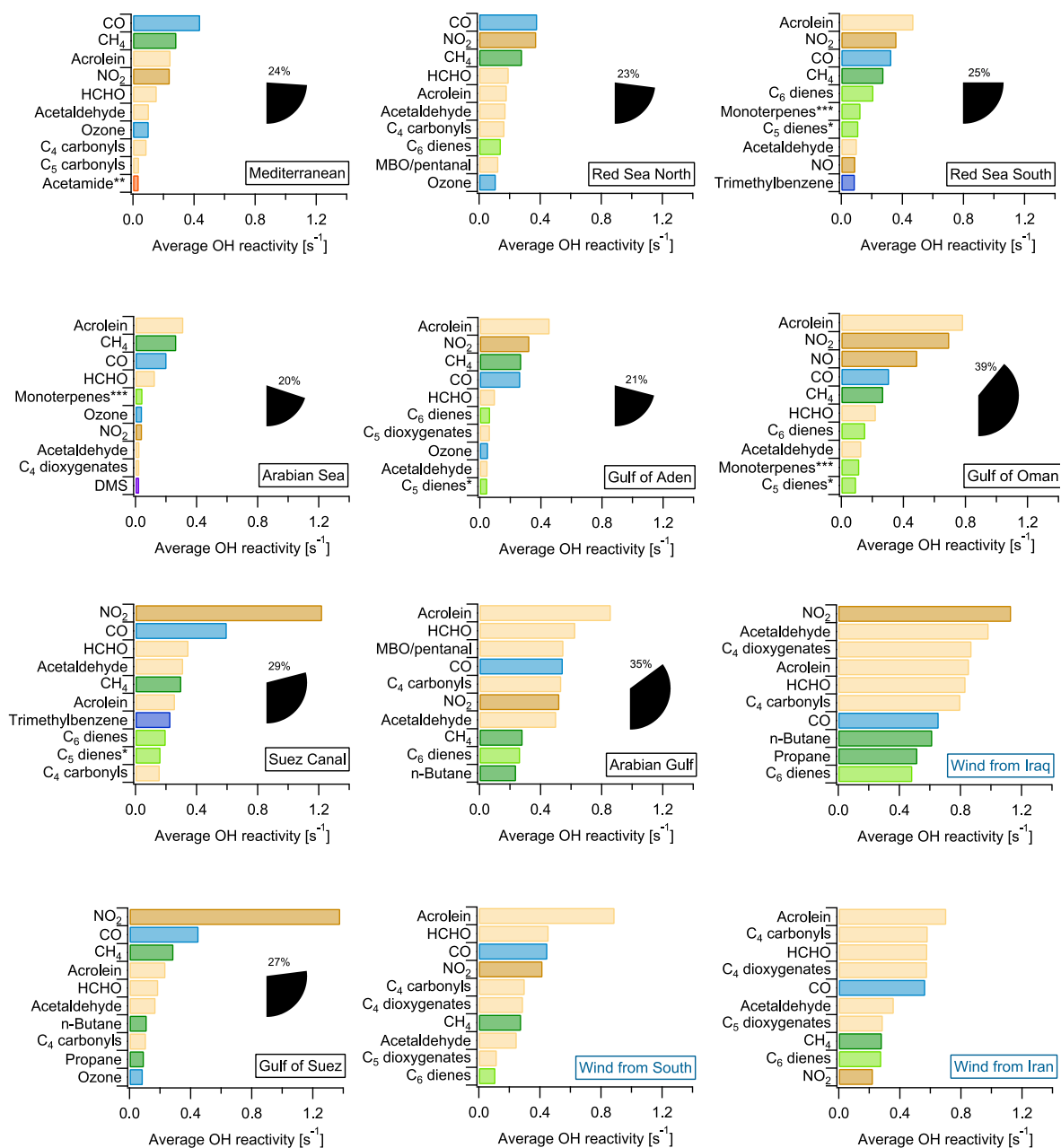


Figure 3.8: Regional average OH reactivity of each of the 10 most important contributors to OH reactivity. The percentage of total OH reactivity from these 10 compounds is shown as pie wedges. The Arabian Gulf was split by air mass origin (plots with blue labels). *C₅ dienes do not include isoprene. **Acetamide or *N*-methyl formamide. ***"Monoterpenes" may include anthropogenic C₁₀ trienes. Abbreviations: MBO: 2-Methyl-3-buten-2-ol.

served in this part of the ocean before (Warneke and Gouw, 2001) and will be discussed elsewhere for the AQABA campaign (Edtbauer et al., 2019, in preparation), appears among the 10 most important OH sinks here despite a reactivity of only 0.02 s^{-1} . This is evidence for relatively clean air due to the influence of open ocean air, although even here emissions from shipping are evident from the CO and NO₂ contributions. In the Mediterranean, methane was the second-most important single contributor to total OH reactivity after CO.

Generally, anthropogenic VOCs and their oxidation products dominated OH reactivity around the Arabian Peninsula. For example, acrolein was among the 10 most important contributors almost everywhere during AQABA (Fig. 3.8). Acrolein is a major product of the oxidation of 1,3-butadiene, which is among the most abundant alkenes emitted from anthropogenic sources (Grosjean et al., 1994). The C₄ carbonyls (butanal or methyl ethyl ketone (MEK)), are major contributors to total OH reactivity over the Arabian Basin, and both can be directly emitted from fossil fuel combustion (Schauer et al., 2002) or be the result of ambient oxidation processes. Carbonyl photolysis has been found recently to be a possible source of ozone formation in an oil and gas production area (Edwards et al., 2014).

3.3.4 OH reactivity and ozone

Ozone production regimes

Ozone and OH reactivity are connected via a chemical cycle that involves NO_x and VOCs (Ren et al., 2013; Sillman, 1999): OH oxidizes VOCs to form peroxy radicals, which, in turn, oxidize NO to NO₂. NO₂ thus formed is subsequently photolyzed to result in ozone production. Ozone formation is, however, neither linearly dependent on NO_x concentration nor VOC reactivity, and a decrease in one parameter does not necessarily lead to a decrease in ozone formation (Pusede and Cohen, 2012).

Defining ozone production regimes in terms of the OH reactivities of VOCs and NO_x is a way of assessing the sensitivity of ozone production to the prevailing conditions (Kirchner et al., 2001; Sinha et al., 2012). The method and underlying chemistry has been extensively evaluated for different conditions and compared to other methods in Kirchner et al. (2001). The amount of peroxy radicals produced by VOC oxidation is linked to the OH reactivity of VOCs. The OH reactivity of VOCs was calculated here as the difference of measured total OH reactivity (in 5 min time resolution) and OH reactivity of measured NO_x. Only data at daytime (06:00–18:00 local time) was considered, because the method is inherently limited to daytime chemistry. Figure 3.9 shows ozone production regime plot examples, where “s” denotes the relative reactivity of OH towards NO_x and VOCs. Based on the analysis of Kirchner et al. (2001), which was developed for urban VOC mixtures, in between the lines labelled $s = 0.2$ and $s = 0.01$, ozone production is favored by a suitable ratio of NO_x and OH reactivity of VOCs, whereas $s > 0.2$ indicates VOC limitation, and $s < 0.01$ NO_x limitation.

The Arabian Sea with its comparably clean air was a region with partially NO_x limited ozone production (Fig. 3.9a). Here, 20 % of the datapoints do not fall within the regime of ozone production, mostly due to NO_x limitation. This is reflected in relatively low ozone mixing ratios. The Gulf of Suez (Fig. 3.9b) is characterized in part by a strong VOC limitation associated with high NO_x (69 % of datapoints in-

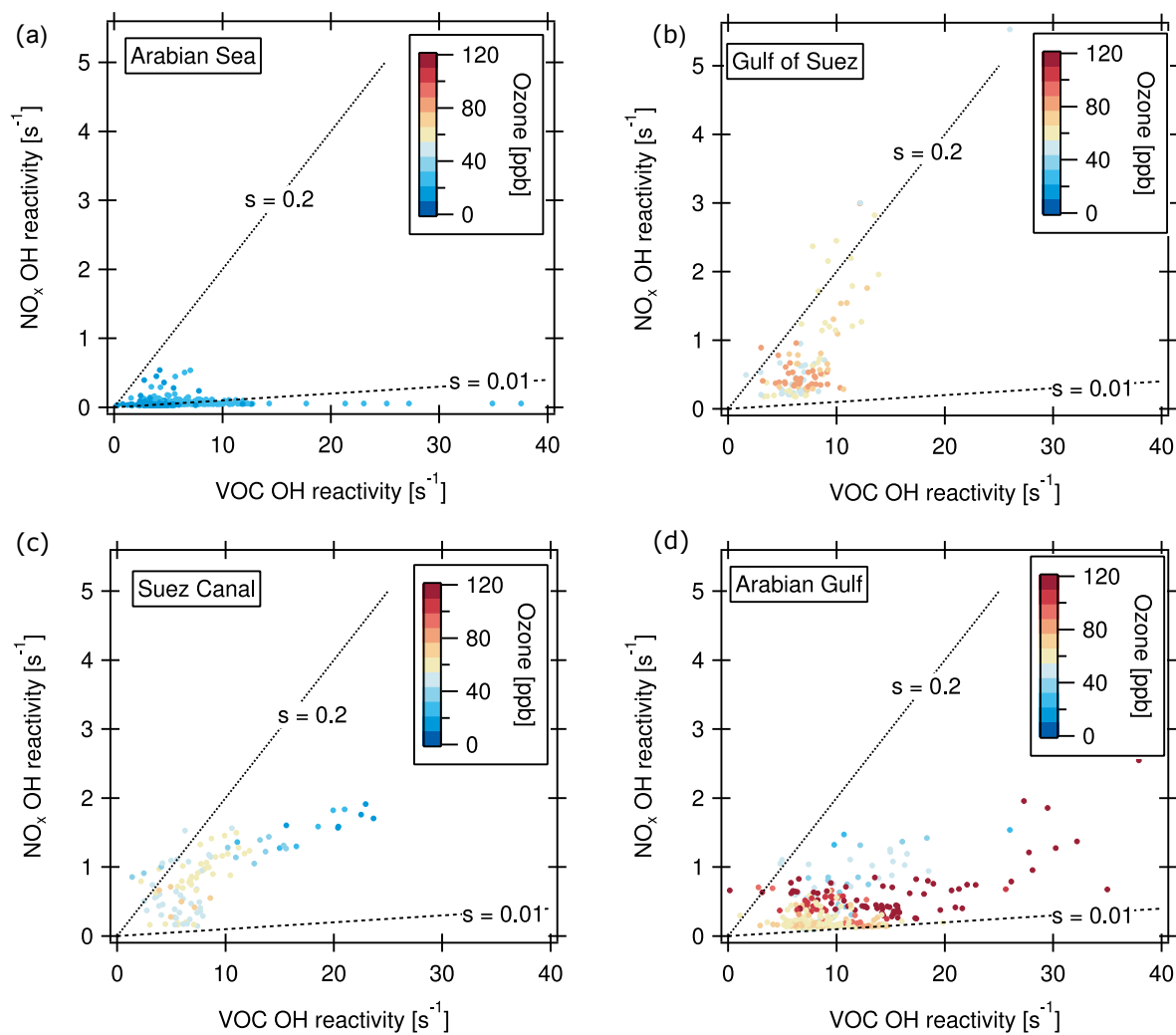


Figure 3.9: Ozone production regimes for (a) Arabian Sea, (b) Gulf of Suez (c) Suez Canal, and (d) Arabian Gulf. “ s ” denotes the relative reactivity of OH towards NO_x and VOCs. For $s > 0.2$: VOC limitation, for $s < 0.01$: NO_x limitation of the ozone formation.

dicate an ozone formation regime). This NO_x can be attributed to emissions from other vessels at close proximity while waiting at the entrance of the Suez Canal. The low ozone mixing ratios associated with high NO_x in the fresh combustion emissions (Fig. 3.9b/c) point to ozone titration, which will be discussed in greater detail in the following section. In the Suez Canal (Fig. 3.9c), the datapoints are also grouped more towards VOC sensitivity whereas the opposite is true for the Arabian Gulf (Fig. 3.9d). Nevertheless, in both the Suez Canal and the Arabian Gulf, almost all datapoints (97 % in the Arabian Gulf and 91 % in the Suez Canal) fall into the regime of ozone formation, meaning that a suitable ratio of VOC and NO_x molecules for ozone formation was present nearly all the time. The same is true for the other environments (not shown in graph) with favored ozone formation 97 % of the time in the Mediterranean, 93 % in the northern Red Sea, 88 % in the southern Red Sea, 87 % in the Gulf of Aden, and 82 % in the Gulf of Oman.

The ozone production favoring conditions with both high NO_x - and VOC-attributed OH reactivities may be contributing factors to the high ozone levels observed and modeled above the Arabian Gulf (Fountoukis et al., 2018; Lelieveld et al., 2009). Ozone formation favorable conditions resulting in ozone mixing ratios up to 145 ppb have been reported from other sites influenced by oil and gas production (Edwards et al., 2014; Wei et al., 2014). Moradzadeh et al. (2019) found that a hydrocarbon processing plant at the shore of the Arabian Gulf impacted ozone levels even in 300 km distance. Generally, emissions in lower latitudes (e.g. below 30°N as in the Arabian Gulf) lead to more efficient formation of tropospheric ozone than in higher latitudes, because the meteorological conditions lead to faster reaction rates and strong convection (Zhang et al., 2016).

OH reactivity/ozone correlations

The relationship between ozone and total OH reactivity during the AQABA campaign is depicted in Fig. 3.10. Data from most regions display a negative correlation between ozone mixing ratio and total OH reactivity. This is exemplified for the Mediterranean, the Suez Canal and Gulf of Suez in Fig. 3.10a (correlation for Suez Canal: slope = -0.2; $r^2 = 0.61$). Additionally, there is a large group of datapoints located at lower OH reactivity (below 10 s^{-1}) and ozone mixing ratios of 50 to 70 ppb.

The reason for the negative correlation seen in parts of the data is displayed in Fig. 3.10b. Higher OH reactivities in this part of the plot coincide with higher NO_x , stemming from the exhaust plumes of vessels passing close by. In these ship plumes, high levels of VOCs are co-emitted with NO_x . This combination leads to elevated total OH reactivity. At the same time, ozone is depleted by the NO emissions in the fresh ship plumes ($\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$, Sillman, 1999). This effect is seen when an emission source co-emitting NO_x and VOCs is very close (Akimoto, 2016), as ozone values recover rapidly downwind through NO_2 photolysis and mixing. The ozone titration effect has similarly been observed in negative ozone-CO correlations (Parrish et al., 1998).

The bulk of datapoints between 50 and 70 ppb of ozone associated with lower OH reactivity and no trend is, on the other hand, more representative of a campaign background/average, uninfluenced by immediate emission sources and with lower NO_x (Fig. 3.10b). Here, a possible longer-term effect of the co-emission of VOC and NO_x from marine transport and other anthropogenic sources can be seen. As

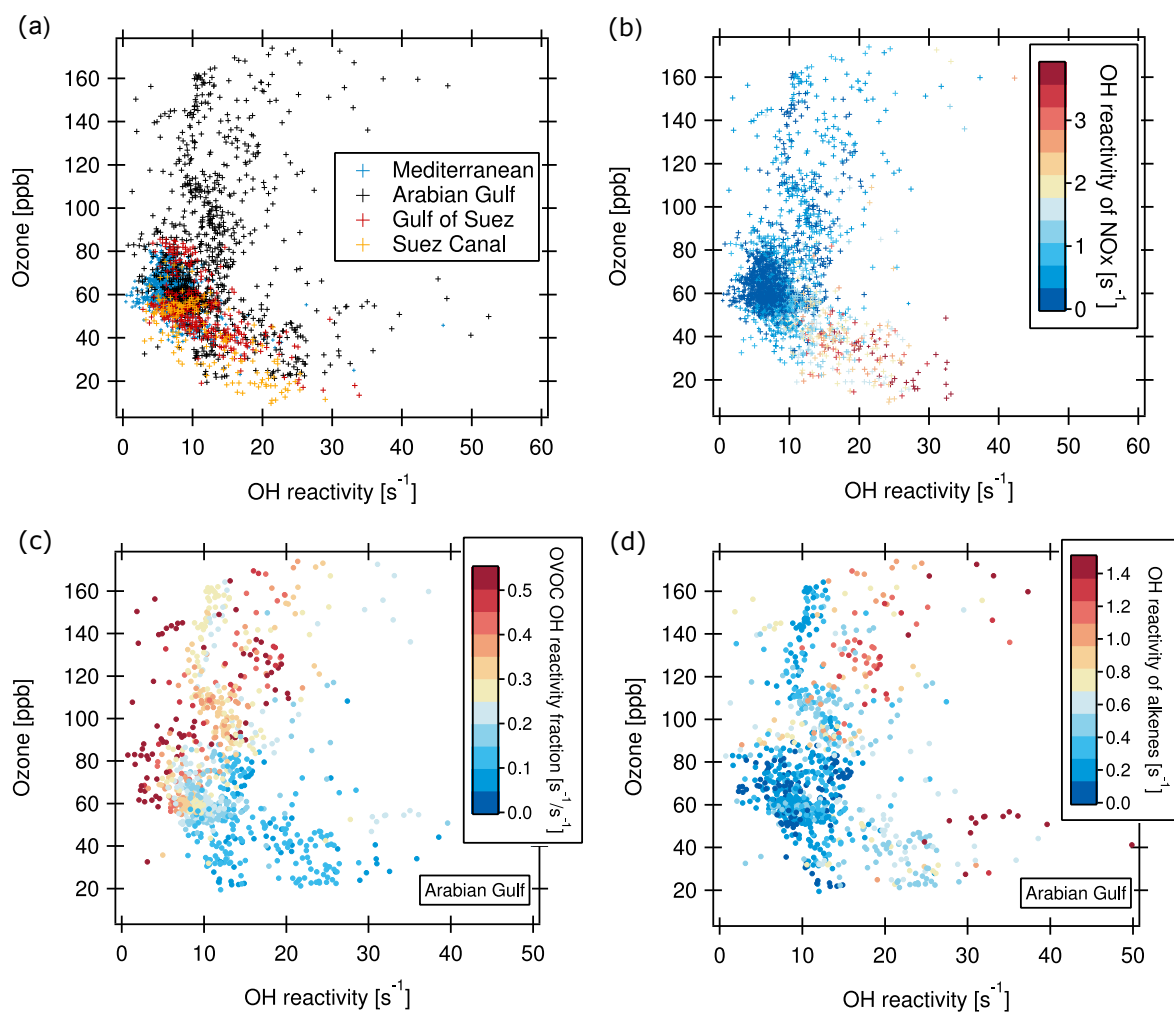


Figure 3.10: (a) Ozone vs. total OH reactivity for four regions. (b) Same as (a), but with OH reactivity of NO_x as color scale (no datapoints when NO_x values are missing). (c) Ozone vs. OH reactivity for the Arabian Gulf with the fraction of OVOC in total OH reactivity as color scale. (d) Ozone vs. OH reactivity for the Arabian Gulf with OH reactivity of alkenes as color scale.

a secondary pollutant and being suppressed by NO, ozone can often be elevated at distance to the pollution sources (Sudo and Akimoto, 2007). Large quantities of ozone can be produced during long-range transport under sunlight influence (Akimoto, 2016; Moradzadeh et al., 2019; Parrish et al., 1998)). Consequently, in the seaways around the Arabian Peninsula, ozone mixing ratios were mostly between 50 and 80 ppb, which is the range of daytime values in polluted Beijing (Williams et al., 2016; Yang et al., 2017).

Over the Arabian Gulf, the same negative relationship between OH reactivity and ozone as in the Suez Canal, Gulf of Suez and Mediterranean existed in those datapoints where ozone was below 70 ppb. In contrast, at ozone mixing ratios above ca. 80 ppb, no trend or a slightly positive correlation between ozone mixing ratio and OH reactivity can be ascertained (Fig. 3.10a). Ozone mixing ratios above 70 ppb over the Arabian Gulf were associated with a high fraction of OVOCs (Fig. 3.10c), indicating more photochemically processed air. Additionally, when OH reactivity was high at the same time as ozone, alkene OH reactivity was also elevated (Fig. 3.10d). This points to a mixing in of fresh emissions (associated with short-lived alkenes) into photochemically aged, oxidized air contaminants (high OVOCs and high ozone) over the Arabian Gulf. Polluted air masses from urban or industrial areas on land were probably oxidized during their transport to the coast/sea, where they were mixed with emissions from oil and gas extraction facilities, as has been discussed in detailed case studies of such occasions in Sect. 3.3.2.

3.4 Summary and conclusions

In July and August 2017, during the AQABA campaign, the first ship-based direct measurements of total OH reactivity were conducted using the Comparative Reactivity Method. The total OH reactivity in ambient air around the Arabian Peninsula was predominantly related to anthropogenic influence. Particularly, reactive hydrocarbons from oil and gas extraction/production and inorganic reactants such as NO_x and CO from fuel combustion by shipping were major OH sinks during the whole campaign. Total OH reactivity over the Arabian Basin varied, with periods below the detection limit over the Arabian Sea, regional medians of 7.9–8.5 s⁻¹ under permanent maritime traffic influence over the seaways of the Red Sea, Gulf of Aden and Gulf of Oman, and episodes of up to 32.8 ± 9.6 s⁻¹ when air masses were influenced by emissions from oil/gas extraction facilities, urban centers and/or ships in close proximity. The largest regional median OH loss rate of 18.8 s⁻¹ was observed over the Arabian Gulf when air originated from Iraq/Kuwait, where large oil fields and refineries at the shore provided high emissions. Over the Suez Canal, median OH reactivities of 10.8 s⁻¹ and up to 26.6 ± 8.2 s⁻¹ were attributed to local emissions from a petroleum storage facility, a power plant and traffic on sea and land. The cleanest environment was the Arabian Sea, where the marine biogenic compound dimethyl sulfide was among the 10 most important known contributors to OH reactivity.

In all the regions around the Arabian Peninsula, OVOCs were the class of compounds that provided the largest identified OH sink. They were formed efficiently because photochemistry was highly active due to intense solar irradiation and high temperatures in summer. Photochemically aged air mixed with fresh nearby emissions over

the Arabian Gulf, leading to extremely high ozone mixing ratios. Using ozone production regime plots, we found that the ratio of VOC- and NO_x -attributed OH reactivities was favorable for ozone formation nearly all along the ship track. In the Arabian Gulf, large OH reactivity from VOCs due to oil and gas sources together with NO_x from marine traffic lead to a regime of ozone production 97 % of the time. The only regions where ozone production was limited for a significant fraction of time were the Gulf of Suez with VOC limitation when affected by NO_x -rich plumes, and the Arabian Sea with a slight NO_x limitation due to clean air from the open Indian Ocean. Ozone versus OH reactivity correlation plots were found to be a valuable tool in identifying different chemical regimes with regards to ozone formation and loss: ozone destruction in NO_x -rich ship plumes was clearly distinguishable from a mix of fresh petroleum extraction emissions with photochemically aged air.

Studies of ambient total OH reactivity often show a significant “missing” or unattributed fraction of OH reactivity, although this tends to be smaller in anthropogenic environments (Williams and Brune, 2015). In an attempt to close the OH reactivity budget, the OH reactivity of compounds with unidentified structure from PTR–ToF–MS measurements was calculated using averages of the reaction rate constants of all possible structures attributed to each chemical formula. These species were important OH sinks, accounting for 22–51 % of the regional speciated OH reactivity. With this approach, the measured total OH reactivity can be explained within the uncertainty for the Suez Canal, the southern Red Sea, the Gulf of Oman and the Arabian Gulf. Significant unattributed fractions remain in the Gulf of Suez, the northern Red Sea and the Gulf of Aden. Overall, ≈ 100 chemical species needed to be identified to explain the measured total OH reactivity within the uncertainty, while the 10 most important compounds contributed 20–39 % of the reactivity. Unattributed reactivity in plumes from hydrocarbon processing facilities may be due to branched and/or higher hydrocarbons not captured with the techniques available on board the *Kommandor Iona*. In order to get a more comprehensive picture of the chemical species relevant for OH chemistry in the region, measurements with even greater chemical detail in the hydrocarbons would be necessary.

The range and composition of OH reactivity (and the ozone mixing ratios) around the Arabian Peninsula were, despite the marine measurement locations, broadly comparable to observations from highly populated urban areas, except for an unusually large contribution of OVOCs (Dolgorouky et al., 2012; Kim et al., 2016; Kovacs et al., 2003; Mao et al., 2010; Praplan et al., 2017; Williams et al., 2016; Yang et al., 2017). The “urban-like” OH reactivity is related to intensive international ship traffic in the seaways in the Arabian Basin and to major emissions from oil and gas industries on sea platforms and at the coasts. Oil and gas related VOCs were important sources of OH reactivity, and could be a relevant factor for the extremely high ozone concentrations and the photochemical air pollution usually seen in summer in the region (Barkley et al., 2017; Farahat, 2016; Lelieveld et al., 2009; Smoydzin et al., 2012). Most predictions assume that oil and natural gas production will increase in the Middle East during the coming decades (Balat, 2006; Holz et al., 2015; Khatib, 2014; Overland, 2015). Similarly, ship emissions around the Arabian Peninsula have been projected to grow on the short term due to intensifying traffic (Eyring et al., 2007), although new emission regulations set by the International Maritime Organization (IMO, 2019), effective from 2020, might lead to a long-term decrease. Given that

the conditions favor ozone production and will increase to do so due to rising temperatures (Lelieveld et al., 2012; Lelieveld et al., 2016a; Wasimi, 2010), emission regulations in the region appear to be the only way to prevent a further increase in photochemical air pollution in the future.

Supplement. The supplement related to this article is available online at: www.atmos-chem-phys-discuss.net/acp-2019-416/acp-2019-416-supplement.pdf

Data availability. The data used in this study will be available from August 2019 to all scientists agreeing to the AQABA protocol at <https://doi.org/10.5281/zenodo.3354117>.

Author contributions. EP and NW were responsible for OH reactivity measurements and data. EP conducted further data analysis and wrote the first draft of the manuscript. AE, EB, LE and CS contributed VOC and NMHC measurements and data. Ozone and SO₂ data were provided by JC and PE, formaldehyde and NO_x data by DD, BH, IT and HF, methane and carbon monoxide by JP. DW calculated the back trajectories. JL designed and realized the campaign. JW supervised the study. All authors contributed to manuscript writing and revision, read and approved the submitted version.

Competing interests. The authors declare that they have no conflict of interest.

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OH reactivity of the urban air in Helsinki, Finland, during winter

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Contribution to this publication by Eva Y. Pfannerstill: Contributed to the design and evaluation of the instrument characterization experiments, assisted with the data analysis and provided input to the writing of the manuscript.

Abstract. A new instrument to measure total OH reactivity in ambient air based on the Comparative Reactivity Method (CRM) has been built and characterised at the Finnish Meteorological Institute in Helsinki, Finland. The system is based on the detection of pyrrole by a gas chromatograph with a photoionization detector and designed for long term studies. It was tested in a container close to the SMEAR III semi-urban station in Helsinki during the winter in February 2016. The sampling location next to the delivery area of the institute was influenced by local vehicle emissions and cannot be considered representative of background conditions in Helsinki. However, effects of nitrogen oxides on the measurements could be investigated there. During this campaign, 56 compounds were measured individually by 1) an in-situ gas chromatograph coupled to a mass spectrometer (GC/MS) and by 2) off-line sampling in canisters and on adsorbent filled cartridges taken at the container and subsequently analysed by GC/MS and liquid chromatography, respectively. In addition, nitrogen oxides were measured at the same location, while ozone, carbon monoxide and sulfur dioxide concentrations have been retrieved from the SMEAR III mast data. The comparison between the total OH reactivity measured and the OH reactivity derived from individual compound measurements are in better agreement for lower reactivity levels. Possible explanations for the differences are discussed in detail.

4.1 Introduction

The hydroxyl radical (OH) is the most important oxidant in our atmosphere (Denman et al., 2007; Lelieveld et al., 2016b). Yet it is difficult to measure directly and to constrain correctly its concentration in models. OH reacts with nearly all atmospheric trace gases and its lifetime is therefore short (from a few seconds to below 10 ms). OH reactivity is defined as the inverse of its lifetime and can be derived by summing all the individual compounds (*i*) reacting with OH multiplied by their corresponding OH reaction rate coefficients ($k_{i,\text{OH}}$):

$$R_{\text{OH}} = \sum_i k_{i,\text{OH}}[i] \quad (4.1)$$

Kovacs and Brune (2001) originally proposed measurement of total OH reactivity as a holistic approach to verify whether the compounds that are routinely measured (in particular volatile organic compounds, VOCs) are sufficient to account for the directly measured reactivity and OH concentrations in models. The basic assumption is that if reactive compounds are missing from the models, the OH concentrations in photochemical and global climate models will be overestimated, leading to inaccurate predictions.

The first OH reactivity measurement method relied on the direct observation of OH and its decay by laser induced fluorescence (LIF, Kovacs et al., 2003; Kovacs and Brune, 2001). Later, Sinha et al. (2008) proposed an alternative relative rate approach based on the measurement of a VOC by mass spectrometry and termed the Comparative Reactivity Method (CRM). With this method the oxidation of a reference compound (not present naturally in the air) in an OH field is monitored with and without ambient air present. This method has been then adopted by several groups (e. g. Dolgorouky et al., 2012; Kim et al., 2011; Michoud et al., 2015; Yang et al., 2016) and has been deployed at various sites (e. g. Hansen et al., 2015; Williams et al., 2016; Zannoni et al., 2015; Zannoni et al., 2016).

Generally, studies made in urban environments have found that the difference between the total OH reactivity measured and the OH reactivity calculated from individually measured atmospheric compounds (called unexplained or *missing* reactivity) is below 40 % and in some cases within the experimental error (e. g. Hansen et al., 2015; Kovacs et al., 2003; Lee et al., 2009; Lou et al., 2010; Ren et al., 2003; Ren et al., 2006a; Sadanaga et al., 2005; Shirley et al., 2006; Whalley et al., 2016; Yoshino et al., 2006; Yoshino et al., 2012). In contrast, from forested sites large fractions of the OH reactivity could not be explained. Di Carlo et al. (2004) first reported such data from the temperate forest and since then similar findings have been reported from other tropical and boreal forests (e. g. Edwards et al., 2013; Nölscher et al., 2012a; Nölscher et al., 2016; Sinha et al., 2008; Sinha et al., 2010). These findings on the variability of OH reactivity from ambient air at various locations and from biogenic emissions have been the main drivers for the development of a new CRM system at the Finnish Meteorological Institute (FMI) suitable for semi-autonomous longer term measurements at boreal forest sites. OH reactivity measurements have been comprehensively reviewed recently (Yang et al., 2016) and the immediate research goals for the OH reactivity community summarized (Williams and Brune, 2015). It is clear that most work to date has been performed in intensive campaigns due to the complexity of the instrumentation. Here we endeavour to con-

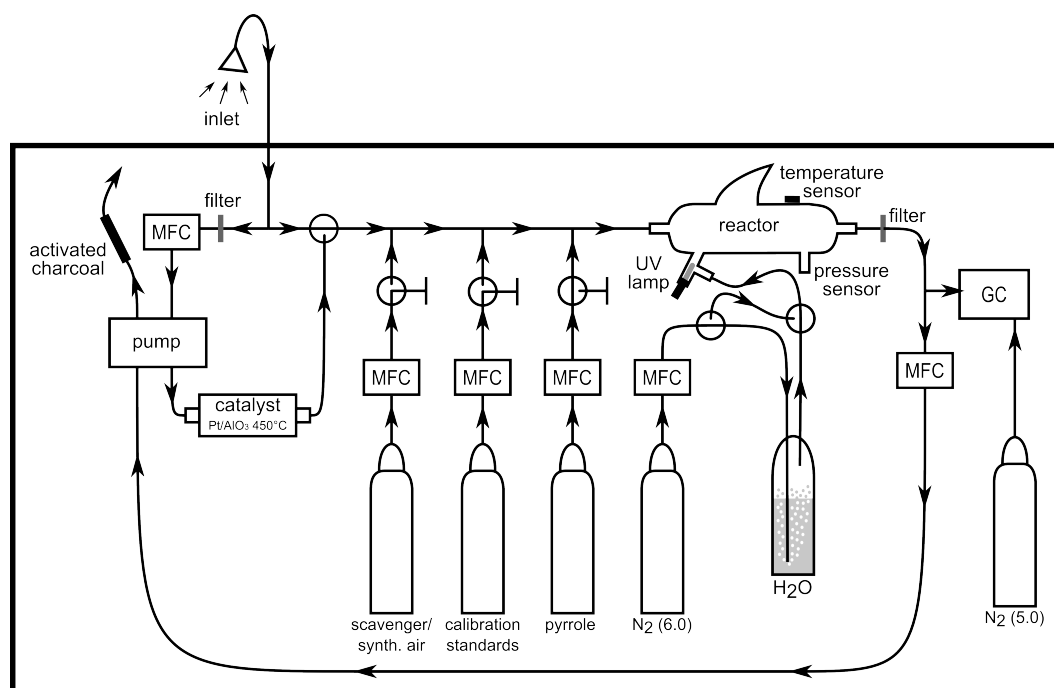


Figure 4.1: Scheme of the CRM-FMI setup (MFC: Mass Flow Controller, GC: Gas Chromatograph).

struct a robust, sensitive, accurate, and precise system suitable for seasons spanning measurement intervals and we test the system with as little intervention as possible during a month of measurements.

4.2 Methods

4.2.1 The Comparative Reactivity Method (CRM)

Sinha et al. (2008) developed the CRM method in order to provide more affordable and transportable OH reactivity measurements requiring less ambient air inflow than those based on LIF. Its principle relies on the addition of a given compound (pyrrole, C_4H_5N) to both ambient air and zero air and exposing the mixtures to OH. The radicals are produced by the photolysis of water with a UV lamp ($\lambda < 185$ nm). A scheme of the setup is depicted in Fig. 4.1 with a gas chromatograph using a photoionization detector (GC-PID, GC955, Synspec b.v., Groningen, The Netherlands) as the detector rather than the original proton transfer reaction mass spectrometer (PTR-MS), similar in concept to Nölscher et al. (2012b). The whole system is therefore easy to transport for field campaigns and does not require a lot of space.

By comparing the consumption of pyrrole in both ambient and zero air mixtures after exposure to OH, it is possible to estimate the total reactivity of the compounds present in ambient air. Assuming pseudo-first order conditions ($[Pyrrole] \gg [OH]$), the total OH reactivity in the reactor, R_{eqn} , can be derived from the following formula:

$$R_{eqn} = \frac{C_3 - C_2}{C_1 - C_3} \cdot k_{OH,pyr} \cdot C_1 \quad (4.2)$$

where C_1 is the concentration of pyrrole in the presence of an effective OH scavenger, C_2 the concentration of pyrrole in zero air (all OH reacts with pyrrole), C_3 the concentration of pyrrole in ambient air, and $k_{\text{OH,pyr}}$ the reaction rate for the reaction of pyrrole with OH.

A two minute program was used to sample and quantify pyrrole with GC-PID. C_2 and C_3 measurements were alternated sequentially every 8 minutes and the first point measured after switching the valve was discarded (stabilisation period). These alternate measurements take into account natural changes in the relative humidity (RH), a key parameter to determine the amount of OH produced as zero air is generated by using a catalyst (platinum on alumina, Pt/AlO₃) at 450 °C to remove VOCs without altering RH significantly (see also section 4.3.1).

Under field conditions C_1 is measured approximately every other week by adding up to 60 ml min⁻¹ of a 0.600 % mixture of propane in nitrogen as an OH scavenger (AGA, Espoo, Finland). This has been shown to be more reliable and quicker than the original method of measuring C_1 under completely dry conditions, without scavenger (Michoud et al., 2015). C_1 takes into account the photolysis of pyrrole by UV (ca. 9–25 %).

The minimum sampling flow is 325 ml min⁻¹ during C_2 measurements (zero air only), and about 650 ml min⁻¹ during C_3 measurements (half of which goes to the reactor). The nitrogen flow is 145 ml min⁻¹ and the pyrrole input flow is about 4 ml min⁻¹ from a gas cylinder (5.27 ppmv ± 10% in 6.0 N₂, Westfalen AG, Münster, Germany). Therefore the total flow through the reactor is 472 ml min⁻¹ and the dilution factor D is 1.45 (ratio of sampling and total flows). The system is controlled and the data recorded with a custom-made software written in Python (pyCRM).

4.2.2 Laboratory characterization

For the characterization of the CRM system in the laboratory, the following additional instruments were used: APNA-370 Ambient NO_x Monitor (Horiba, Ltd.), Thermo 49i ozone monitor (Thermo Scientific), and Thermo 49i ozone monitor with ozone generator. NO (50 ppmv) was mixed with synthetic air (grade 5.0, AGA, Espoo, Finland) to produce concentrations in the reactor up to 100 ppbv. NO₂ levels in the reactor up to 65 ppbv were produced from a gas standard (VSL, 48.3 ppmv) connected to a calibrator (Sonimix 3012, LNI Swissgas, Geneva, Switzerland).

4.2.3 Measurement site

OH reactivity, NO_x, and VOCs were sampled from 29 January to 26 February 2016, close to FMI in Helsinki, roughly 85 metres away from the mast of the third Station for Measuring Ecosystem-Atmosphere Relations (SMEAR III, Järvi et al. (2009)). This is a semi-urban site situated 4 km north from the center of Helsinki. The measurements cover various meteorological conditions. In addition carbon monoxide (CO), sulfur dioxide (SO₂), and ozone (O₃) mixing ratios were retrieved from the SMEAR III mast data* (35 m a. s. l.).

Figure 4.2 shows an orthophotograph of the sampling site combined with a wind rose. The surroundings can be divided in three sectors: 1) A communal garden containing large leaf-trees such as lindens and maples and other vegetation lies in the South to North West direction; 2) our institute building, the Kumpula campus of

*Available at <http://avaa.tdata.fi/web/smart/smea>

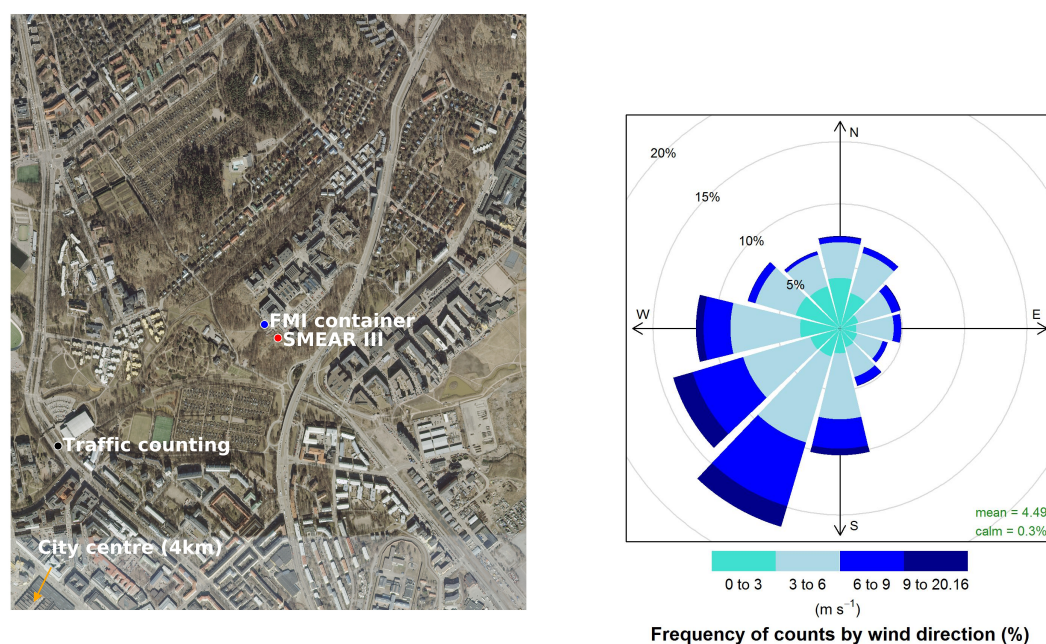


Figure 4.2: Left: Orthophotograph from the surrounding of the sampling site in the Kumpula Campus in Helsinki (Source: National Land Survey of Finland Topographic Database 04/2014). Right: Wind rose for the whole measurement period.

the University of Helsinki, and various housing are located in the North West to North East direction; 3) the main road to the city centre runs in the North East to South direction (where also further housing is located). Note that another important street is located behind the communal garden, where traffic is counted by the Helsinki City Planning Department as indicated in Fig. 4.2.

In-situ measurements

Since the instruments were located in a container situated close to the institute delivery area, our measurements were periodically subject to local truck and car exhausts containing high levels of NO_x , which impact the CRM OH reactivity. In order to assess correctly the NO_x correction (see sections 4.3.1 and 4.3.1), the APNA-370 NO_x Monitor was placed in the same container as the CRM system. Additionally C_6 – C_{10} hydrocarbons were measured with an in situ thermal desorber (TurboMatrix, 650, Perkin-Elmer) connected to a GC (Clarus 680, Perkin-Elmer) coupled to a mass spectrometer (Clarus SQ 8 T, Perkin-Elmer). The sampling lines for each instrument were about 5 m long unheated Teflon lines sticking out of the container's roof (ca. 3 m height) for ca. 0.5 m.

Off-line analysis

In order to comprehensively quantify VOCs as to better quantify the expected OH reactivity, we collected additional daily samples for 24-hours. C_2 – C_6 hydrocarbons were collected in pre-evacuated 0.85-liter electro-polished stainless steel canisters using flow restrictors and carbonyls were collected on DNPH adsorption cartridges (C_{18} coated with 2,4-dinitrophenyl hydrazine, Sep-Pak, Waters).

After collection, canisters were pressurized with N_2 (grade 6.0, AGA, Espoo, Finland and analysed with GC (HP6890) using a Flame Ionization Detector (FID) as described

by Hellén et al. (2003). DNPH cartridges were eluted with 3 ml of acetonitrile and the resulting solutions directly injected into the liquid chromatograph (1100 Series, Agilent Technologies) equipped with a UV absorption detector (LC/UV). Calibration was performed using a commercially available standard (CARB Method 1004 DNPH Mix 1, Supelco) to produce four different concentration levels (30, 60, 150, and 1500 ng/ml). A more detailed description of the method can be found in Hellén et al. (2004).

4.2.4 Box model

For accurate determination of the OH reactivity using the CRM method some corrections need to be applied to the raw data that can be derived from model calculations. Therefore, we used a simple box model based on IUPAC recommended rate coefficients (Atkinson et al., 2004; Atkinson et al., 2006) and amended according to Michoud et al. (2015), in order to simulate the chemistry in the CRM system reactor. Additional alterations to the model are described in the following sections. In the present study, we used the model to investigate characterization of the instrument when only NO_x or O_3 was present in the reactor and derived a pseudo-first order correction factor (see section 4.3.1). Because propane (C_3H_8) was used in parts of these experiments, it is included in our model as an OH sink only (without its full degradation scheme, as Michoud et al. (2015) showed that the simple box model delivers results similar to those from the full Master Chemical Mechanism scheme). The chemical reactions included in the model are listed in Table S1 from the Supplementary.

The model is run with varying initial concentrations assuming standard conditions until steady-state is reached. Experimental C_1 is used as the initial pyrrole concentration. The OH concentration is set as the difference between experimental C_1 and experimental C_2 and the same value is used for the initial hydrogen atom (H) concentration as OH is formed from the photolysis of water. Note that H converts almost instantly to HO_2 . N_2 and O_2 concentrations take into account dilution of ambient air with humid N_2 . Other input parameters such as temperature and relative humidity are measured values.

4.3 Results and discussion

4.3.1 Instrument characterization

Several correction factors need to be applied to raw CRM data. Sinha et al. (2008) and Sinha et al. (2009) described how changes of water concentration and the deviation from pseudo-first-order kinetics should be taken into account. These have been reported as well in other studies based on the CRM method (Dolgorouky et al., 2012; Michoud et al., 2015). Dolgorouky et al. (2012) and Michoud et al. (2015) reported as well correction factors for OH recycling in the reactor due to the presence of NO_x as some of the UV light used to generate OH radicals enters the reactor and photolyses compounds there. Attempts to alter the reactor design led to a significant reduction of OH levels in the reactor (Keßel, 2016), therefore this effect is usually minimized by increasing the distance between the tip of the UV lamp and the reactor, while maintaining a pyrrole-to-OH ratio (pyr:OH) around 2. The following subsec-

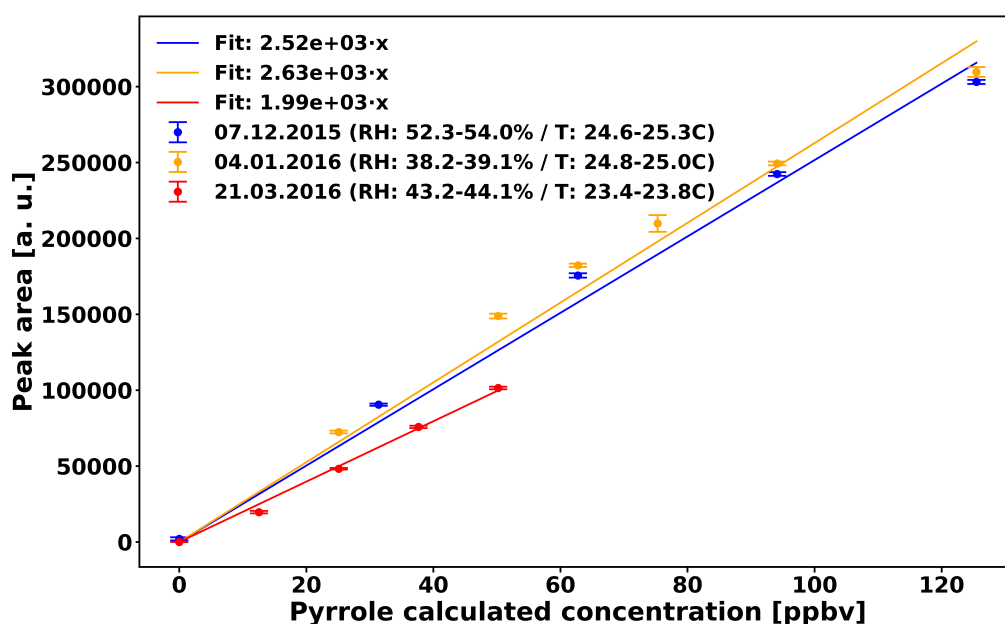


Figure 4.3: Pyrrole calibration curves.

tions describe how these correction factors were derived for our system. Additionally, we describe GC signal variations due to pressure and temperature changes, and show how ozone (O_3) also affects the measured signal. The experimental correction factors discussed in the following sections have been derived for a specific UV lamp position. After the tests presented here were done, the connection holding the lamp in the reactor broke and had to be replaced, affecting the lamp position. Therefore, further tests for the specific configuration used in the present study could not be performed.

Pyrrole calibration

Pyrrole was introduced into the system (in the dark) at known mixing ratio up to 95 ppbv (0 to 8.5 ml min^{-1} flow in a total flow of 465 ml min^{-1}) and the signal recorded to derive a calibration curve through the intercept ($s \cdot x$, Fig. 4.3).

The calibration uncertainty (U_s , relative standard deviation) is about 1.0 % for all three calibration curves. The main reason for the slope change in March is a decreasing signal for the PID detector of the GC. The highest uncertainty on the pyrrole concentration due to the flows and the dilution in the system (U_{dil}) is about 8 % for the lowest pyrrole level. Because C_2 and C_3 values in the present study are usually in the lower range of the calibration curve, this value is used to derive measurement uncertainties. In addition, the pyrrole standard concentration has a 10 % uncertainty ($U_{pyr,standard}$), so that the total uncertainty on pyrrole levels (U_p) is derived as

$$U_p = \sqrt{U_{dil}^2 + U_{pyr,standard}^2} = 12.8 \% \quad (4.3)$$

Relative humidity correction

Variation of the relative humidity (RH) between zero air and ambient measurements will affect the OH levels in the reactor. Figure 4.4 depicts the RH dependence of the pyrrole signal during zero air measurements (C_2) with a factor of $-0.134 \text{ ppbv/\%}$

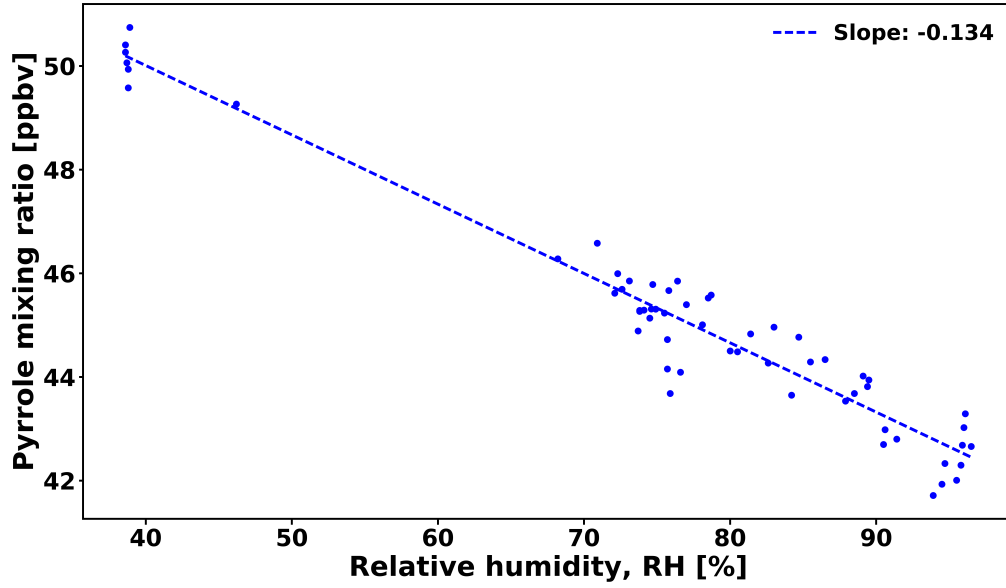


Figure 4.4: Pyrrole concentration during zero air measurements (C_2) as a function of the measured relative humidity (RH). The dashed line is a first-order polynomial fit to the data.

(uncertainty $U_\sigma = 3.2\%$), which is applied throughout the ambient measurements and laboratory tests for the characterisation of our system.

Nitrogen oxide correction

As described by Michoud et al. (2015), NO produces additional OH radicals via the following reaction:



For the tests with NO, propane (C_3H_8) was injected at a constant level (2.6 or 1.1 ppmv) throughout the experiment and the NO level in the reactor varied from 0 to 77 ppbv. The experimental decrease in C_3 due to the presence of NO is depicted in Fig. 4.5 (left) for various pyr:OH ranging from 2.27 to 4.45. The change in C_3 expected due to the apparent increase in reactivity (up to 18.7 s^{-1}) due to NO addition ($\Delta C_{3,\text{eqn}}$) is taken into account, derived from equation (4.2) and the dilution factor D , assuming that $R_{\text{eqn}} = R_{\text{NO}}/D$.

$$\Delta C_{3,\text{NO},\text{exp}} = (C_{3,0} - C_{3,\text{NO}}) + \Delta C_{3,\text{NO},\text{eqn}} \quad (4.5)$$

$$\Delta C_{3,\text{NO},\text{eqn}} = \frac{C_1(R_{\text{NO}}/D + C_2 k_{\text{OH},\text{pyr}})}{R_{\text{NO}}/D + C_1 k_{\text{OH},\text{pyr}}} \quad (4.6)$$

with $C_{3,0}$ the level of pyrrole in the absence of NO and $C_{3,\text{NO}}$ the measured level of pyrrole with a given concentration of NO.

Figure 4.5 (top) also shows the expected ΔC_3 values from the box model, which agree with the experimental data within their uncertainties, except for the test with the highest pyr:OH (in green). It is not clear though why the results of this test differ from others. Nevertheless, one possible explanation is that the water used to modify pyr:OH for that experiment was not flushed long enough with synthetic air,

introducing impurities in the system, while another experiment using water (in cyan) was flushed for a day before the experiment.

The coefficients retrieved from the quadratic fits ($d \cdot x^2 + e \cdot x$) of the experimental data (dashed lines) are plotted as a function of pyr:OH in the two additional panels of Fig. 4.5 (bottom, in gray for the higher reactivity experiment and in black for the lower reactivity experiments). Coefficients for fits in the box model data (not shown in the top panel for clarity), are plotted as well in blue for the higher reactivity value and in green for the lower reactivity value. Linear regressions (solid lines) are used to derive functions of pyr:OH for the second and first order fit coefficients (d and e , respectively) for the model data (blue and green for high and low reactivity, respectively). They show that the correction does not depend on pyr:OH, in contrast with the findings of (Michoud et al., 2015). They also suggest that the correction due to the presence of NO is larger for low OH reactivity in the reactor, which has not been discussed in previous publications on CRM.

The fit functions are of the form

$$d = d_1 \cdot (\text{pyr} : \text{OH})^2 + d_2 \cdot (\text{pyr} : \text{OH}) \quad (4.7)$$

$$e = e_1 \cdot (\text{pyr} : \text{OH})^2 + e_2 \cdot (\text{pyr} : \text{OH}) \quad (4.8)$$

for the second and first order coefficients d and e , respectively. The final parametrization for this correction factor is of the form

$$\Delta C_{3,\text{NO}} = d \cdot [\text{NO}]^2 + e \cdot [\text{NO}] \quad (4.9)$$

with $\Delta C_{3,\text{NO}}$ the correction applied to C_3 due to the presence of NO.

The experimentally derived factors agree well with the model with the exception of the test performed at the highest pyr:OH as discussed previously. Because it seemed to be an outlier and pyr:OH during ambient measurement was situated between 1.7 and 2.6, it was decided to use a correction function independent of pyr:OH based on the tests at pyr:OH 3.59 and 2.27 with $d = -1.61 \cdot 10^{-3}$ and $e = 3.46 \cdot 10^{-1}$ (black line). The uncertainty of this correction ($U_{\Delta C_{3,\text{NO}}}$) depends on the uncertainty of the fit ($U_{\text{fit},\text{NO}} = 1.8\%$) and the concentration of NO as given by the following equation:

$$U_{\Delta C_{3,\text{NO}}} = \sqrt{U_{\text{fit},\text{NO}}^2 + U_{[\text{NO}]}^2} \quad (4.10)$$

Nitrogen dioxide correction

Nitrogen dioxide (NO_2) can be photolysed in the reactor to produce NO, which generates additional OH as previously seen (Eq. (4.4)). Various concentrations of NO_2 were introduced in the reactor using a standard gas cylinder and a dilutor. Figure 4.6 shows how NO_2 affected the measured signal (ΔC_3). As Michoud et al., 2015 found no pyr:OH dependency, this correction function was derived only for a pyr:OH close to 1.7. Because adding NO_2 to the gas mixture increases OH reactivity, R_{NO_2} , (up to 15.2 s^{-1}) $\Delta C_{3,\text{NO}_2,\text{exp}}$ also takes into account the expected change in C_3 due to the additional OH reactivity ($\Delta C_{3,\text{eqn}}$, derived from equation (4.2), assuming $R_{\text{eqn}} = (((R_{\text{NO}_2}/D) - F_3)/F_1)^{(1/F_2)}$, with D the dilution factor and F_1 , F_2 , and F_3 the correction coefficients derived from model runs assuming the presence of NO_2 only (section 4.3.1).

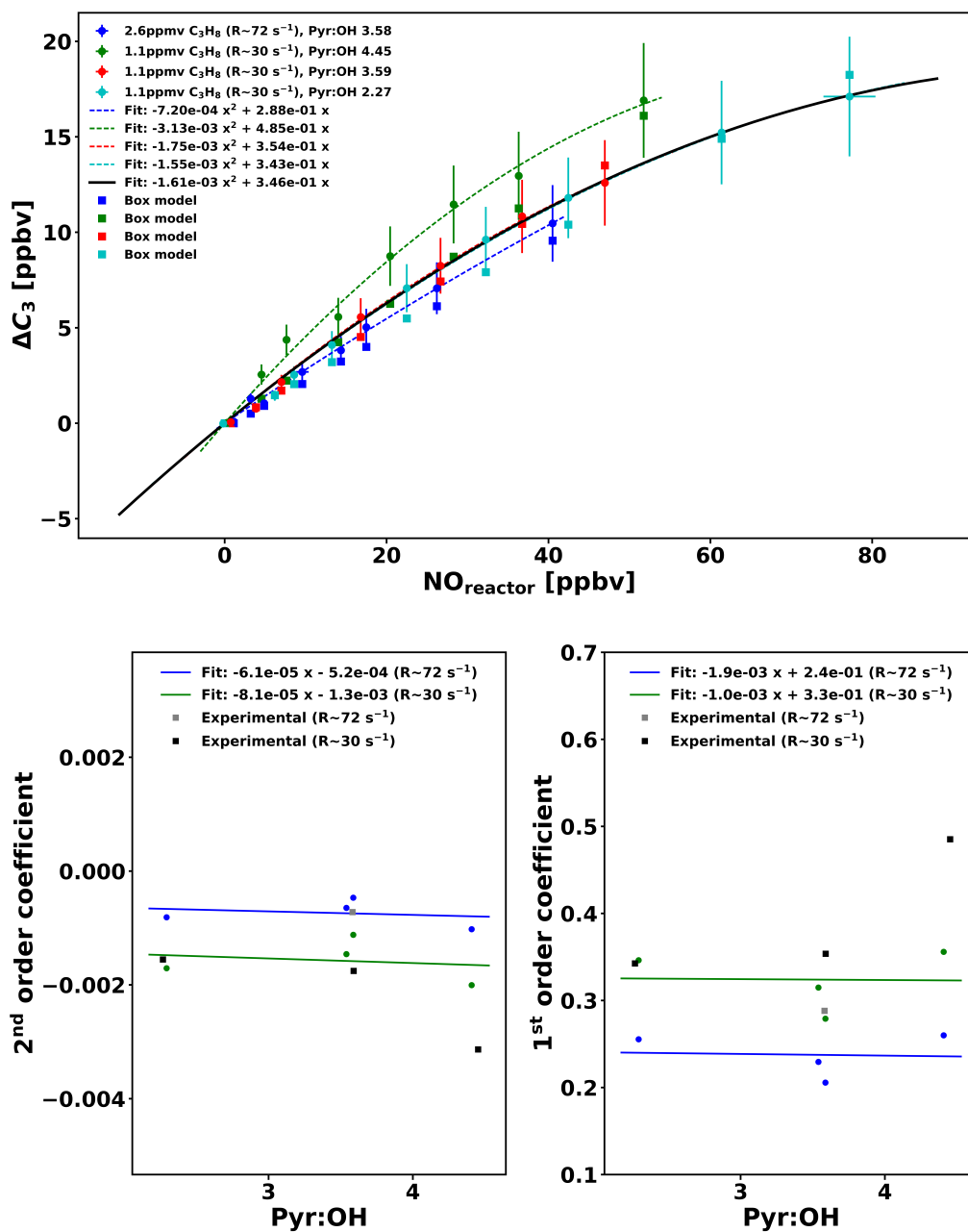


Figure 4.5: Top: Change of measured signal (ΔC_3) as a function of pyr:OH and NO in the reactor (circles) with derived fits and corresponding results from model runs (squares). Bottom (2 panels): Experimental and modelled fit second (left) and first order (right) coefficients as a function of pyr:OH.

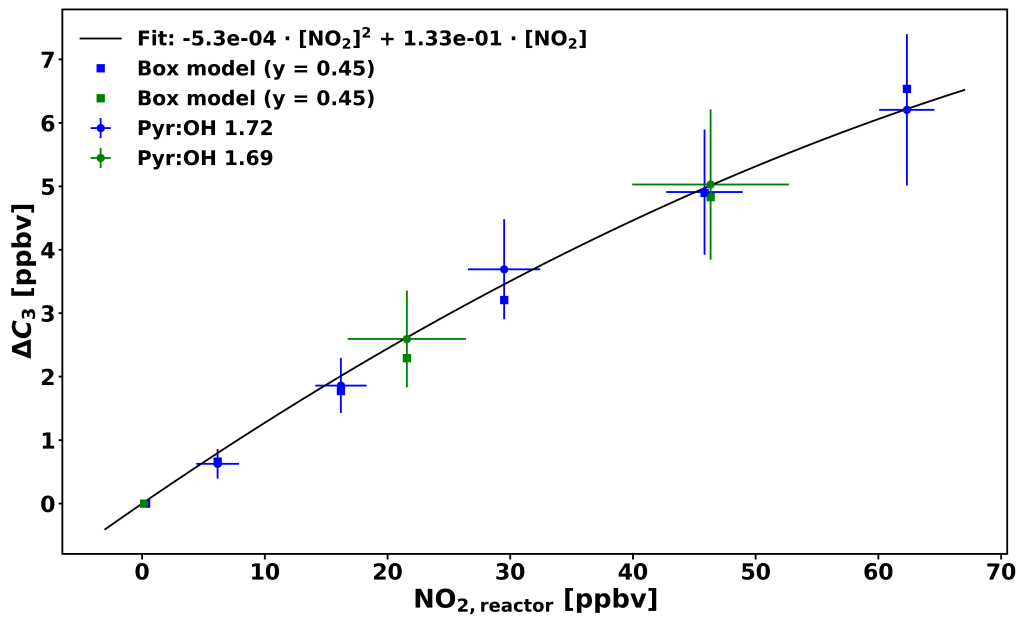


Figure 4.6: Change of measured signal (ΔC_3) as a function of NO_2 present in the reactor (circles) and corresponding results from model experiments (squares). The initial conversion degree of NO_2 in NO and O in the model is described by y .

$$\Delta C_{3,\text{NO}_2,\text{exp}} = (C_{3,0} - C_{3,\text{NO}_2}) + \Delta C_{3,\text{NO}_2,\text{eqn}} \quad (4.11)$$

$$\Delta C_{3,\text{NO}_2,\text{eqn}} = \frac{C_1(R_{\text{eqn}} + C_2 k_{\text{OH},\text{pyr}})}{R_{\text{eqn}} + C_1 k_{\text{OH},\text{pyr}}} \quad (4.12)$$

with $C_{3,0}$ the level of pyrrole in the absence of NO_2 and C_{3,NO_2} the measured level of pyrrole with a given concentration of NO_2 .

By fitting a quadratic function ($f_1 \cdot x^2 + f_2 \cdot x$) to the data, we obtain

$$\Delta C_{3,\text{NO}_2} = f_1 \cdot [\text{NO}_2]^2 + f_2 \cdot [\text{NO}_2] \quad (4.13)$$

with $\Delta C_{3,\text{NO}_2}$ the correction factor for C_3 due to the presence of NO_2 , while $f_1 = -5.3 \cdot 10^{-4}$ and $f_2 = 1.33 \cdot 10^{-1}$. The uncertainty of this correction is $U_{\text{fit},\text{NO}_2} = 3.7\%$.

Figure 4.6 also includes results from box model runs. By assuming a 45 % conversion of NO_2 into NO and O, the model is able to reproduce the signal variation satisfactorily. Michoud et al. (2015) reported an experimental conversion of NO_2 to NO of 24 % but did not attribute it fully to photolysis of NO_2 but to other possible surface processes as well.

Correction for ozone

Additionally, we examined the interference by ozone (O_3), which can also increase the OH levels in the reactor due to O_3 photolysis through the following mechanism:



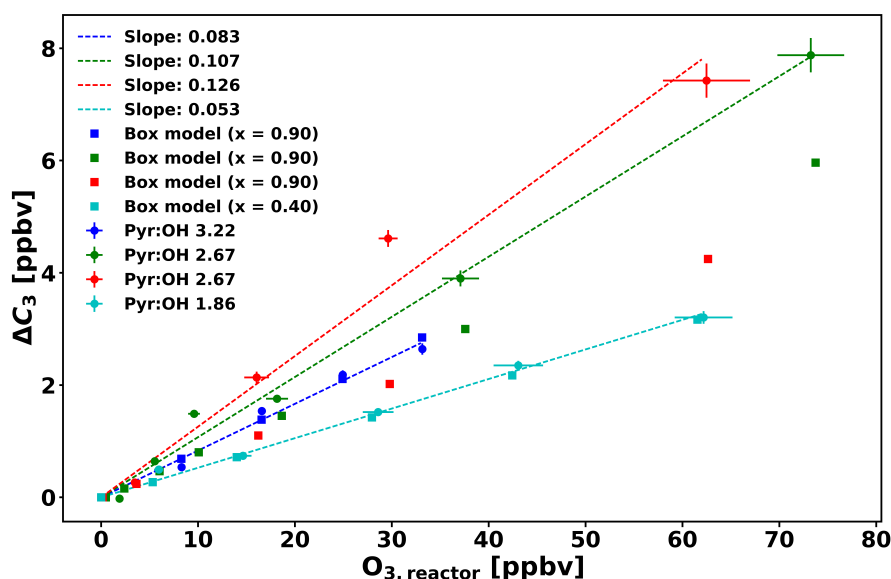


Figure 4.7: Change of measured signal (ΔC_3) as a function of O_3 present in the reactor (circles) at various pyr:OH ratios with derived fits (dotted lines) and corresponding results from model runs (squares). The initial conversion degree of O_3 in $O(^1D)$ (and O_2) is described by x . Right: Slopes as a function of pyr:OH ratio and the derived parametrization.

Sinha et al. (2008) reported that the O_3 concentration in their reactor was of a few ppmv, so that ambient ozone levels would not affect the OH concentration. However, we found that the UV lamp in our system produces only about 170 ppbv of ozone in the reactor, so that an ambient level of 30 ppbv represents almost a change of 20 %. The most likely explanation for the difference is the lamp position. Sinha et al. (2008) reported pyrrole photolysis up to 25 %, which suggests that the lamp was located much closer to the reactor leading to a higher photolysis of O_2 from ambient and zero air. This previously unreported correction has been identified in other CRM systems as well during an intercomparison campaign at the SAPHIR chamber (Forschungszentrum Jülich, Germany; Fuchs et al. (2017a)).

The signal change as a function of the amount of O_3 present in the reactor, $\Delta C_{3,O_3,exp}$, is shown in Fig. 4.7 (left).

$$\Delta C_{3,O_3,exp} = C_{3,0} - C_{3,O_3} \quad (4.16)$$

with C_{3,O_3} the pyrrole signal in the absence of O_3 and C_{3,O_3} the measured pyrrole signal with a given concentration of O_3 in the reactor.

Model calculations using the box model are included in Fig. 4.7. These results are obtained varying the conversion from O_3 to $O(^1D)$ in the reactor from 90 % (RH ca. 37 %) to 40 % (RH ca. 55 %). This dependence on RH of the correction factor for the presence of ozone might be due to effects of adsorbed water on the reactor surface on UV light reflection as experienced in ozone monitors (Wilson and Birks, 2006). At low RH, while the model run agrees with the experimental data of the test conducted at pyr:OH 3.22, it differs largely with the tests conducted at pyr:OH 2.67. Even taking into consideration a change in background reactivity during the test (results in green) and increasing the conversion of O_3 to $O(^1D)$ in the model to 100 % for

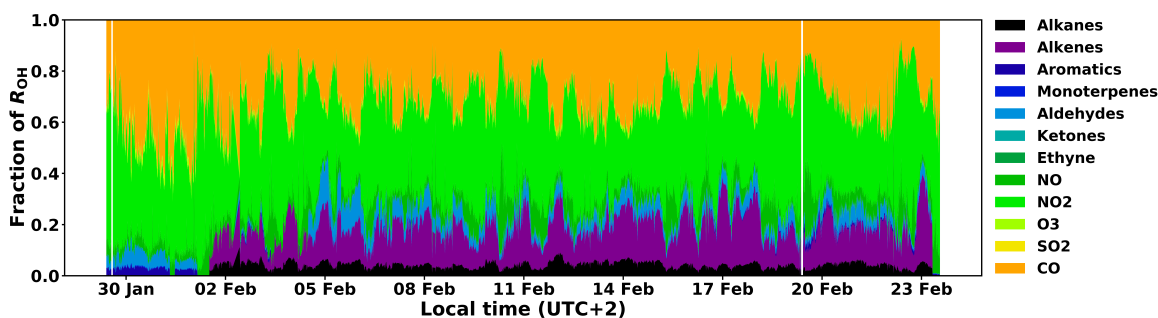


Figure 4.8: Fraction of OH reactivity for (group of) compounds analysed individually. (Not all volatile organic compounds (VOCs) were measured at the beginning of the campaign.)

these tests does not improve the agreement. Both tests have been conducted on the same day and might have suffered from a similar contamination as the outlier test for NO correction (see section 4.3.1).

Given the pyr:OH range and the relative humidity levels for the ambient measurement, it has been decided to apply the ozone correction factor derived from the test at pyr:OH 1.86 with a slope of 0.053 ($U_{\text{fit},\text{O}_3} = 2.2\%$).

Correction for pseudo-first-order conditions

As equation (4.2) assumes a pseudo-first-order (i. e. $[\text{Pyrrole}] \gg [\text{OH}]$) but the pyrrole-to-OH ratio (pyr:OH) used for the measurements range from 1.7 to 2.6, it is necessary to correct for this.

This correction has been derived from the simple box model taking OH recycling reactions into account (*simple model*, see section 4.2.4). Michoud et al. (2015) showed that this correction can vary depending on the chemical composition of the sampled air and pyr:OH.

An empirical approach such as described by Michoud et al. (2015) is not appropriate for this particular dataset, as the (known) reactivity is not dominated by one particular species. Roughly one third of the reactivity comes from CO, another third from NO_x , and the last third from various organics (Fig. 4.8) and no standard available would reproduce that specific mixture.

Nevertheless, we have derived here a correction factor assuming R_{input} values of 0, 3, 9, 27, and 81 s^{-1} , assuming that NO_2 , CO, and a generic VOC (with a reaction rate constant with OH of $5.0 \cdot 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, Michoud et al. (2015)) all contribute to one third of the reactivity. Using the campaign average C_1 as the initial pyrrole concentration and $C_1 - C_{2,\text{model}}$ as initial OH concentration and varying both reactivity and pyr:OH, the model predicts how much pyrrole should be observed ($C_{3,\text{model}}$). $C_{2,\text{model}}$ is the model result when the reactivity is 0 s^{-1} . Even though O_3 does not contribute to the reactivity, it influences the chemistry in the reactor and the average value of 23.44 ppbv for the campaign has been used. Photolysis rates of 45 % for NO_2 and 40 % for O_3 are used in the model, respectively (see sections 4.3.1 and 4.7). Figure 4.9 represents R_{input} (calculated from input concentrations) compared to $R_{\text{eqn,model}}$ (modelled, eq. (4.18)) for various pyr:OH with fit functions of the form $F_1 \cdot x^{F_2} + F_3$ (eq. (4.19), see Sinha et al., 2008).

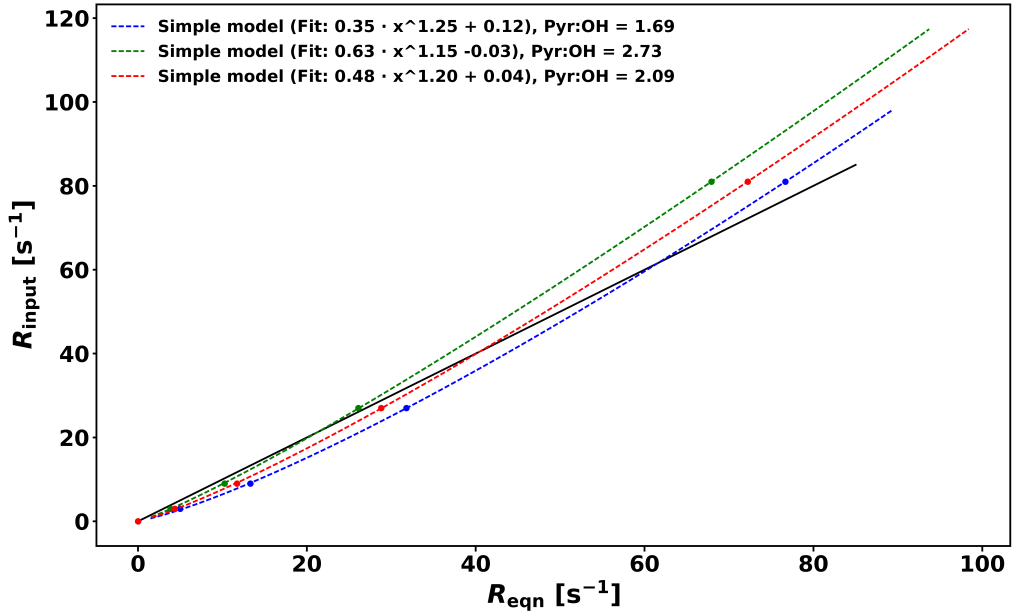


Figure 4.9: Scatter plots used for deriving pseudo-first-order correction. Scatter plot of R_{input} (calculated from input concentrations) against $R_{eqn,model}$ and the derived fit functions. The 1:1-line is depicted in black.

$$F = R_{true} / R_{model} \quad (4.17)$$

$$R_{eqn,model} = \frac{C_{3,model} - C_{2,model}}{C_1 - C_{3,model}} \cdot k_{OH,pyr} \cdot C_1 \quad (4.18)$$

$$R_{input} = F_1 \cdot R_{eqn,model}^{F_2} + F_3 \quad (4.19)$$

with $F_1 = 0.477$, $F_2 = 1.200$, and $F_3 = 0.043$ for the correction of ambient data. The model results lie close to the 1:1-line, overestimating R_{input} at low values and underestimating it at higher values. To correct for ambient data, we use the average fit (in red) and use the highest uncertainty (found at low values) of $U_F = 10.7\%$. The box model has also been used to derive a correction factor assuming the presence of NO_2 only (see Fig. 4.10 and section 4.3.1). The function at $pyr:OH$ 1.69 has been used ($R_{input}(NO_2) = 0.61 \cdot R_{eqn,model}^{1.07} + 0.14$) as $pyr:OH$ for the determination of NO_2 correction factor was close to 1.7.

Measurement precision

Measurement precision, U_{prec} , has been derived by mixing a known amount of test standard into the zero air (Keßel, 2016). These measurements have been performed with propane, carbon monoxide, and an air standard containing mostly α -pinene. The reactivity derived by Eq. (4.2) is calculated for every C_3 value measured and the standard deviation ($\sigma_{R_{eqn}}$) computed. The precision is obtained by dividing $\sigma_{R_{eqn}}$ with the mean of R_{eqn} ($\overline{R_{eqn}}$) for stable conditions. The results are depicted in Fig. 4.11. The precision varies with $\overline{R_{eqn}}$ values and is described by the following function:

$$U_{prec} = \phi_1 + \phi_2 \cdot \exp(-\phi_3 \cdot \overline{R_{eqn}}) \quad (4.20)$$

with $\phi_1 = 0.15$, $\phi_2 = 4.46$, and $\phi_3 = 0.40$.

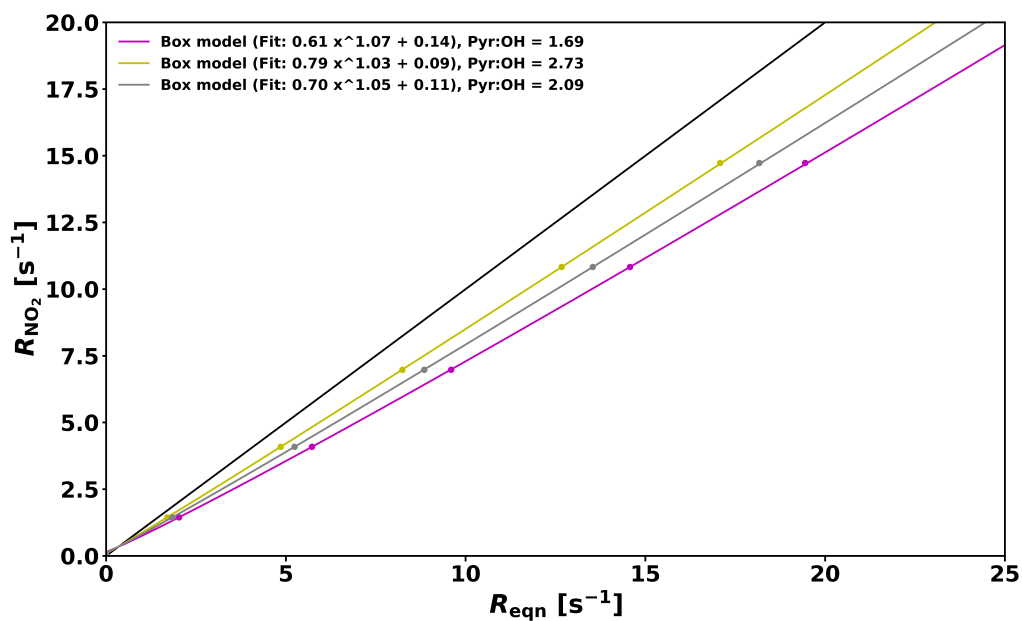


Figure 4.10: Scatter plots used for deriving pseudo-first-order correction in the presence of NO₂ only at various pyr:OH. The 1:1-line is depicted in black.

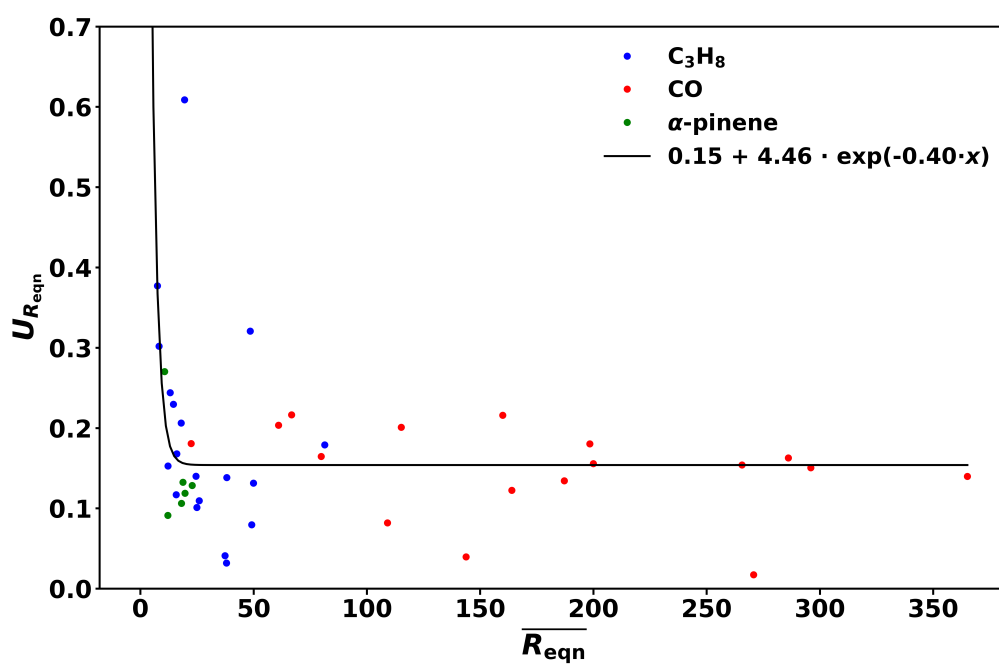


Figure 4.11: Precision of the measurement (standard deviation) as a function of R_{eqn} for various gas standards.

Summary

Equations (4.21) to (4.24) were used to derive experimental total OH reactivity values (R_{exp}) for the campaign presented in the next section. The correction factors $\Delta C_{3,\{NO,NO_2,O_3\}}$ were applied consequently to all data and equations (4.25) and (4.26) were applied to derive uncertainties for each measurement point.

$$R_{\text{exp}} = R_{\text{CRM}} \cdot D \quad (4.21)$$

$$R_{\text{CRM}} = (F_1 \cdot R_{\text{eqn}}^{F_2} + F_3) \cdot F \quad (4.22)$$

$$R_{\text{eqn}} = \frac{(C_3 + \Delta C_3) - C_2}{C_1 - (C_3 + \Delta C_3)} \cdot k_{\text{OH,Pyr}} \cdot C_1 \quad (4.23)$$

$$\Delta C_3 = \Delta C_{3,NO_2} + \Delta C_{3,NO} + \Delta C_{3,O_3} \quad (4.24)$$

$$U_{R_{\text{exp}}} = \sqrt{U_p^2 + U_s^2 + U_\sigma^2 + U_{\Delta C_3}^2 + U_{k_{\text{OH,Pyr}}}^2 + U_D^2 + U_F^2 + U_{\text{prec}}^2} \quad (4.25)$$

$$U_{\Delta C_3} = \sqrt{U_{\text{fit,NO}}^2 + U_{[\text{NO}]}^2 + U_{\text{fit,NO}_2}^2 + U_{[\text{NO}_2]}^2 + U_{\text{fit,O}_3}^2 + U_{[\text{O}_3]}^2} \quad (4.26)$$

with $U_{k_{\text{OH,Pyr}}}$ is 15 % (Keßel, 2016), and U_D is 2.8 % ($U_D^2 = U_{\text{totalflow}}^2 + U_{\text{samplingflow}}^2$, with $U_{\text{totalflow}} = U_{\text{samplingflow}} = 2\%$), while other uncertainties have been discussed previously. Note that the uncertainty on $k_{\text{OH,Pyr}}$ is larger than its variation with temperature (comparing air inside and outside the container).

4.3.2 Ambient measurements in Helsinki

In order to assess the performance of our system, we tested it in real conditions in a container next to our institute building. Atmospheric conditions (temperature and pressure), trace gas concentrations (NO_x from the container and O_3 from the SMEAR III mast), as well as the measured and calculated total OH reactivity (with 1-hour averages) are shown in Fig. 4.12. Ambient temperatures range from -7 to 4 °C and the wind during the measurement period came mostly from the vegetated sector, as shown in the right panel of Fig. 4.2.

The measured reactivity with all correction factors is displayed as R_{exp} (green). The limit of detection (LOD) was calculated individually for every C_2 measurement by using $C_3 = C_2 + 3 \cdot \sigma_{C_2}$ with σ_{C_2} the standard deviation of measured C_2 . Their average is $3.4 (\pm 2.2, 1\sigma) \text{ s}^{-1}$, which is lower than reported in other systems (e. g. Nölscher et al., 2012b). Measured total OH reactivity values below LOD are marked as crosses. The median total OH reactivity value for the whole measurement period (above LOD) is 7.6 s^{-1} , which is comparable to the reactivity found in Houston in summer (Mao et al., 2010) and to suburban areas reviewed by Yang et al. (2016), but lower than urban areas compiled in the same review. Due to the sampling location right next to the delivery area of our institute, it is not surprising that local vehicle emissions combined with low temperatures, weak photochemical activity, as well as slow mixing possibly allow for longer lifetimes of reactive compounds.

The calculated reactivity has been derived summing up the OH reactivity of NO_x , O_3 , CO, SO_2 , as well as 56 more individual compounds analysed with online GC/MS, off-line sampling in canisters and on DNPH cartridges followed by analysis with GC-FID and LC/UV, respectively. All the reaction rate coefficients for their reactions with OH

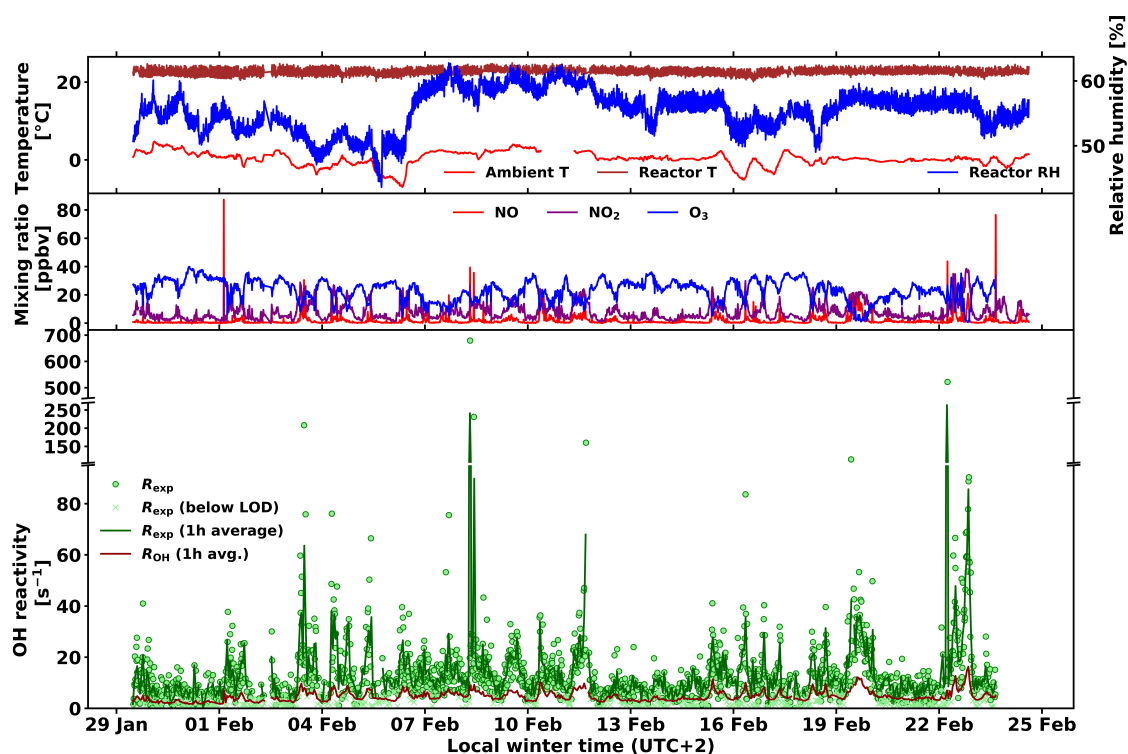


Figure 4.12: Temperature and pressure (top panel), NO, NO₂, and O₃ (middle panel), and total OH reactivity (bottom panel) measured (R_{exp} in green) with its 1-hour average (solid green line) as well as 1-hour averages of calculated OH reactivity from 61 individual species (R_{OH} , solid red line) for the whole measurement period.

are summarised in Table S2 from the Supplementary. The median value of the calculated OH reactivity is 4.0 s^{-1} . The measured total OH reactivity is generally higher than the calculated OH reactivity, with a better agreement for low reactivity periods.

NO peaks ($> 30 \text{ ppbv}$) due to truck emissions driving next to our container are reflected in the total OH reactivity measurements by extremely high values, while the calculated peak values are much lower. This could be partly explained by the fact that important co-emitted reactive species were not measured or measured at the tower and not next to the container (such as CO), which does not represent levels from the truck emissions. Most VOCs and OVOCs had a 24-hours sampling periods, which cannot reflect very high peaks in short time periods. Furthermore, two elements contribute to the difficulty of measuring such high OH reactivity at high NO_x: on one hand the catalyst for the zero air might not be removing all NO_x, decreasing C₂ and leading to overestimated reactivity values, and on the other hand the dependence of the NO correction factor on R (decreasing for high reactivity values).

Filtering these reactivity peaks and averaging all the hourly data during the campaign for weekdays and weekend a diurnal pattern on weekdays only (Fig. 4.13). Note that values below detection limit have been replaced by half the detection limit for these averages. These results indicate that the reactivity is mostly driven by traffic emissions (early morning and afternoon rush hour peaks) as has been seen previously in Mexico (Shirley et al., 2006) and Beijing (Williams et al., 2016), for instance. Comparison with vehicle count statistics measured less than 1 km away in the main wind direction for the campaign (except for a short period between 1 February at noon

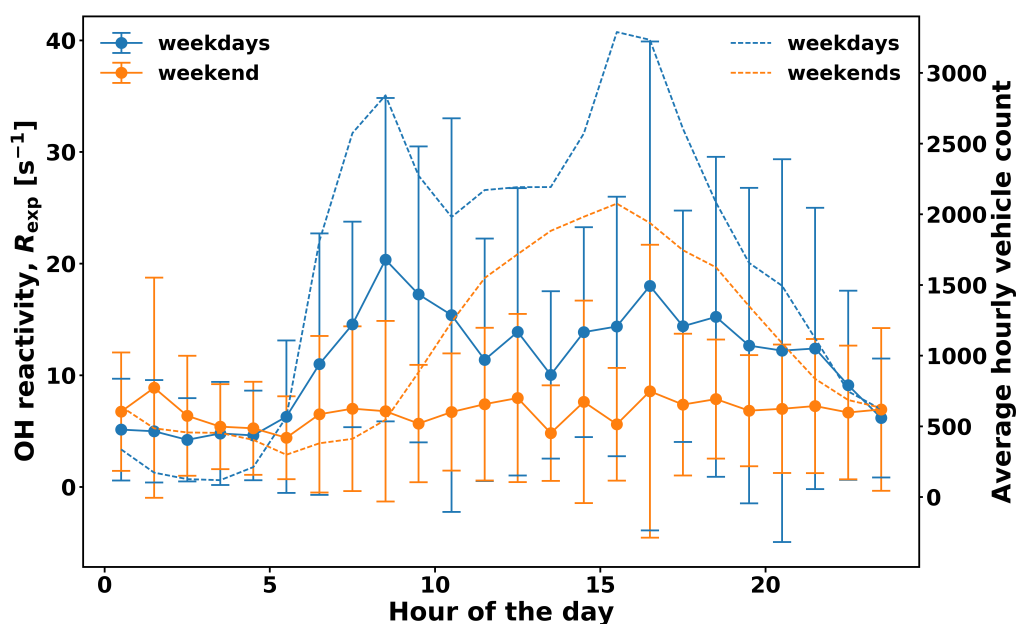


Figure 4.13: Diurnal pattern of measured OH reactivity (left axis) and hourly vehicle count (right axis) for weekdays and weekends.

and 2 February at 3 pm) show comparable trends during the night and in the morning rush hour. The increase of traffic in the afternoon for weekdays and weekends is not captured as clearly by OH reactivity measurement, possibly due to a higher planetary boundary layer, reducing concentration of compounds emitted by traffic.

Finally, the total relative uncertainty is displayed in Fig. 4.14. The main contributions to the uncertainty are due to the correction factors for NO, NO₂ and O₃, while other correction factors and uncertainties contribute only to a small extent to the overall total OH reactivity uncertainty. Low values ($< 20 \text{ s}^{-1}$) are greatly affected by the precision of the measurements, which is the case for most of the ambient measurement values in this study. This is largely due to the scatter of the 16-minutes time resolution data, which can be reduced by 1-hour averaging.

4.4 Conclusions

The CRM system developed at FMI was characterized in the laboratory and deployed in a test campaign next to the SMEAR III semi-urban site in Helsinki during winter months. The correction factors derived were consequently applied and the measured OH reactivity was higher than the OH reactivity derived from the individual measurements of 61 compounds at higher reactivity values. This implementation of the Comparative Reactivity Method delivers reasonable data and the higher measured total OH reactivity values compared to calculated ones can be at least partially explained by local influence (truck emissions) that was not captured fully (in particular for CO that was not measured at the container).

The first deployment close to the semi-urban background site SMEAR III in Helsinki during winter showed that the system was able to capture a traffic-related diurnal

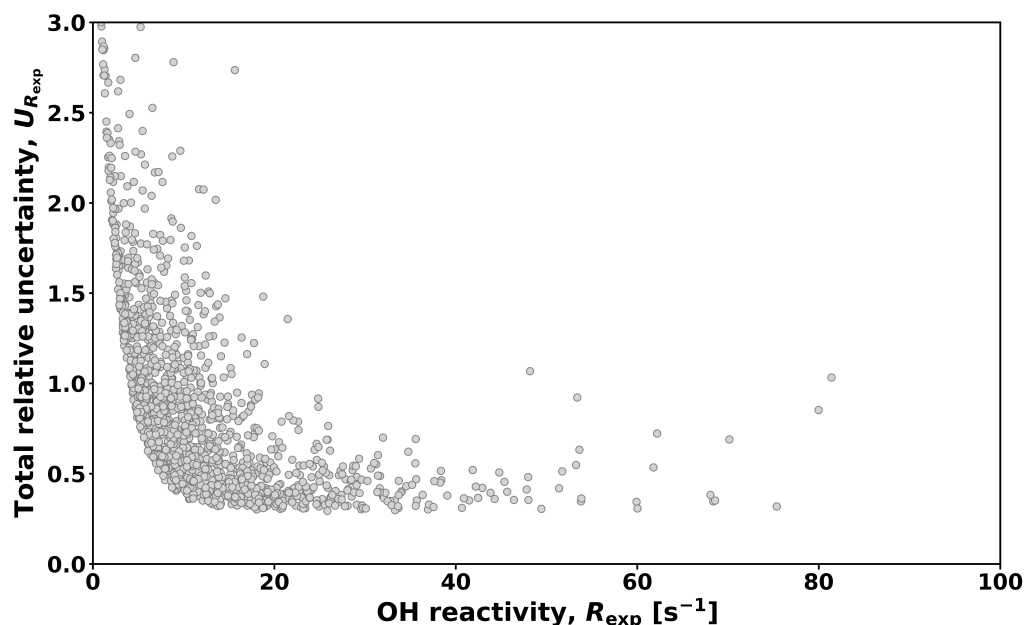


Figure 4.14: Total relative uncertainties for R_{exp} . A few points at extremely high and extremely low reactivity values have been left out.

pattern during weekdays. As the system has been primarily designed for studies in the boreal forest (ambient air and tree emissions), measurement uncertainties will be reduced in these as correction factors for NO and NO₂ can be neglected due to low NO_x concentrations.

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Comparison of OH reactivity measurements in the atmospheric simulation chamber SAPHIR

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Contribution to this publication by Eva Y. Pfannerstill: Conducted measurements and data analysis for the MPIC CRM instrument during the two intercomparison campaigns in 2015 and 2016, wrote parts of the CRM instrument description and contributed to the writing of results and discussion.

Abstract. Hydroxyl (OH) radical reactivity (k_{OH}) has been measured for 18 years with different measurement techniques. In order to compare the performances of instruments deployed in the field, two campaigns were conducted performing experiments in the atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich in October 2015 and April 2016. Chemical conditions were chosen either to be representative of the atmosphere or to test potential limitations of instruments. All types of instruments that are currently used for atmospheric measurements were used in one of the two campaigns. The results of these campaigns demonstrate that OH reactivity can be accurately measured for a wide range of atmospherically relevant chemical conditions (e.g. water vapour, nitrogen oxides, various organic compounds) by all instruments. The precision of the measurements (limit of detection $< 1 \text{ s}^{-1}$ at a time resolution of 30 s to a few minutes) is higher for instruments directly detecting hydroxyl radicals, whereas the indirect comparative reactivity method (CRM) has a higher limit of detection of 2 s^{-1} at a time resolution of 10 to 15 min. The performances of the instruments were systematically tested by stepwise increasing, for example, the concentrations of carbon monoxide (CO), water vapour or nitric oxide (NO). In further experiments, mixtures of organic reactants were injected into the chamber to simulate urban and forested environments. Overall, the results show that the instruments are capable of measuring OH reactivity in the presence of CO, alkanes, alkenes and aromatic compounds. The transmission efficiency in Teflon inlet lines could have introduced systematic errors in measurements for low-volatile organic compounds in some instruments. CRM instruments exhibited a larger scatter in the data compared to the other instruments. The largest differences to reference measurements or to calculated reactivity were observed by CRM instruments in the presence of terpenes and oxygenated organic compounds (mixing ratio of OH reactants were up to 10 ppbv). In some of these experiments, only a small fraction of the reactivity is detected. The accuracy of CRM measurements is most likely limited by the corrections that need to be applied to account for known effects of, for example, deviations from pseudo first-order conditions, nitrogen oxides or water vapour on the measurement. Methods used to derive these corrections vary among the different CRM instruments. Measurements taken with a flow-tube instrument combined with the direct detection of OH by chemical ionisation mass spectrometry (CIMS) show limitations in cases of high reactivity and high NO concentrations but were accurate for low reactivity ($< 15 \text{ s}^{-1}$) and low NO ($< 5 \text{ ppbv}$) conditions.

5.1 Introduction

Most gas species in the atmosphere are transformed by their reaction with the hydroxyl radical (OH). These processes lead to the formation of oxidised, secondary pollutants such as ozone and aerosol. Due to the large number of organic OH reactants (Goldstein and Galbally, 2007), several methods have been developed in order to measure OH reactivity (the inverse OH lifetime). OH reactivity (k_{OH}) is the sum of OH reactant concentrations ($[X]$) weighted by their reaction rate coefficient with OH ($k_{\text{OH}+X}$):

$$k_{\text{OH}} = \sum_i k_{\text{OH}+X_i} [X_i]. \quad (5.1)$$

Predicting trace gas loadings and lifetimes requires a comprehensive understanding of the atmosphere's chemical cycling and oxidative capacity, which is aided by the measurement of total OH reactivity. Measurements can be compared to calculations from OH reactant concentrations in order to quantify unexplained reactivity. In addition, the total loss rate of OH can be calculated if OH concentrations are concurrently measured in order to analyse the OH budget by comparing the total OH loss rate with the sum of OH production rates.

The measurement of OH reactivity has been shown to be extremely useful (Yang et al., 2016). Up to several tens per second unexplained reactivity was identified in biogenic-dominated environments such as in a forest in Michigan (Di Carlo et al., 2004; Hansen et al., 2014), in the Amazonian rainforest (Nölscher et al., 2016) and in a boreal forest in Finland (Nölscher et al., 2012a). The magnitude of missing reactivity appears to be dependent on the biogenic source, time of the day and season (Nölscher et al., 2016; Williams et al., 2016). However, the agreement between measured and calculated reactivity is also a valuable result, because it indicates that all trace gases that are relevant for the photochemistry were measured. This was the case in environments that were influenced by anthropogenic OH reactants as in New York (Ren, 2003) and in the North China Plain (Fuchs et al., 2016), in isoprene-dominated environments during daytime in a Mediterranean forest (Zannoni et al., 2016) and in a chamber study (Nölscher et al., 2014). In addition, the gap between measured and calculated OH reactivity could be closed in some field studies if oxygenated VOCs (volatile organic compounds) derived from model calculation were additionally taken into account (e.g. Chatani et al., 2009; Kaiser et al., 2016; Lou et al., 2010; Whalley et al., 2016). First attempts were also made to measure OH reactivity fluxes (Nölscher et al., 2013).

The application of OH reactivity measurements for the analysis of the OH budget also provided new results. A gap in the understanding of OH recycling processes was found in a field study in Nashville in 1999 (Martinez et al., 2003), in China in 2006 (Hofzumahaus et al., 2009), in Borneo in 2008 (Whalley et al., 2011) and in chamber experiments investigating the oxidation of isoprene by OH (Fuchs et al., 2013). Because of the close connection between oxidation of organic compounds by OH and ozone production, OH reactivity can help to calculate local ozone production rates (Sinha et al., 2012).

Several methods to measure OH reactivity have been developed since the first measurements were made by Penn State University (PSU) (Kovacs and Brune, 2001). The different methods fall into two categories. One method determines the OH reactivity

directly from the time-dependent decay of measured OH that is artificially produced. The other method determines k_{OH} indirectly from the concentration change of a reference species, which competes with atmospheric reactants in their reaction with artificially produced OH.

In the instrument developed by Kovacs and Brune (2001), the decay of OH is measured in a flow tube through which ambient air is drawn by the direct detection of OH using laser-induced fluorescence. OH is continuously produced by water photolysis. The time-resolved OH decay is measured by varying the reaction time using a movable injector to produce OH. A compact aircraft instrument was later developed by PSU and deployed for the first time in 2006 (Mao et al., 2009). Similar instruments were built at Indiana University (Hansen et al., 2014) and at the University of Leeds (Ingham et al., 2009). The latter apparatus was recently replaced by an instrument applying a pump-probe technique (see below).

In an alternative instrument, a flow-tube set-up is combined with a chemical ionisation mass spectrometer (CIMS), which detects sulfuric acid (H_2SO_4) following the chemical conversion of OH to H_2SO_4 (Berresheim et al., 2000; Muller et al., 2018). In this instrument developed by the German Meteorological Service (DWD), OH is produced by water photolysis in the flow tube. The reaction of OH with ambient OH reactants is terminated by chemically removing OH by its reaction with sulfur dioxide, which is injected at two positions within the flow tube, giving one reaction time for the OH decay. The remaining OH concentrations for the two injection positions are measured to calculate the OH reactivity.

Sadanaga et al. (2004) developed an instrument that uses a pump-probe technique, called laser photolysis – laser-induced fluorescence (LP-LIF). OH is produced by ozone photolysis using radiation of short laser pulse at 266 nm at a low repetition rate of 1 to 2 Hz. The OH decay is observed by laser-induced fluorescence with a high time resolution. The pump-probe technique has the advantage that the flow conditions do not need to be exactly known in order to determine a reaction time. This technique is now used by several groups such as Tokyo Metropolitan University (Sadanaga et al., 2004), the University of Leeds (Stone et al., 2016), the University of Lille (Parker et al., 2011) and Forschungszentrum Jülich (FZJ) (Lou et al., 2010). The indirect technique for the measurement of OH reactivity was pioneered by Sinha et al. (2008). The comparative reactivity method (CRM) is based on the detection of pyrrole that reacts with artificially produced OH in clean or ambient air. The pyrrole competes with the ambient OH reactants, so that the pyrrole concentration depends on the ambient OH reactivity. In most CRM instruments, pyrrole is detected by proton transfer reaction mass spectrometry (PTR-MS) but can also be detected by gas chromatography (GC) (Nölscher et al., 2012b). The CRM method is more commonly used than the direct OH measurement techniques because of the commercial availability of PTR-MS instruments. It is applied by the Max Planck Institute Mainz (MPI) (Sinha et al., 2008), IMT Lille Douai, formally called Mines Douai (MDOUAI) (Hansen et al., 2015; Michoud et al., 2015), Laboratoire des Sciences du Climat et de l'Environnement (LSCE) (Zannoni et al., 2015), Indian Institute of Science Education and Research Mohali (Kumar and Sinha, 2014), the Finnish Meteorological Institute (Praplan et al., 2017), Peking University (Yang et al., 2017), the University of Leicester and University of California, Irvine (Kim et al., 2016).

Only two side-by-side comparisons have been performed between two CRM instruments in a remote environment (Zannoni et al., 2015) and between a CRM and a

pump-probe instrument in an urban environment (Hansen et al., 2015). Both comparisons show generally good agreement between measurements within 20 to 50 %.

In 2014, a workshop was held at the Max Planck Institute for Chemistry in Mainz in order to assess the current status and future of OH reactivity measurements. At the workshop, a comparison campaign was suggested to investigate the performance of instruments under different atmospheric chemical conditions (Williams and Brune, 2015). Large environmental chambers are ideal for this purpose, as they ensure that all instruments sample air with the same chemical composition. In addition, chemical conditions can be systematically varied. This was demonstrated in several comparison exercises in the atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich (e.g. Dorn et al., 2013; Schlosser et al., 2009) as well as in the EUPHORE chamber (e.g. Pang et al., 2014). Here, we report the results of two k_{OH} comparison campaigns that were conducted in the SAPHIR chamber. The two comparisons were not blind: quick-look data were presented from some groups during the campaigns. After first data submission without the knowledge of the final results from other participants or OH reactant concentrations, data were allowed to be revised. Only final data are presented in this paper, but changes after the first data submission are described.

A large number of OH reactivity instruments applying different techniques were successfully used in these campaigns (CRM instruments of MPI, IMT Lille Douai and LSCE; a flow-tube LIF instrument from PSU; a CIMS instrument from DWD and LP-LIF instruments from Lille, Leeds and FZJ, Table 5.1). The CRM instrument from the Finnish Meteorological Institute was also used in the campaign, but measurements by this instrument failed due to technical problems and no valid data could be acquired.

5.2 Experiments in the SAPHIR chamber

5.2.1 The SAPHIR chamber

The outdoor atmospheric simulation chamber SAPHIR is made of a double-wall Teflon (FEP) film and has a cylindrical shape (5 m diameter, 18 m length). The Teflon chamber is mounted inside a steel frame that is equipped with a shutter system that allows for experiments in the dark or in the presence of sunlight. The space between the inner and outer Teflon film is continuously purged with nitrogen (Linde, purity > 99.9999 %) to prevent contamination from outside. In addition, the pressure inside the chamber is 45 Pa higher than ambient pressure. Small leakages and air sampling by instruments require the air to be replenished to maintain the pressure difference. This leads to a small dilution of trace gases by 3 to 5 % per hour. The dilution can be as high as 60 % per hour if the replenishment flow needs to be high. Ultra-pure air (Linde, purity > 99.9999 %) is used to purge the chamber with a high flow (up to $250 \text{ m}^3 \text{ h}^{-1}$) in order to clean the chamber. The high flow rate is also required to humidify the chamber air with steam from boiling water that is supplied by a Milli-Q water device. Ozone produced by a silent discharge ozoniser can be added to the chamber air. Two fans ensure that the air is well mixed, so that all instruments always sample the same air mass (e.g. Dorn et al., 2013; Schlosser et al., 2009).

Table 5.1: Specification of instrument parameters of OH reactivity instruments in these campaigns.

Instrument	Technique	Time res./ s	1 σ LOD ^y s ⁻¹	1 σ accur. ^a (@ k_{OH})	Flow rate/ L min ⁻¹	[OH]/ 10 ¹⁰ cm ⁻³	Inlet res. time/s	Inlet line	Reference
MDOUAP ^b	CRM ^c	600	1	18 %	0.37 ^d	72 ^{e,f}	5	1/4" PFA	Michoud et al. (2015)
LSCE ^b	CRM ^c	600	1	35 %	0.23 ^d	78 ^{e,f}	6	1/4" PFA	Zannoni et al. (2015)
MPI ^{b,g}	CRM ^c	900	1.6 ^b 1.3 ^g	37 %	0.38	75 ^{e,f}	6	1/4" PFA (heated) ^b 1/2" PFA (heated) ^g	Sinha et al. (2008)
PSU ^b	FT-LIF ⁱ	30	0.5 ^j	23 % (< 2 s ⁻¹) 8 % (10 to 100 s ⁻¹) 7 % (> 100 s ⁻¹)	100	0.5 ^e	1	1" PFA	Kovacs and Brune (2001) Mao et al. (2009)
Lille ^b	LP-LIF ^h	30 to 60	0.4	8 %	9.5	0.6 ^k	4	1/2" PFA	Parker et al. (2011)
Leeds ^b	LP-LIF ^h	100	0.4 to 1.0	6 %	16	3 ^k	2.5	1/2" PFA	Stone et al. (2016)
FZJM ^b	LP-LIF ^h	40 to 160	0.2	10 %	15	0.7 ^k	0.5	10 mm steel (Silconert coating)	Lou et al. (2010)
FZJS ^{b,g}	LP-LIF ^h	60	0.1	10 %	20	0.8 ^k	0.5	10 mm steel (Silconert coating)	Fuchs et al. (2016) Lou et al. (2010)
DWD ^g	FT-CIMS ^l	60 to 300	0.5	1 s ⁻¹ (< 30 s ⁻¹) 2 s ⁻¹ (30 to 40 s ⁻¹)	2280 ^m	0.01 ^e	no additional inlet line		Berresheim et al. (2000)

^a Limit of detection/accuracy as stated by the operator.^b October 2015.^c Comparative reactivity measurement.^d Faster flow of 1 L min⁻¹ in inlet line.^e Produced continuously by water photolysis (185 nm radiation of a Pen-Ray lamp).^f Derived from the difference in the C1 and C2 measurement.^g April 2016.^h Laser flash photolysis and laser-induced fluorescence.ⁱ Flow-tube and laser-induced fluorescence.^j Limit of detection without the dilution, which amplifies this number by a factor of 5.^k Peak value produced by flash ozone photolysis (266 nm of a quadrupled Nd:YAG laser).^l Flow-tube and chemical-ionisation mass-spectrometry.^m Sampling rate from the chamber.

Table 5.2: Specification of instruments measuring OH reactant concentrations in the two campaigns.

OH reactant	Measurement	1 σ accuracy	1 σ precision	Reaction rate constant
CO	Piccarro CRDS, GC (RGA)	15 ppbv, 8 %	5 ppbv	IUPAC
NO	chemiluminescence	5 %	4 pptv	IUPAC
NO ₂	chemiluminescence	5 %	4 pptv	IUPAC
O ₃	UV photometer	5 %	1 ppbv	IUPAC
CH ₄	Piccarro CRDS	1 ppbv	1 ppbv	IUPAC
<i>n</i> -pentane	GC-FID	13 %	20 pptv	IUPAC
1-pentene	GC-FID, PTR-TOF-MS	13, 4 %	20, 19 pptv	Atkinson (1997); MCM
toluene	GC-FID, PTR-TOF-MS	13, 7 %	20, 7 pptv	IUPAC
<i>o</i> -xylene	GC-FID, PTR-TOF-MS	13, 2 %	10, 3 pptv	Mehta et al. (2009)
isoprene	GC-FID, PTR-TOF-MS	13, 6 %	20, 33 pptv	IUPAC
MVK	GC-FID	13 %	30 pptv	IUPAC
MACR	GC-FID	13 %	30 pptv	IUPAC
MVK + MACR	PTR-TOF-MS	6 %	22 pptv	
α -pinene	GC-FID	13 %	10 pptv	IUPAC
limonene	GC-FID	13 %	10 pptv	Gill and Hites (2002)
myrcene	GC-FID	13 %	10 pptv	Kim et al. (2011)
β -pinene	GC-FID	13 %	10 pptv	Gill and Hites (2002)
camphene	GC-FID	13 %	10 pptv	Atkinson et al. (1990)
Δ^3 -carene	GC-FID	13 %	10 pptv	Atkinson et al. (1986)
β -ocimene	GC-FID	13 %	10 pptv	Kim et al. (2011)
β -phellandrene	GC-FID	13 %	10 pptv	IUPAC
sum monoterpenes	PTR-TOF-MS	4 %	5 pptv	
β -caryophyllene	GC-FID, PTR-TOF-MS	13, 6 % ^a	10, 15 pptv	IUPAC
HCHO	Hantzsch monitor	5 %	18 pptv	IUPAC
CH ₃ CHO	GC-FID, PTR-TOF-MS	13, 6 % ^b	200, 40 pptv	IUPAC

^a PTR-TOF-MS measurements 40 % lower than GC-FID in 2016.^b PTR-TOF-MS measurements 50 % higher than GC-FID in 2016.

The use of high-purity air ensures that there are no measurable gaseous OH reactants present in the chamber after the purging procedure. Small amounts of mostly unidentified organic compounds and nitrogen oxide compounds like HONO (< 100 pptv) can be observed in some cases during the humidification. The total OH reactivity measured by the OH reactivity instrument that is permanently installed at the chamber shows that the reactivity is typically well below 1 s⁻¹ after humidification. In fact, instruments measured on average no significant OH reactivity in these campaigns in the clean chamber (see below).

If the chamber is exposed to sunlight, well-characterised sources for HONO, formaldehyde and acetaldehyde lead to an increase in OH reactivity (production rates are typically 200 pptv h⁻¹). Photolysis of HONO (Rohrer et al., 2005) is also the dominant source of OH and nitrogen oxides in the chamber. The source strength depends on the relative humidity, temperature and radiation. The overall increase in OH reactivity is of the order of 0.2 s⁻¹ per hour, and is much smaller than the reactivity from added OH reactants in these campaigns.

OH reactants were added either from gas mixtures via calibrated flow controllers or as liquids that were injected into a heated inlet line with a syringe. The vapours were transported by a flow of synthetic air into the chamber. In addition, a recently built plant chamber allows for the quantitative transfer of mixtures of biogenic organic compounds from up to six trees into the SAPHIR chamber (Hohaus et al., 2016). Environmental parameters in the plant chamber can be fully controlled.

5.2.2 Calculated OH reactivity

A number of instruments for the detection of OH reactants took measurements concurrently with the OH reactivity instruments (Table 5.2). Nitrogen oxides (NO and NO₂) were detected by a chemiluminescence instrument (Eco Physics TR 780). CO was measured using a Picarro cavity ring-down instrument (Picarro G2301) and by gas chromatography (GC, Trace Analytical RGA 3). Both measurements agreed within 5 %. Data from the cavity ring-down instrument were used here for calculations of the OH reactivity due to its higher accuracy. This instrument also measured methane and water vapour concentrations. Organic compounds were detected by PTR-TOF-MS (proton transfer reaction time-of-flight mass spectrometry, Ionicon) and GC (Agilent 7890N). Measurements agreed for those species that could be detected by both instruments, such as isoprene better than 20 % with some larger discrepancies for acetaldehyde and β -caryophyllene in the second set of experiments in 2016 (Table 5.2). Differences between measurements need to be regarded as additional uncertainties in the calculation of OH reactivity.

PTR-TOF-MS measures the sum of methyl vinyl ketone (MVK) and methacrolein (MACR) and the sum of monoterpenes. In order to calculate OH reactivity, PTR-TOF-MS measurements were used taking the relative distribution of MVK and MACR and monoterpenes as measured by GC, because PTR-TOF-MS has a high time resolution. Formaldehyde was additionally measured by a Hantzsch monitor (Aero Laser AL 4001). All reaction rate constants used for the calculation of OH reactivity are taken from IUPAC (International Union of Pure and Applied Chemistry) recommendations (IUPAC, 2018) if not stated differently in Table 5.2. Temperature and pressure are assumed to be the same in the instruments and the SAPHIR chamber. This approach is applicable as indicated by temperature and pressure measurements in the instruments. The overall 1 σ uncertainty of the calculated OH reactivity is around 20 % in most experiments but can be higher (e.g. 40 % in case of the experiment with sesquiterpenes) depending on the uncertainty in the OH reactant measurements, the agreement between simultaneous measurements by different instruments and the uncertainty in reaction rate constants.

5.2.3 Experiments performed in 2015

Two campaigns were conducted for this comparison. The first one took place in October 2015. All instruments listed in Table 5.1 were used in this campaign with the exception of the CIMS instrument.

In the experiments, the chamber was flushed with high-purity air before each experiment, until trace gas concentrations were below the limit of detection of instruments (Table 5.2). The chamber air was humidified to approximately 75 % relative humidity (RH) at the beginning of each experiment, except for the experiment on 6 October 2015, when the experiment was started with 25 % RH and the humidity was increased to 90 % RH in three steps. Relative humidity typically dropped to 40 to 50 % during the experiment due to temperature changes and dilution. Ozone was also added at the beginning of the experiments to allow OH production in the LP-LIF instruments if ozone was not expected to affect the chemical composition of the chamber air (e.g. by ozonolysis reaction or by the conversion of NO to NO₂). Initial ozone mixing ratios were typically between 50 and 80 ppbv.

Table 5.3: Conditions during the experiments. Maximum concentrations during the experiments are given. Maximum values for OH reactivity are approximate values that do not refer to a specific instrument. Photolysis reactions were possible if the chamber roof was open (mostly only part of the experiment). A mixture of aromatic compounds, alkenes and NO_x species is summarised as “urban” conditions.

Date	Added OH reactants	$k_{\text{OH}}/\text{s}^{-1}$	CO/ ppbv	$\Sigma\text{VOC}/\text{ppbv}$	NO ₂ / ppbv	NO/ ppbv	O ₃ / ppbv	$j_{\text{NO}_2}/10^{-3}\text{s}^{-1}$
5 October 2015	CO	200	33500	< LOD	< 0.01	< 0.1	85	dark
6 October 2015	CO, CH ₄ , NO ₂	25	3300	11 000	12	< 0.03	85	dark
7 October 2015	CO, CH ₄ , NO	60	4100	13 500	< 1	120	< LOD	dark
9 October 2015	monoterpenes ^a	25	< LOD	11	< 0.01	< 0.05	295 ^b	dark
11 October 2015	CO, isoprene MVK ^c , MACR ^c	35	1650 2.3	9 3.2	0.06	0.7	50	3.0
12 October 2015	urban ^d , NO ₂	40	< LOD	50	55	2.8	50	3.2
13 October 2015	CO, urban ^d , NO ₂	35	900	48	12.5	1.2	50	1.6
14 October 2015	monoterpenes ^e	15	< LOD	6	< 0.08	< 0.01	65 ^b	dark
15 October 2015	CO, TME ^f , NO	100	5400	40	15	30	45	dark
16 October 2015	β -caryophyllene, CH ₃ CHO, MVK, MACR	30	< LOD	1.5 1.9 11	< 0.04	< 0.04	43 ^b	dark
7 April 2016	CO	60	16 000	< LOD	< 0.05	< 0.01	80	dark
8 April 2016	<i>n</i> -pentane, NO	35	< LOD	60	< LOD	15	< LOD	dark
9 April 2016	isoprene, NO ₂ MVK, MACR	45	< LOD	15 7	8	0.5	115	4.5
11 April 2016	urban ^d , NO ₂ CH ₃ CHO	50	< LOD	96 45	28	6	110	4.5
12 April 2016	urban ^d , NO CH ₃ CHO	60	< LOD	94 67	< LOD	32	< LOD	dark
13 April 2016	monoterpenes ^a	40	< LOD	19	< 0.05	< 0.02	185 ^b	dark
14 April 2016	monoterpenes ^a , NO ₂	40	< LOD	16	29	2.8	70	4.3
15 April 2016	CO, β -caryophyllene	65	11 500	4	< 0.5	< 0.04	45 ^b	dark

^a α -pinene, limonene, myrcene (liquid volume ratio 0.68 : 0.11 : 0.21).

^b Added at later times for ozonolysis.

^c Photochemically formed.

^d *o*-xylene, toluene, 1-pentene (liquid volume ratio 1 : 1 : 1).

^e Identified compounds of plant emissions: α -pinene, β -pinene, limonene, myrcene, camphene, Δ^3 -carene, ocimene, β -phellandrene.

^f 2,3-dimethyl-2-butene.

OH reactivity was typically increased in several steps to maximum values of approximately 50 s⁻¹ at the end of the experiment (maximum 150 s⁻¹). The time between two injections of trace gases was approximately 45 min. In addition, chemical conditions were changed during the course of some experiments, such as opening or closing the chamber roof or adding nitrogen oxides or water vapour. Chemical conditions in the different experiments are summarised in Table 5.3.

Some experiments aimed to primarily test the instruments' performances: linearity with CO (5 October 2015), the influence of humidity (6 October 2015) and the presence of NO (7 October 2015). The last test was repeated on 15 October. However, due to an operational error, ozone was added at the beginning of the experiment, so that a mixture of NO and NO₂ was present. In order to reduce the ozone concentration, 2,3-dimethyl-2-butene (TME), which reacts rapidly with ozone, was injected twice.

The other experiments focused on the instruments' performances in the presence of specific OH reactants and atmospheric mixtures of reactants. In part of these experiments, OH reactants were also oxidised by either OH or ozone. In five experiments,

biogenic reactants were present: isoprene (11 October 2015), isoprene oxidation products MVK and MACR (16 October 2015), a mix of monoterpenes (α -pinene, limonene, myrcene, 9 October 2015) and a sesquiterpene (β -caryophyllene, 16 October 2015). In another experiment with biogenic reactants, emissions from plants (3 pine and 3 spruce) were transferred into the chamber at a flow rate of $11 \text{ m}^3 \text{ h}^{-1}$. In two experiments, an urban environment was simulated by a mixture of 1-pentene, *o*-xylene and toluene together with NO_2 (12 and 13 October 2015). On 16 October 2015, acetaldehyde was injected.

5.2.4 Experiments performed in 2016

In the second campaign in 2016, only three instruments measured OH reactivity: a CRM instrument (MPI), a LP-LIF instrument (FZJS) and the CIMS instrument from DWD. The CRM and LP-LIF instruments were the same as in the 2015 campaign. The CIMS instrument sampled air with a high flow rate (2280 L min^{-1}), requiring the chamber to be operated with a high replenishment flow. As a consequence, all trace gases were diluted at a high rate of approximately 60 % per hour. Oxidation products could not accumulate. Accordingly, the experimental procedure was different in these experiments compared to those in 2015: humidification was done two to four times over the course of an experiment in order to maintain a sufficiently high water vapour concentration for the production of OH in the LP-LIF and CIMS instruments (typical range of relative humidity between 25 and 80 %). If ozone was present in the experiment, ozone was also injected several times. Initial ozone concentrations were around 100 ppbv and dropped to 20 ppbv before re-injection. Similar chemical conditions as in the first campaign were tested in order to achieve comparable results. Tests were done with single, anthropogenic OH reactants (CO, pentane) in the presence (8 April 2016) and in the absence (7 and 15 April 2016) of NO, with biogenic reactants (isoprene, MVK, MACR on 9 April 2016, a monoterpene mixture on 13 and 14 April 2016, β -caryophyllene on 15 April 2016) and with a mixture of anthropogenic reactants (11 and 12 April 2016). The same monoterpene and urban reactant mixtures were used as in the experiments in 2015 and in 2016.

5.2.5 Data coverage

The CRM instrument from the Finnish Meteorological Institute (FMI) was used in the first campaign, but no valid measurements could be acquired due to technical problems of this instrument. Data were submitted for all other instruments for nearly all experiments and are included in the comparison. A leak in the OH injection system of the MDOUAI CRM instrument was found after the third experiments and this leak possibly led to systematic errors in the measurements in this experiment. Data from the experiment on 7 October 2015 were therefore rejected for this instrument. The sampling system of the CRM instrument from LSCE was changed on the second day of the campaign (6 October 2015). Measurements from this experiment were rejected. On 12 October 2015, the flow-tube instrument from PSU did not take measurements, except for the last 2 h due to technical problems. All other instruments took measurements at all times during the campaign.

5.2.6 Procedure of data comparison

The measurement comparison was not strictly blind, but some rules were applied to which all participants had agreed prior to the campaign. The general outline of the campaign was as follows:

- ◆ Before the official campaign started, a test experiment with CO was performed in the SAPHIR chamber. During this experiment, the participants were informed about the added CO concentrations in order to test the functionality of their instruments (4 October 2015, not included in the comparison, and 7 April 2016).
- ◆ During the campaign, participants were informed about the types of trace gases which were planned to be added to the chamber air before the experiments. Concentrations of reactants, however, were not disclosed to the participants.
- ◆ During the campaign, participants had the opportunity to present quick-look data of measured values at daily meetings, but data were not exchanged or distributed.
- ◆ After the campaign, all participants independently submitted their evaluated data to a neutral person at Forschungszentrum Jülich who was not involved in reactivity measurements. Only after all data were received, the measured trace gas concentrations and the k_{OH} data on all participants were made available.
- ◆ After data disclosure, some participants applied corrections to their data and submitted a revised data set together with an explanation for the correction.
- ◆ The comparison in this paper is based on the final data versions.

Changes of data that were made as a result of the comparison are described in the next section for each instrument.

5.3 Instruments for the detection of OH reactivity

5.3.1 Comparative reactivity method (CRM)

The comparative reactivity method (CRM) is an indirect method for the measurement of OH reactivity developed by Sinha et al. (2008). The measurement principle relies on the competition of the reaction of OH with either a known pyrrole concentration or ambient OH reactants. Pyrrole acts as a reference species that is typically not present in ambient air. A small flow of humidified, ultra-pure nitrogen (flow rate approximately $240 \text{ cm}^3 \text{ min}^{-1}$) passes over a Pen-Ray lamp, leading to formation of OH by water photolysis at 185 nm with concentrations of approximately 1 to $3 \times 10^{12} \text{ cm}^{-3}$ (Table 5.1). Water photolysis, however, not only produces OH but also HO_2 radicals. The higher reactivity of OH compared to HO_2 , also towards surfaces, may lead to HO_2 concentrations exceeding the concentration of OH in the reactor. Ambient OH reactants and/or pyrrole react with OH in a reaction volume (94 cm^3) made of glass, with the inner surface covered by Teflon. The instrument is alternately switched between two measurement modes: the small flow of pyrrole (approx. 2 to $3 \text{ cm}^3 \text{ min}^{-1}$) is mixed into a flow of purified air (C2-mode) (approximately $300 \text{ cm}^3 \text{ min}^{-1}$) or into a flow of ambient air (air sampled from the chamber in these experiments) (C3-mode). As OH exclusively reacts with pyrrole in the C2-mode, maximum reduction of the pyrrole concentration is achieved, whereas the pyrrole concentration is higher in the C3-mode, when ambient OH reactants are also present.

Table 5.4: Correction applied to the raw data. Some corrections are non-linear and depend on several parameters (such as the pyrrole and OH concentrations). Values are given for typical atmospheric conditions. The instrument zero for the MDOUI CRM was due to a contamination in the inlet system that was only present in this campaign. Corrections due to deviations from a pseudo first-order reaction assumption depend on the actual OH reactivity value and specific VOC (see text for details). Typical numbers are given for 10 and 60 s⁻¹. Interferences are present from NO, NO₂ and O₃ in some instruments. The correction often depends on the concentrations of the interfering species in a non-linear way. Therefore, only typical values can be given here.

Instrument	Instrument zero ^a / s ⁻¹	Humidity ^a	Deviation from pseudo first-order ^a s ⁻¹ (@ k _{OH})	s ⁻¹ / 10 ppbv NO ^a	s ⁻¹ / 10 ppbv NO ₂ ^a	Dilution factor ^b	Other
MDOUI	-15 ^c	< 1 s ⁻¹	-0.5 (@ 10 s ⁻¹) -3 (@ 60 s ⁻¹)	10	3	1.32	
LSCE	0	< 1 s ⁻¹	-1.6 (@ 10 s ⁻¹) -9.6 (@ 60 s ⁻¹)	17.5	1.9	1.45	
MPI	0	< 1 s ^{-1,d}	-2 to -2.5 (@ 10 s ⁻¹) -12 to -14 (@ 60 s ⁻¹)	20	1.6	1.3 to 1.9	O ₃ interference 6 to 8 s ^{-1,a,e} (@ 50 ppbv O ₃)
PSU	-3.4 ± 0.3	0	0	3 ^f	0	5 ^g	
Lille	-4.1 ± 0.4	0	0	0 ^h	0	0, < 1.7 ⁱ	non-linearity -30 to -35 % ^{b,j} ~ -2.5 s ^{-1,a,j}
Leeds	-2.3 ± 0.4	0	0	0	0	1.07 ^k	
FZJM	-2.7 ± 0.2	0	0	0 ^h	0	1.01 ^k , < 3 ⁱ	
FZJS	-1.3 ± 0.2	0	0	0 ^h	0	1.01 ^k , < 7 ⁱ	
DWD	-8.3 ± 0.2	0	0	> 8	0	0	NO contamination ^l

- ^a Absolute change.
^b Relative change.
^c Determined from periods of experiments without reactants, contamination in the inlet line only in this campaign.
^d Up to 4 s⁻¹ during fast humidity changes in 2016.
^e Absolute change due to recycling of OH by ozone.
^f Correction of the decay (Shirley et al., 2006).
^g Only applied in this campaign to reduce sampling flow rate from the chamber.
^h Bi-exponential fit for NO > 20 ppbv – only applied on 7 October (Lille, FZJS, FZJM) and 15 October 2015 (FZJS, FZJM).
ⁱ Only applied for dilution for high reactivity (Lille: > 150 s⁻¹, FZJS/FZJM: variable dilution for > 60 s⁻¹) on 5 October 2015.
^j Deviations from single-exponential OH decay, likely due to misaligned photolysis beam in this campaign.
^k Correction for added flow with O₃, when no O₃ was present in the experiment.
^l Presence of 0.14 ppbv NO contamination within the instrument corrected for k_{OH} > 2.5 s⁻¹.

In order to calculate the OH reactivity, the initial pyrrole concentration needs to be known (typically 1 to $2 \times 10^{12} \text{ cm}^{-3}$). Because a small fraction of the radiation of the Pen-Ray lamp enters the reaction volume, a small fraction of the pyrrole is photolysed (typically less than 10%). Therefore, the pyrrole concentration is measured when zero air is sampled and when the light of the Pen-Ray lamp is turned on (C1-mode). This is typically done once a day.

The design of the reaction volume is identical for all instruments, because they were all manufactured by the Max Planck Institute for Chemistry in Mainz. Three CRM instruments are included in this comparison, by MPI, IMT Lille Douai (MDOUAI) and LSCE. The instruments differ mainly in the exact operational conditions such as flow rate, pyrrole and OH concentration and the inlet lines (Table 5.1). The transformation of raw data into k_{OH} values requires corrections (Michoud et al., 2015) that have been characterised for each CRM instrument (Table 5.4). These corrections, described below, can significantly differ between instruments due to the different operating conditions.

The pyrrole concentration is monitored by proton transfer reaction mass spectrometry (PTR-MS) in nearly all instruments but can also be detected by GC (Nölscher et al., 2012b). This is done for the instrument from the Finnish Meteorological Institute. A number of corrections need to be applied to the signals measured in the different modes due to a variety of factors (Michoud et al., 2015):

- ◆ The OH production rate in the two measurement modes can be different if the water vapour concentration is not the same in both modes.
- ◆ OH can be significantly reformed by the reaction of HO_2 that is present at high concentrations in the reactor with ambient NO.
- ◆ The reaction deviates from pseudo first-order conditions.
- ◆ Ambient OH reactant concentrations are diluted due to the additional nitrogen flow. The dilution factor is calculated from measured flow rates.

Corrections are usually determined from instrumental characterisation in the laboratory and in the field, with the assumption that they are representative of ambient air measurements. Typical values of corrections are listed in Table 5.4.

All groups operating a CRM used empirical functions to correct for deviations from the pseudo first-order decay for the final data evaluation (Michoud et al., 2015). The exact value, however, depends on the chemical composition of OH reactants (see below). Different representative mixtures are taken to characterise of this correction for the various CRM instruments and operating conditions are optimised to reduce the correction dependence on the chemical composition. The error associated to this correction can then be factored into the measurement uncertainty (Michoud et al., 2015).

Additional instrument-specific corrections are described in the following section.

MPI CRM instrument

The correction of measurements taken with the CRM by MPI for deviations from a pseudo first reaction uses results from numerical simulations. However, this can only be applied if the relative importance of the most abundant reactive compounds in the sampled air is known (Sinha et al., 2008). The model correction was not applicable in this comparison, because no data on the concentration ratios of the main OH reactants were known in contrast to typical situations in field campaigns. In this campaign, the empirical correction procedure was also chosen as an alternative

correction procedure that was shown to be advantageous by Michoud et al. (2015). Tests with isoprene, methanol, ethane, propane, propene and toluene were done to determine the correction factor.

In addition to the corrections applied by all groups operating a CRM instrument, measurements by the MPI CRM were corrected for the presence of ambient ozone. The necessity of this correction was recognised after the first comparison of results from the 2015 campaign. This correction was not applied in the first version of submitted data. The procedure to correct data was then determined in laboratory characterisation experiments. The correction was applied to data from the 2016 campaign from the beginning.

OH is reformed in the reaction of HO_2 with O_3 in the reaction volume of the CRM, where O_3 is present in sampled ambient air but is also produced in the photolysis of oxygen by the 185 nm radiation of the Pen-Ray lamp. The assumption is that the effect of OH reformation on the measurement is typically insensitive to the exact concentration of ambient ozone, which is not present in all modes of the measurement cycle. If this assumption is not true, the OH reactivity is underestimated depending on the ambient ozone concentration. This was observed for the MPI CRM instrument in this campaign. Therefore, measurements were corrected by an empirical function derived from laboratory measurements after the first data submission. Although the ozone concentration in the reaction volume was similar to the concentration in the other two CRM instruments, no ozone dependence was seen for the MDOUAI and LSCE instruments. The exact reason is not clear but might be related to different HO_2 concentrations in the instruments. The insensitivity of other CRM instruments to the ozone interference indicates that operating conditions exist for which the interference is negligible. Further investigations should be performed to characterise these conditions.

In addition to the ozone correction, errors in the calculation of the dilution factor and the calibration of the pyrrole sensitivity were noticed for the MPI CRM instrument after the first data submission in 2015. Although corrections were made after knowledge of OH reactant concentrations and measurements of other instruments, unreasonable data already suggested the need for these corrections before. Also, the correction for the presence of NO_2 was again characterised for conditions when also O_3 was present and slightly changed in the final data. Furthermore, the correction due to the deviations from pseudo first-order decay were changed in the final data because a reanalysis of the concentration of test compounds used for the characterisation revealed higher impurities than certified by the manufacturer.

The total increase in OH reactivity measurements between the first and final submission was typically within the range of a factor of 1.5 to 3 but was a factor of 4 to 5 for low OH reactivities around 10 s^{-1} in the presence of ozone mixing ratios of 40 ppbv.

MDOUAI CRM instrument

The performance of the MDOUAI CRM instrument was worse in this campaign than previously observed due to additional sources of noise from the PTR-MS instrument and the inlet system. It was recognised that the pump (Teflon surfaces) in the sampling line upstream of the CRM instrument, which is necessary to avoid a pressure drop between ambient pressure and the CRM reactor (Michoud et al., 2015), released contaminants which caused an additional OH reactivity of 15 s^{-1} on average during measurements. This instrument zero was subtracted from all measurements.

The value was determined daily in each experiment between the humidification of chamber air and the injection of OH reactants. Deviations from pseudo first-order behaviour of the kinetics were characterised by tests with isoprene, propene, ethene, ethane and propane. Data were not revised after the first data submission.

LSCE CRM instrument

At the beginning of the campaign, a pressure change was observed for the two measurement modes of the CRM instrument at the exit of the reactor that could affect the measurements. The total flow rate in the sampling line was increased and only a small part was sampled into the reaction volume in order to avoid a change in pressure. Therefore, the sampling flow was not directly injected into the CRM reactor, but it was first pulled through a pump with Teflon surfaces. The flow was restricted by a valve (Teflon surfaces) before the air entered the reactor. This sampling flow system was used for the first time during this campaign and may have reduced the performance of the instrument.

Corrections were applied to the raw data as described by Michoud et al. (2015) to obtain the OH reactivity values. Specifically, the correction for the deviation from the pseudo first-order conditions was determined from laboratory and field tests using certified concentration of gas standards containing propane and isoprene. The same procedure was applied in a previous field campaign in an isoprene-dominated environment (Zannoni et al., 2016). Previous field deployments of the same instrument were conducted in environments with low NO_x concentrations, for which a correction for OH recycling by NO was not needed. For this reason, a correction for high NO_x concentrations was determined in laboratory tests after the campaign in SAPHIR and data from the experiments from LSCE were revised after the first submission for experiments, when NO_x was injected.

Instrument operators decided to use the part of the experiments before OH reactants were added to subtract a background signal, when positive, non-zero values were on average measured (5, 7, 9 and 16 October 2015) in their first data evaluation. However, this correction was not applied in the final data set, because it was agreed not to use knowledge of the chemical conditions for the data evaluation if it is not required.

Changes in the revised OH reactivity measurements were smaller than $\pm 20\%$ except for measurements at high NO mixing ratios on 7 October 2015, when changes were up to 80 s^{-1} as no correction for the NO interference was applied in the first submitted data.

5.3.2 Direct OH loss rate measurement by laser-photolysis – laser-induced fluorescence (LP–LIF)

All other instruments measured the decay of OH in the presence of ambient OH reactants in a flow tube. In most of the instruments, OH radicals are detected by LIF (Heard and Pilling, 2003).

All methods measuring the OH decay have a higher time resolution compared to the CRM instruments (Table 5.1), because no time is used up when switching between ambient and purified air. In general, fewer corrections are required to derive the OH reactivity from the measured OH decay.

Four LP–LIF instruments were used in the campaigns: instruments from University of Lille and University of Leeds and two instruments from FZJ, one of which is per-

manently installed at the SAPHIR chamber (FZJS) and the other of which is used for mobile field deployment (FZJM).

In the laser-photolysis instruments, ambient air passes (flow rate 10 to 20 L min⁻¹) through a flow tube. Part or all of the air is drawn into an OH fluorescence detection cell. The exact position and design of the flow tube and the fluorescence cell differ among the instruments. OH is produced by flash photolysis of ozone with subsequent reaction of O(¹D) with water vapour. Radiation is provided by a quadrupled Nd:YAG laser pulse at 266 nm, which is operated at a low repetition rate of 1 to 2 Hz. The OH concentration is measured with a high frequency of 3 to 8.5 kHz, so that the decay of OH can be observed with a high time resolution between two photolysis shots. Tens of consecutive decays are summed up to increase the signal to noise ratio.

The OH radicals decay in a pseudo first-order reaction with ambient OH reactants, so that the time-resolved OH signal can be fitted to a single-exponential function that directly gives the OH reactivity. Differences between the fitting procedures of the instruments are described in the Supplement. The accuracy of the time basis of the OH decay is only determined by the accuracy of the photon-counting electronics.

Measurements need to be corrected for an instrument zero that is subtracted from all measurements. This zero loss rate in the flow tube is due to the wall loss reactions and likely limited by the diffusion of OH. Values are typically of the order of a few s⁻¹ (Table 5.4) and are regularly determined by sampling high-purity zero air.

Conversion of HO₂ to OH in the presence of ambient NO can influence the measurements. As there is no concurrent production of HO₂ in the ozone photolysis, LP-LIF instruments are less affected by this recycling process compared to instruments that use water photolysis for OH production. It is expected that this recycling process only becomes relevant for NO mixing ratios higher than 20 ppbv for typical atmospheric chemical compositions of ambient air (Lou et al., 2010). In this case, the single-exponential decay of OH turns into a bi-exponential decay that can clearly be identified in the summed decays. If a bi-exponential decay is observed, the faster decay time can be attributed to the OH reactivity. The underlying assumption is that the timescale of OH formation is slow compared to the OH loss. This is reasonable for typical atmospheric conditions but may not be applicable in all cases, specifically in artificial air mixtures. In field experiments, bi-exponential behaviour in the OH decay due to OH recycling at high NO concentrations in ambient air measurements has been observed by the FZJS and Lille instruments. A bi-exponential function was applied to measurements in a campaign in China for the FZJS instrument (Lou et al., 2010). Measurements of the Lille instrument that showed bi-exponential behaviour during a campaign on the campus of the University of Lille were evaluated by applying a single-exponential function. Measurements were evaluated by only using the first part of the decay curve that contained information on the faster decay (Hansen et al., 2015). No significant difference between this procedure and the results from a bi-exponential fit was found. The fitting of the data using a single- or bi-exponentially decay function is discussed later in the paper, as differences were observed in the returned value of the OH reactivity in this campaign at high NO_x (> 20 ppbv) depending on the type of fit used.

In the normal operational procedure, no dilution or only a small amount needs to be taken into account for most of the instruments. If there is insufficient ambient ozone to generate a measurable OH signal, then an addition of O₃-containing flow needs

to be added to the flow tube and a small dilution correction needs to be made. This was required in experiments without the presence of ozone in the chamber air.

The number of data points on the decay curve that are above the noise level decreases with increasing OH reactivity, so that the accuracy and precision of the measurements start to decrease for exceptionally high OH reactivity values (for example higher than 60 s^{-1} for the FZJ LP-LIF instrument). In addition, initial inhomogeneities in the OH distribution in the flow tube due to inhomogeneities of the laser photolysis beam can impact the shape of the observed OH decay curve for these high reactivity values. For this reason, an additional dilution flow can be applied in order to reduce the OH reactant concentrations and improve the data quality. This was done in some instruments (FZJ, Lille) in this campaign, when the measured reactivity exceeded a threshold (e.g. $> 150\text{ s}^{-1}$ for the Lille instrument) but is not required as indicated by measurements by the Leeds LP-LIF instrument.

Imperfect alignment of the photolysis laser can enhance the inhomogeneities in the initial OH distribution, so that deviations from a single-exponential OH decay can also occur at low reactivity values. This was observed in this campaign in the Lille and Leeds LP-LIF instruments but recognised only at the end of (Lille) or after (Leeds) the campaign. As a consequence, the evaluation procedures were changed for measurements in this campaign in order to account for this effect.

Data from FZJS and FZJM instruments were not revised after the first data submission and no instrument-specific description is required here. The Lille and Leeds instruments required a campaign-specific data evaluation that was applied before (Lille) or after (Leeds) the first data submission.

Lille LP-LIF instrument

Quick-look data presented from the LP-LIF instrument from Lille systematically deviated from measurements of the other instruments. The overestimation of approximately 30 % was confirmed by determining the reaction rate constant of the reaction between CO and OH in test experiments, in which a mixture of CO in synthetic air was sampled. This overestimation was due to two reasons: (1) misalignment of the photolysis laser leading to deviations from single-exponential behaviour of the OH decay curve, likely due to an inhomogeneous initial OH concentration (see above); (2) the procedure of analysing the decay by adapting the length of the decay curve used for the fit. The length is limited to 15 times the first estimate of the inverse reactivity (Hansen et al., 2015) in order to avoid noise from the background signal over longer periods of time. As a consequence, the fitted zero decay time appeared to change if the length of the curve used for the fit was shortened for zero-air measurements like done for the high reactivity values. This was then used to account for the deviations in the reactivity measurements by determining an artificial zero decay time as a function of the fit length. In the final data, this zero decay time, which depends on the fit length and therefore reactivity value, was subtracted from the measurements (Fig. S1 in the Supplement). With this method, correct reactivity values could be calculated for the laboratory test experiments with CO. The drawback is that the accuracy is lower for high reactivity values due to the decreasing number of points used for the fit.

This correction would not be needed for a good alignment of the photolysis laser. It is therefore only needed for the data evaluation of this campaign but could be used to deal with similar alignment problems in the future.

Leeds LP-LIF instrument

Similar behaviour of the decay curves to that observed for the Lille LP-LIF instrument was recognised for the Leeds LP-LIF instrument after the campaign. In the decay, a fast component was followed by a slower component rather than single-exponential behaviour. This behaviour was also apparent during the zero decay measurements conducted with zero air for this campaign. As a consequence, the fit of the single-exponential function was started after the fast section of the decay curve for the data evaluation (fit range between 150 and 400 ms) for low reactivity values ($k_{\text{OH}} < 10 \text{ s}^{-1}$). An accurate determination of the OH reactivity was more difficult for high reactivity values ($k_{\text{OH}} > 10 \text{ s}^{-1}$), when values became similar to the fast component of the decay. A single-exponential function between 100 and 200 ms was fitted to the measured decay curve in this case.

Similar to the procedure that was applied to the data from the Lille LP-LIF instrument, zero-air measurements were evaluated using the same fit ranges as for evaluating low and high reactivity values. A decay time of $(2.3 \pm 0.4) \text{ s}^{-1}$ was obtained for the low reactivity case. This is close to the real loss rate of OH in the instrument without OH reactants (instrument zero). A higher value of $(4.8 \pm 0.6) \text{ s}^{-1}$ was determined if the fit range was shifted to an earlier start as it is for evaluating decays for high reactivity values. These two values were subtracted as instrument zeros when either one of the fit ranges were used. The higher value acts as a correction for the overlap of the faster instrumental component and the OH decay due to chemical reactions. For decays taken on the 7 and 15 October 2015 when NO was present, a fit range between 105 and 150 ms was chosen, giving an instrument zero of $(5.1 \pm 1.1) \text{ s}^{-1}$.

The difference between the revised data, when this evaluation scheme was applied, and the initially submitted data is mainly due to the higher instrument zero that was subtracted for $k_{\text{OH}} > 10 \text{ s}^{-1}$, so that these values are 2.5 s^{-1} lower than before. Deviations of the OH decay from single-exponential behaviour for conditions without OH recycling in the instrument were not observed in other field campaigns in the past. This correction is specific for the data from this campaign.

5.3.3 Direct OH loss rate measurement by flow-tube technique with laser-induced fluorescence (PSU instrument)

The flow-tube LIF instrument from PSU also measures the decay of OH radicals. In contrast to LP-LIF instruments, OH is continuously produced by water photolysis at 185 nm in this instrument using a Pen-Ray lamp with concurrent HO_2 production as in the CRM instruments.

In the PSU instrument, the reaction time is varied by a movable injector, which is used to change the distance between OH injection and the point of OH detection (Kovacs and Brune, 2001; Mao et al., 2009). The reaction time is calculated from the velocity measured with a hot-wire anemometer and the known distance travelled for each position of the injector. Within each scan, more than 100 data points were used to calculate the decay. Finally, during normal operation in the field, the PSU instruments sample ambient air with a high flow rate ($> 100 \text{ L min}^{-1}$). This exceeds the flow rate which can be consumed during operation of the SAPHIR chamber; therefore the PSU instrument had to apply a high dilution flow in this campaign. Only 20 L min^{-1} were sampled from the chamber, to which 80 L min^{-1} of high-purity synthetic air provided by the SAPHIR air supply system was added. The dilution factor was determined

from monitored flow rates and was verified in several tests during the campaign, in which the ratio of flows was varied. Using a dilution flow has two drawbacks. Firstly, the calculated OH reactivity is very sensitive to the exact ambient and dilution flows. Secondly, any error in the instrument zero decay due to wall loss or trace impurities in the dilution air is amplified by the ratio of the dilution flow to the ambient flow, in this case a factor of 5. Thus the typical limit of detection of 0.5 s^{-1} becomes 2.5 s^{-1} . As for the CRM instruments, measurements by the PSU instrument can be affected by OH recycling from the reaction of ambient NO with HO_2 , which is concurrently produced with OH by water photolysis. The correction of OH recycling in the PSU instrument is based on correcting each point in the decays for the recycling calculated from measured NO and HO_2 before applying the fit to determine the OH reactivity (Shirley et al., 2006).

Changes made after the first data submission in the data by the PSU instrument were mostly smaller than $\pm 10\%$. These small changes were due to improvements in the data evaluation algorithms that were made between the first and final submissions. These included improvements in the procedure, how data on measurements from instruments that were used for the corrections were synchronised to the OH reactivity measurements and refinement of instrument parameters such as air velocity and location of the injector.

In addition, the change in the correction procedure for OH regeneration due to the reaction of HO_2 with NO led to the final data being 2.5 times higher than the first data submission at the highest NO mixing ratios on 7 October 2015. Initially a new optimisation fitting procedure was developed and used for the first data submission, but laboratory and modelling studies showed that the method in Shirley et al. (2006) was superior and less uncertain. Thus, the method in Shirley et al. (2006) was used for the revised final data submission.

These changes were specific for this campaign because the instrument was not exactly the same instrument as used in previous and future campaigns. It was assembled from parts of the original PSU instrument and parts (mainly the laser system for the OH detection) provided by the Max Planck Institute for Chemistry in Mainz and the University of California, Berkeley.

5.3.4 Direct OH loss rate measurement by flow-tube technique with chemical ionisation mass spectrometry (DWD instrument)

The measurement scheme of the CIMS instrument by DWD is similar to that of the flow-tube LIF instrument by PSU. However, only one reaction time is currently realised to measure the OH decay (Berresheim et al., 2000; Muller et al., 2018). Excess OH (10^8 cm^{-3}) is produced by water photolysis in front of the flow tube with concurrent production of HO_2 . The reduction of its concentration by reacting with ambient OH reactants is measured at two set time periods. This is achieved by terminating this reaction by chemical conversion of OH after a specific reaction time. For this purpose, a high concentration of sulfur dioxide is added at two injection points, so that OH is converted to sulfuric acid. After the OH titration, a high concentration of propane is injected to scavenge any OH present. The injection of sulfur dioxide is alternately switched between these two points. The reaction time is determined by adding known amounts of OH reactivity (e.g. propane) in front of the flow tube.

OH wall losses from the flow tube are quantified by using humidified synthetic air. If the OH lifetime in the instrument is of the order of the travel time between the two injection points, no reasonable measurement is possible. In the current set-up, an upper limit of OH reactivity values of 40 s^{-1} is achieved.

Additionally, measurements by the CIMS instrument can also be affected by OH recycling from the reaction of ambient NO with HO_2 that is concurrently produced with OH by water photolysis. Corrections for OH recycling in the CIMS are based on laboratory characterisation at the Hohenpeissenberg station (ambient pressure $\sim 900\text{ hPa}$). An empirical function corrects for the systematic underestimation seen in CIMS OH reactivity measurements, which is dependent on both the magnitude of OH reactivity and the levels of NO present. The function has been derived for propane, isoprene and ethene for NO concentrations up to 15 ppbv (Muller et al., 2018). Under the assumption that any complex mixture in the SAPHIR chamber behaves like the three OH reactant mixture above, the NO correction was applied to the SAPHIR campaign data set for k_{OH} larger than 2.5 s^{-1} . The fit function optimised for OH reactivity up to 40 s^{-1} and NO ranging from 0 to 15 ppbv leads to a systematic overestimation of OH reactivities below 2.5 s^{-1} (Fig. S3), not representing laboratory observations. Therefore no correction is applied to $k_{\text{OH}} < 2.5\text{ s}^{-1}$. The OH recycling efficiency is partly dependent on the reaction time between the two injection zones. As the NO correction was determined at the laboratory at Hohenpeissenberg Observatory at a pressure of 900 hPa , an uncertainty of $+10\%$ exists for its application at the SAPHIR chamber, as a result of lower flow rates (i.e. longer reaction time in CIMS) at 1000 hPa .

In addition to ambient NO, the CIMS measurements were influenced by an NO impurity in the SO_2 cylinder, leading to the presence of 0.14 ppbv NO in the CIMS flow tube at all times in this campaign. The presence of the NO impurity became evident from the inspection of the CO experiments (7 and 15 April 2016) where a systematic, repeatable underestimation in OH reactivity was found for reactivities above 20 s^{-1} . Therefore, an NO correction function was applied to the whole data set, also for experiments without NO in the chamber, e.g. in experiments with monoterpenes (13 April 2016) and sesquiterpenes (15 April 2016).

The DWD CIMS instrument is a relatively new instrument that had only been used in a remote environment at the monitoring station at Hohenpeißenberg. Therefore, the correction procedure had been developed for chemical conditions experienced in this campaign and were further refined after the first data submission. They would also be required if the instrument took measurements in similar environments.

The wall loss of OH in the instrument and the time in which the air travelled between the two titration points were initially determined from zero-air phases of the experiments on each day. In order to provide data which are fully independent from the experiments, measurements were revised after data from the other instruments were known. The parameters were determined by an external flow tube with propane and synthetic air concentrations only once before the start of the campaign. This resulted not only in a constant change in the data due to the change in the zero decay time (wall loss) but also a scaling of data due to the change in the calculated reaction time (Table S1 in the Supplement). Final data are on average 10% lower than initially submitted.

5.4 Results and discussion

A summary of OH reactivity measurements of all instruments together with calculated OH reactivity is shown in Figs. 5.1 to 5.4 and the results are discussed in detail in the following subsections. For comparing data, the calculated reactivity is taken as the reference value if no oxidation products were formed during the experiment. In all other cases, one of the LP-LIF instruments (FZJS) is taken as reference. This instrument was chosen because its measurements have a high precision and time resolution. Regression lines were determined using the fitexy procedure by Press (1992). This method takes into account the measurement errors of both instruments and is symmetric, i.e. the fitted parameters are independent of whichever of the two instruments is assigned to be the dependent or independent variable.

5.4.1 OH reactivity measurements with zero air

Ultra-pure air was present in the chamber at the beginning of each experiment. As discussed above, it can be assumed that there was no OH reactivity present in this case. For normal operation of the LIF instruments, ozone and water vapour need to be present. A small contamination from OH reactants could appear during the humidification process of the chamber air. Measurements from previous experiments in the chamber indicate that OH reactivity introduced together with water is most often below the limit of detection of the reactivity instrument (approximately 0.2 s^{-1} , e.g. Fuchs et al., 2013) but always less than 1 s^{-1} . This is likely due to either contaminants in the water or contaminants coming off the Teflon film of the chamber with increasing humidity. Therefore, these periods are ideal for testing the instrument zeros and the precision of the measurements.

If an instrument zero needed to be taken into account, it was independently determined from the zero-air phase of the experiments for all instruments except for the MDOUAI CRM instrument. The instrument zeros were typically measured on a daily basis. No systematic change in the value was observed over the course of the campaign for these instruments. The instrument zero of the Leeds LP-LIF instrument was determined only once at the end of the campaign and the zero of the CIMS instrument once at the beginning of the campaign. The same air supply as for the chamber was used in these experiments, except for the CIMS, for which bottled air was used (Linde, purity 99.999 %). The derived values were used to correct all data. No instrument zero is expected for the CRM instruments (except for the contamination in the MDOUAI instrument), because only differences between measurement modes are used to calculate the OH reactivity.

Figure 5.5 shows the histogram of measurements during all zero-air parts in the two campaigns. A Gaussian fit function is fitted to the distribution in order to determine a potential bias in measurements and to estimate the precision of the measurements (Table 5.5). Overall, the distributions of zero measurements give a Gaussian shape. If all data are put together, none of the instruments exhibit a significant bias. Some exceptions are observed for specific experiments for some instruments. This result also demonstrates that no significant OH reactivity was present during these parts of the experiments.

Partly due to the small number of data points, the distribution is noisier for the measurements by the CRM instruments compared to the distribution for the LP-LIF

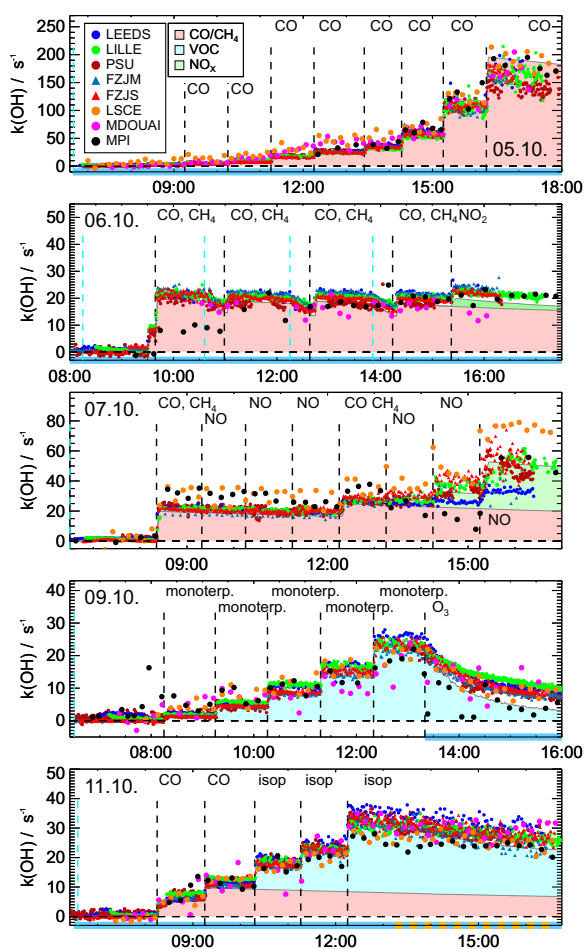


Figure 5.1: Measured (dots) and calculated (coloured areas) OH reactivity during experiments in the SAPHIR chamber 2015. Error bars are omitted for the clarity of the plot but are within the range of the scatter of data. Vertical dashed lines with labels give points in time of the injection of trace gases. Vertical dashed blue lines indicate addition of water, horizontal blue lines the presence of O_3 and horizontal dashed yellow lines illumination of the chamber by sunlight.

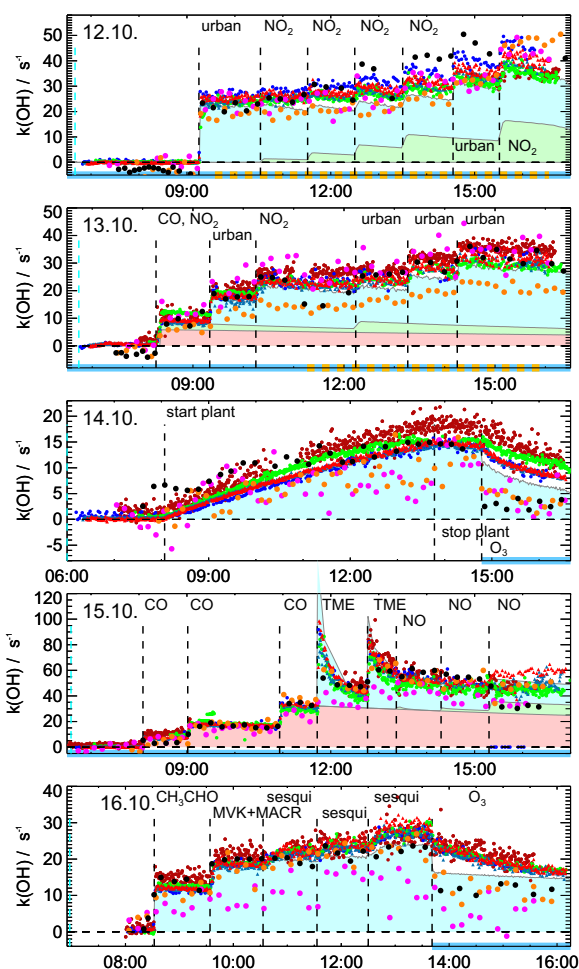


Figure 5.2: Same as Fig. 5.1. For the experiment on 16 October 2015 the subsequent addition of various VOC reactants is shown, so that differences among measurements that only occur for a specific VOC reactant impact the visual agreement at later times, when other VOC reactants were injected.

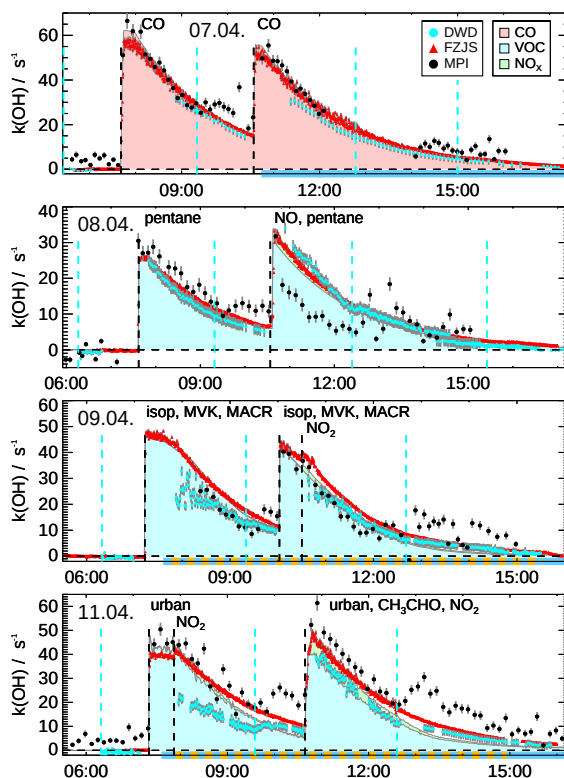


Figure 5.3: Measured (dots) and calculated (coloured areas) OH reactivity during experiments in the SAPHIR chamber 2016. Vertical dashed lines with labels give points in time of the injection of trace gases. Vertical blue lines indicate addition of water, horizontal blue lines the presence of O_3 and horizontal yellow lines illumination of the chamber by sunlight.

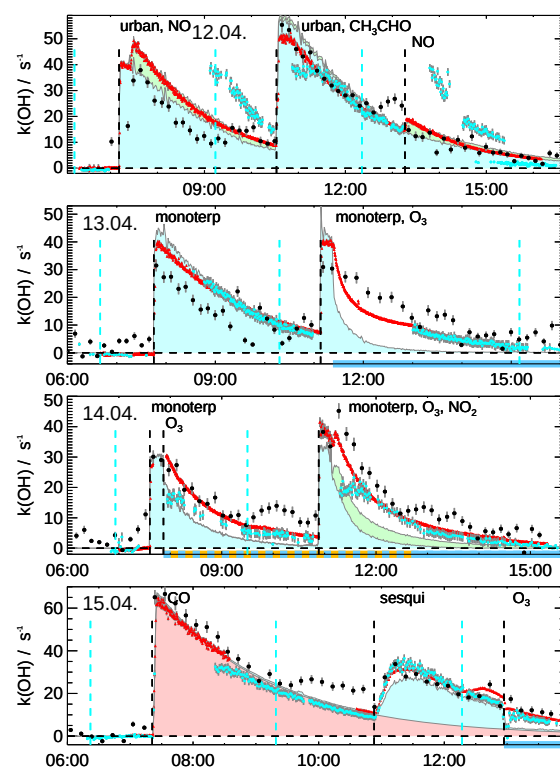


Figure 5.4: Measured (dots) and calculated (coloured areas) OH reactivity during experiments in the SAPHIR chamber 2016. Vertical dashed lines with labels give points in time of the injection of trace gases. Vertical blue lines indicate addition of water, horizontal blue lines the presence of O_3 and horizontal yellow lines illumination of the chamber by sunlight.

instruments. No bias of the MDOUAI instrument can be determined because of the use of zero-air phases of experiments to determine an instrument zero (see above). The bias in the other two CRM instruments varies between experiments (Fig. 5.1): the day-to-day variability is between ± 3 and $\pm 5 \text{ s}^{-1}$ with maximum values of $\pm 10 \text{ s}^{-1}$.

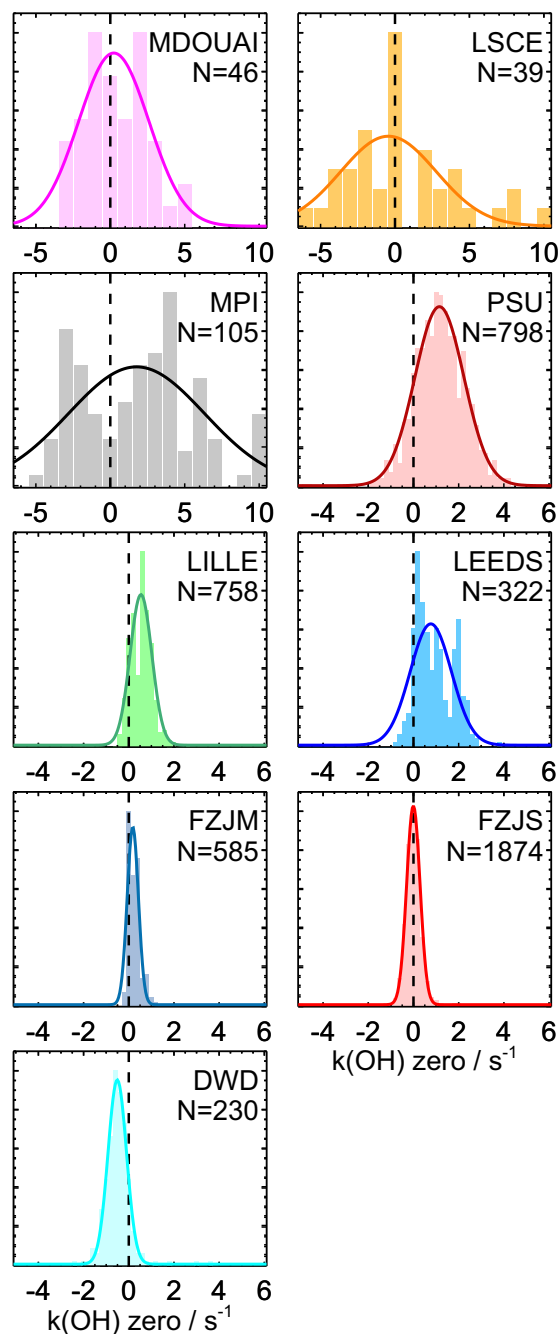


Figure 5.5: Distribution (bars) of OH reactivity measurements before OH reactants were injected into the chamber. MDOUAI, LSCE and MPI measurements are binned to 1 s^{-1} intervals, other measurements to 0.1 s^{-1} intervals. Solid lines show the fit to a Gaussian distribution.

A small bias is also observed in a few experiments for measurements of the Leeds LP-LIF instrument (smaller maximum value around 2 s^{-1}). A small positive bias of approximately 2 s^{-1} is also seen in the PSU measurements after 13 October 2015 for unknown reasons. However, this change is likely affected by the amplification of zero variability and errors due to the dilution procedure that was used.

The width of the distribution can only be regarded as an upper limit for the precision because of the deviation of zero measurements from a Gaussian distribution for some instruments (Table 5.5). Alternatively, the width of the distribution was calculated for a distribution of data after subtraction of the bias observed for each instrument for each individual experiment. The width of this distribution gives a more realistic estimate of the precision of the measurements (Fig. S5). The widths of the corrected distributions for the CRM instruments give a precision of approximately 2 s^{-1} at a time resolution of 10 (LSCE-CRM, MDOUAI-CRM) or 15 min (MPI-CRM), slightly higher than the stated limits of detection of 1 to 1.5 s^{-1} (Table 5.1). The widths of the distributions give a precision between 0.1 and 0.3 s^{-1} for LP-LIF instruments at time resolutions between 30 and 160 s for the different instruments, and a precision of 0.4 s^{-1} for the CIMS (60 to 300 s time resolution) in agreement with their stated limits of detection (Table 5.1). The PSU flow-tube instrument gives a precision of 0.9 s^{-1} . The precision in Table 5.1 of 0.5 s^{-1} is stated for normal operation of the instrument without the dilution and becomes 2.5 s^{-1} when corrected for the dilution amplification.

Table 5.5: Fit results of the distribution of the measurements to a Gaussian function when no OH reactants were present in the chamber. The distribution is either calculated by taking all data as they are measured or by forcing the mean values on each day to zero for an individual instrument. For the MDOUAI instrument, no independent instrument zero was determined.

Instrument	Data points	Width (daily mean zero)/ s^{-1}	Width/ s^{-1}	Bias/ s^{-1}
MDOUAI	46	2.3	N/A*	N/A*
LSCE	39	1.8	3.2	-0.4
MPI	105	2.1	4.6	1.8
PSU	798	0.9	1.1	1.1
Lille	758	0.2	0.5	0.5
Leeds	322	0.3	0.9	0.8
FZJM	585	0.1	0.2	0.2
FZJS	1450	0.2	0.3	0.0
DWD	230	0.3	0.4	-0.5

* Not applicable because measurements during zero-air phases were used as instrument zero.

5.4.2 OH reactivity measurements in the presence of CO and CH₄

During several experiments, only CO and CH₄ were present in the chamber for the entire experiment or part of the experiment. These experiments were performed in the dark, so that there was no photochemistry. The linearity of instruments and behaviour for a chemically simple system can be investigated from these experiments. As can be seen in Figs. 5.1 and 5.3, measurements of all instruments followed the expected changes (expressed by k_{calc}) due to the additions of CO and CH₄. In the tested range of up to $150 s^{-1}$, the agreement is mostly very good. Measurements by the DWD instrument show a clear upper limit of measurable reactivity of $40 s^{-1}$ as expected from the measurement principle (see above). Some instruments exhibited large transient deviations from the expected values (e.g. MPI on 6 October 2015 between 10:00 and 11:00 UTC) but otherwise agree well during the CO and CH₄ experiments.

Although linearity appears not to be a problem for all instruments, even for exceptionally high reactivity values (Fig. S6 and Table S2), the discussion of the results focuses on OH reactivity values below $60 s^{-1}$, which are more relevant for atmospheric measurements. Figure 5.6 shows the correlation of measured and calculated OH reactivities and Table 5.6 gives the result of a regression analysis for all periods, when only CO and/or CH₄ were present in the dark chamber. High linear correlation coefficients ($R^2 > 0.8$) are calculated for all instruments. A linear regression analysis gives slopes between 0.98 and 1.17 for most instruments. Errors of the fitted slopes were always smaller than 0.01, because the precision of data are higher than the scatter of data around the regression line. These results demonstrate the

Table 5.6: Results of the correlation analysis (linear correlation coefficient R^2 and slope and intercept of a weighted linear fit) for different subsets of the data. Errors of fit results (not shown here) are not significant within two digits of the fit parameters. $\langle |\Delta k|/k_{\text{fit}} \rangle$ gives the mean value of the relative difference between measurements and the regression line.

Data subset	Instrument	No. of data points	R^2	Slope	Intercept/ s^{-1}	$\langle \Delta k /k_{\text{fit}} \rangle$
CO, CH ₄ ^a $k(\text{OH}) < 60 \text{ s}^{-1,\text{b}}$	MDOUAI	122	0.79	1.05	0.8	0.33
	LSCE	112	0.81	1.31	−0.1	0.54
	MPI	178	0.91	1.05	0.3	0.32
	PSU	1151	0.97	1.03	1.1	0.19 ^c
	Lille	1506	0.97	1.04	1.3	0.10
	Leeds	829	0.98	1.06	1.3	0.11
	FZJM	795	0.98	1.12	0.2	0.10
	FZJS	2255	0.99	1.01	0.6	0.08
	DWD	295	0.99	0.87	−0.3	0.05
Urban mix ^d , isoprene ^{e,f}	MDOUAI	145	0.85	0.99	0.8	0.17
	LSCE	155	0.86	0.77	−0.1	0.17
	MPI	228	0.80	1.06	−1.1	0.17
	PSU	863	0.94	1.01	1.0	0.11 ^c
	Lille	1355	0.97	0.94	0.4	0.08
	Leeds	677	0.98	1.07	0.1	0.09
	FZJM	993	0.98	0.94	0.1	0.06
	FZJS	reference				
	DWD	719	0.91	0.73	−0.3	0.16
Monoterpenes no oxidation ^{f,g}	MDOUAI	69	0.48	0.56	2.4	0.45
	LSCE	69	0.68	0.82	−0.3	0.37
	MPI	73	0.72	0.70	1.5	0.34
	PSU	502	0.93	1.20	0.2	0.18 ^c
	Lille	639	0.98	1.08	0.4	0.09
	Leeds	318	0.96	1.02	−0.1	0.16
	FZJM	585	0.99	0.96	0.2	0.07
	FZJS	reference				
	DWD	142	0.98	1.01	−0.6	0.09

^a 5, 6, 7, 11, 13 and 15 October 2015; 7 and 15 April 2016;

^b reference: calculated reactivity.

^c scatter amplified by the dilution factor of 5 in this campaign.

^d 12–13 October 2015; 11 April 2016.

^e 11 October 2015; 9 April 2016.

^f reference: measurements by FZJS.

^g 9, 14 October 2015; 13–14 April 2016.

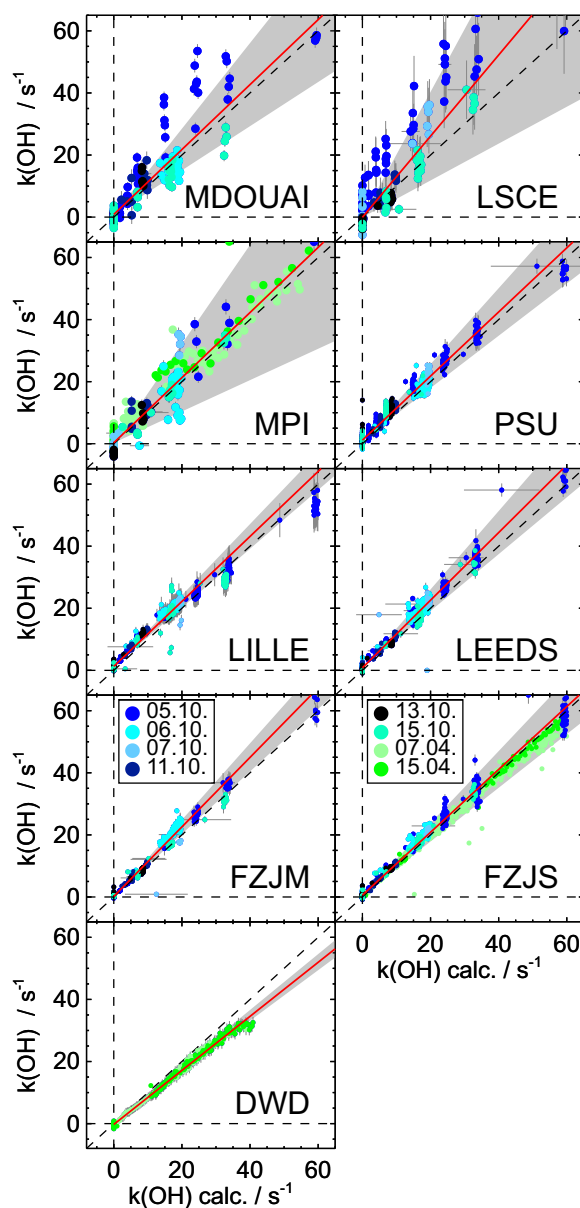


Figure 5.6: Correlation between measured and calculated OH reactivity for experiments in the SAPHIR chamber when only CO, CH₄, O₃ and water vapour were present. Only the subset of the entire data set for values below 60 s⁻¹ is shown. Red lines give the results of a linear regression analysis (Table 5.6). The grey area indicates the mean relative difference between measurements and the regression line. Measurements of the MDOUAI instrument during the first three experiments (5–7 October 2015) have a higher uncertainty due to technical problems.

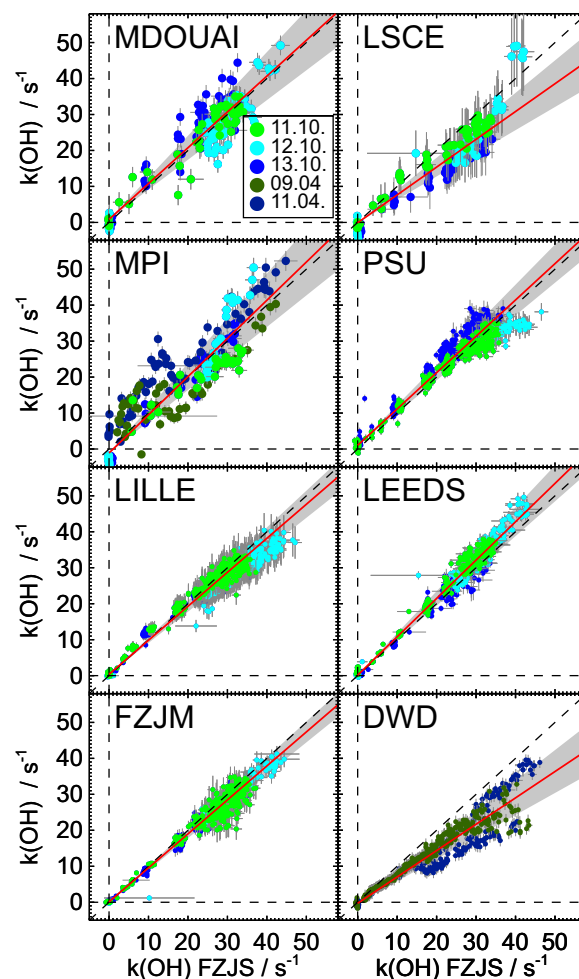


Figure 5.7: Correlation between measured OH reactivities and measurements by the FZJS instrument for experiments in the SAPHIR chamber when either isoprene (11 October 2015), isoprene, MVK and MACR (9 April 2016) or a mixture of propene, xylene and toluene (12–13 October 2015, 11 April 2016) were present in the chamber together with O₃ and water vapour. Lines give results of a linear regression analysis of the combined data set (Table 5.6). The grey area indicates the mean relative difference between measurements and the regression line.

ability of instruments to measure the correct reactivity values. Only the regression analysis for one CRM instrument (LSCE) gives a higher slope of 1.31, mostly due to measurements during the first experiment, whereas better agreement (Table 5.6) is achieved in other experiments. The larger deviation for this instrument is likely due to the correction for deviations from pseudo first-order behaviour (Table 5.4). This was determined from characterisation measurements with a mixture of isoprene and propane, which might not represent chemical conditions well with only CO.

Although the slopes of the regression lines indicate on average a good agreement of the measurements for these chemical conditions, the scatter in the correlation plots (Fig. 5.6) is considerably different for the instruments. The time series in Figs. 5.1 and 5.3 show that the scatter in the correlation plot is caused by statistical noise, and for some instruments by irregular systematic deviations pointing to instrumental instabilities. The mean of the relative absolute difference between measured and calculated OH reactivity is 32 to 48 % for CRM instruments, 19 % for the PSU LIF instrument and between 8 and 11 % for LP-LIF and the CIMS instruments. If the PSU instrument was operated similarly to how it was in the field without the large dilution flow, measurements would have scattered significantly less (at least a factor of 5). Thus, for the instruments as configured for this comparison study, the PSU LIF and LP-LIF instruments appear to have the highest measurement precision.

5.4.3 OH reactivity measurements in the presence of isoprene, MVK, MACR and OH reactants in urban environments

In a second set of experiments, chemical conditions included volatile organic compounds, NO₂ and CO (Table 5.3). The most abundant biogenic species, isoprene and OH reactants were tested, which are representative of alkenes and aromatic compounds found in urban environments (1-pentene, *o*-xylene, toluene). Oxygenated VOCs from isoprene oxidation (MVK and MACR) and acetaldehyde were present in separate experiments in 2015 (Fig. 5.8). In 2016, these species were present in experiments together with isoprene and the urban OH reactant mixture.

Similar results are obtained for isoprene and urban OH reactants. Because these experiments partly included oxidation products that were not measured by instrumentation at the chamber, measurements by the LP-LIF FZJS instrument are taken as the reference value. Measurements of this instrument differ less than 10 % from calculations using measured OH reactant concentrations. This difference is smaller than the 1 σ accuracy of the calculation, so that results would not significantly differ if calculated OH reactivity was used.

For most instruments (except for LSCE CRM and DWD CIMS instruments), the agreement between measurements found for these chemical conditions is about as good as for the experiments with only CO and CH₄ (Fig. 5.7). High linear correlation coefficients between measured and calculated reactivity values are obtained ($R^2 > 0.80$) and slopes of the regression lines are 0.94 and 1.07, showing good absolute agreement (Table 5.6).

The performance of the LSCE instrument is better than in the experiments with only CO and CH₄, but measurements are lower than the reference in this case, whereas measurements are higher in the CO and CH₄ case. As discussed above, the correction for deviation from pseudo first-order kinetics (which is based on a characterisation with propane and isoprene standards) might better represent chemical conditions during the experiment with alkenes, aromatics and isoprene compared to the CO

and CH₄ case. In general, this issue can cause a variability in the agreement between measured and calculated reactivity in this campaign. This indicates that a more intensive characterisation of this correction is required for the specific chemical conditions, specifically if individual OH reactants are studied.

Measurements by the DWD CIMS instrument give larger deviations from calculated reactivity in these experiments compared to results found in the CO and CH₄ case. The experiments on 9 and 11 April 2016 started with high reactivities of about 40 s⁻¹, but only 60 % is measured by the DWD CIMS instrument (Fig. 5.3). The agreement improves when k_{OH} decreases. For values below 10 s⁻¹, the measurements agreed well with calculated reactivities. The exact behaviour of the relationship between measured and calculated reactivity changed for periods of the experiments with different chemical conditions. In addition, an increase in the measured reactivity with increasing water vapour concentration after starting humidification of the chamber air is observed in these experiments. This is less obvious in other experiments (see below).

Part of this large discrepancy could be the result of an instrumental instability, which was seen as an intermittent increase in noise in the CIMS reactant ion counts (NO₃⁻) from 9 April 2016 onwards and coincided with the periods deviating from the FZJS instrument observations (see Supplement). This could be relevant because the reactant ion count is used to normalise the HSO₄⁻ counts, thus obtaining the equivalent OH concentration. At high OH reactivities, when OH signals are smaller, higher noise in the (comparatively) large reactant ion concentrations could thus affect the resultant k_{OH} estimation. The exact reason why there was an increase in noise in reactant ion concentrations remains unclear. Additionally, these two experiments have in common the illumination of the chamber by sunlight and presence of NO₂ in the second part of the experiments. Interestingly, measured and calculated reactivity agree better in these parts of the experiment compared to the first parts. However, there is no obvious reason why these conditions would impact the measurements of this instrument. Chemistry occurring in the inlet system may impact the OH concentration for the more complex chemical composition of air. In the presence of NO (see below), any unaccounted OH recycling would affect the accuracy of the measurements.

In the 2016 experiments, the relationship between measured and calculated reactivities does not change when oxygenated VOCs (MVK, MACR and acetaldehyde) were present compared to the part of the experiments when only the parent VOC was present. This can be seen in the time series of experiments on 9 and 11 April 2016 (Fig. 5.3). In the 2015 campaign, the impact of the presence of these compounds on the instruments was tested in a separate experiment (16 October 2015, Fig. 5.2). Because the compounds were consecutively injected, only the observed change in the measured OH reactivity for each instrument is calculated for the analysis (median of 20 min of measurements before and after the injection). This value can be compared to the expected change in the reactivity that is calculated from measured reactant concentrations (Fig. 5.8).

Measurements of LP-LIF instruments are not affected by these species and agree with the change in calculated reactivity. Also, the flow-tube LIF instrument by PSU and the CRM by MPI give similar values within 10 to 20 %. The change in reactivity measured by the LSCE instrument agrees in the case of MVK and MACR but is less in the case of acetaldehyde. Changes measured by the MDOUAI CRM instrument are up to a factor of 3 lower than observed by the other instruments. Losses on surfaces in the inlet system may explain part or all of the discrepancy. Both instruments used

an additional pump with Teflon surfaces in their inlet system (see also the discussion for monoterpenes/sesquiterpenes).

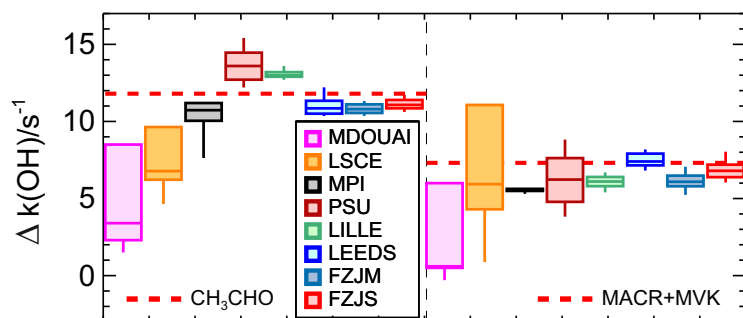


Figure 5.8: Change in reactivity measurements when acetaldehyde and a mixture of MVK and MACR were added to the experiment on 15 October 2015. The box and whisker plot shows the statistics (median and 10, 25, 75, 90 percentiles) of 20 min time intervals 5 min before and after the injections of OH reactants. Dashed red lines give values calculated from the measured change in OH reactant concentrations.

OH proceeds by H-atom abstraction from the aldehydic group, leading to the formation of acyl peroxy radicals, $\text{RC}(\text{O})\text{O}_2$. For instance, the oxidation of acetaldehyde will lead to the formation of the acetyl peroxy radical, $\text{CH}_3\text{C}(\text{O})\text{O}_2$, with a yield of approximately 95 % (Butkovskaya et al., 2004; Cameron et al., 2002). The reaction of acyl peroxy radicals with HO_2 is known to efficiently recycle OH in the atmosphere. For the acetyl peroxy radical, Dillon and Crowley (2008) and Winiberg et al. (2016) recently reported an OH yield of 0.5. Also, one reaction pathway in the reaction of MVK with OH forms an acyl peroxy radical that leads to OH reformation in the reaction with HO_2 with a high yield of 0.64 (Praske et al., 2015). These recycling mechanisms can act as a secondary source of OH in CRM instruments, which in turn can mask a fraction of the OH reactivity from aldehyde species for these instruments, leading to a negative bias. Results of model calculations and laboratory investigations (Fig. S4) performed for the MDOUAI instrument confirm that the OH reactivity of acetaldehyde is underestimated by this instrument, which is consistent with observations during the 16 October 2015 experiment (Fig. 5.2), when acetaldehyde was first introduced in SAPHIR. However, Fig. 5.2 shows that the two other CRM instruments (LSCE and MPI) are less (or not) impacted by OH recycling from $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{HO}_2$. These different behaviours are not well understood and need more investigation.

It is noteworthy that concentrations of acetaldehyde and other aldehydes in the atmosphere are typically smaller than in the experiment in this campaign but can constitute a significant fraction (10 to 20 %) of the total reactivity (e.g. Fuchs et al., 2017a). The maximum error that is caused by the underestimation of the total reactivity measurement by the CRM instrument would be less than 13 % if the results of the experiment of this campaign are extrapolated to atmospheric conditions.

The largest differences are seen in the presence of acetaldehyde for the MDOUAI CRM instrument. In addition, measurements by the LSCE and MDOUAI instruments are more variable compared to those by the other instruments as indicated by the large difference between 25 and 75 percentile values in this case. The presence of oxygenated VOCs may cause additional complications in the reaction system in the CRM that impacts the OH concentration. The oxidation of aldehyde species by

5.4.4 OH reactivity measurements in the presence of monoterpenes and sesquiterpenes

The third type of chemical condition tested in the campaigns was the presence of terpenes. This was done either by injecting a mixture of monoterpenes, a sesquiterpene or by flushing real plant emissions into the SAPHIR chamber. These experiments also included ozonolysis reactions of terpenes. Maximum reactivities (25 s^{-1}) were lower than in other experiments in 2015. Oxidation products of the ozonolysis reactions were not measured, so that it is expected that calculated reactivities are underestimating the real reactivity.

Therefore, one of the instruments (LP-LIF FZJS) is taken as reference for the comparison of the measurements. As seen in the correlation plots (Fig. 5.9) and the results of the regression analysis for data without the presence of ozone (Table 5.6), differences between measurements of the LP-LIF instruments and the other instruments are largest in these experiments compared to the other experiments.

High linear correlation coefficients are obtained ($R^2 > 0.96$) and slopes of the regression lines between 0.96 and 1.08 are calculated for the LP-LIF instruments. No systematic change in the relationship of measurements is observed whether ozone and hence ozonolysis products are present or not. Similarly, measurements between LP-LIF instruments agree in the presence of the sesquiterpene (with and without the presence of ozone and ozonolysis reaction products). Because this experiment started with the addition of other OH reactants (Fig. 5.2), only the measured difference is compared that due to the injection of β -caryophyllene that is observed by each instrument (Fig. 5.10), as done for the oxygenated VOCs (see above). Measurements of the flow-tube LIF instrument (PSU) varied more with respect to the reference measurements in the presence of monoterpenes and sesquiterpenes compared to the other chemical conditions. The level of agreement varies among the

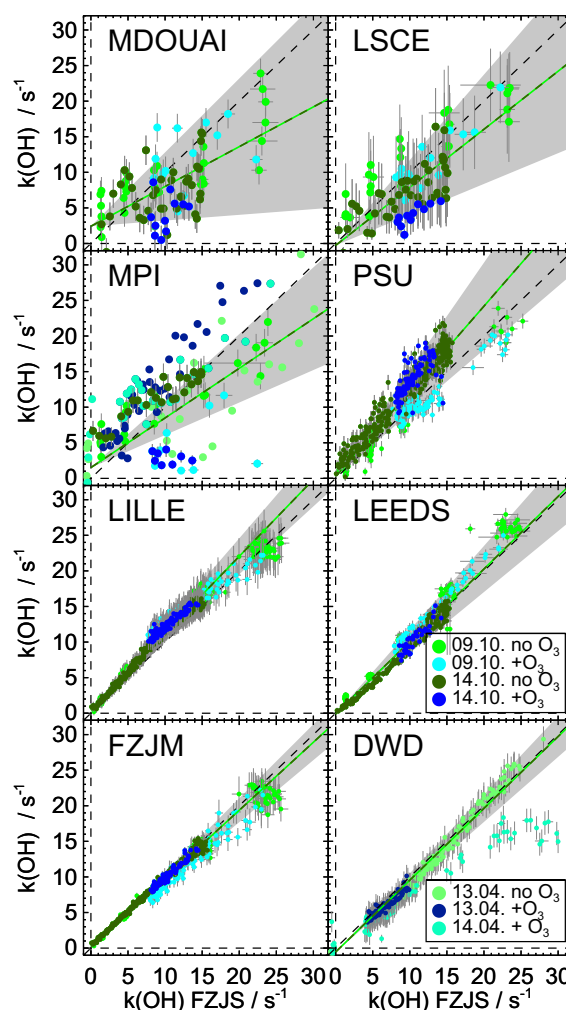


Figure 5.9: Correlation between measured OH reactivities and measurements by the FZJS instrument. This subset of data includes experiments with injections of a mix of monoterpenes (α -pinene), limonene, and myrcene (9 October 2015 and 13–14 April 2016) or with the transfer of real plant emissions, which consists predominantly of monoterpenes (14 October 2015). Times when O_3 was present are indicated by bluish colours. Lines give results of a linear regression analysis of a subset of data when no ozone was present (Table 5.6). The grey area indicates the mean relative difference between measurements and the regression line.

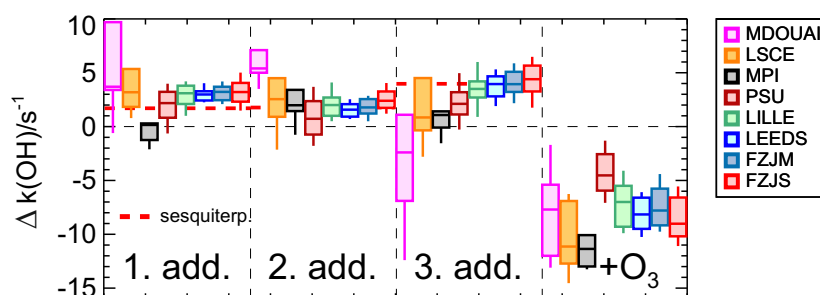


Figure 5.10: Change in reactivity measurements when β -caryophyllene was first added three times and ozone in the last step of the experiment on 16 October 2015. The box and whisker plot shows the statistics (median and 10, 25, 75, 90 percentiles) of 20 min time intervals 5 min before and after each addition. Dashed red lines give values calculated from the measured change in OH reactant concentrations.

three experiments (9, 14 and 16 October 2015): when the monoterpene mixture was injected, measurements by the PSU instrument are 10 to 15 % lower than measurements by the FZJS instrument, but they are 20 % higher when plant emissions are transferred into the chamber. During the continuous transfer small inhomogeneities cannot be fully excluded, but the discrepancies between measurements also remain after the injection and oxidation part of the experiment. The relationship does not depend on the presence of ozone in these two experiments.

In the third experiment, changes in the OH reactivity measured by the PSU instrument due to the increase in sesquiterpene concentration (and ozonolysis products) are up to 40 % smaller than the changes observed by the LP-LIF instruments (Fig. 5.10). The higher and lower values observed in these experiments may not be related to the chemical conditions but instead to the instrument problems. This is indicated by higher values of the PSU instrument compared to measurements by the other instruments in nearly all experiments after 13 October, independent of the chemical conditions (Figs. 5.7 and 5.9). Difficulties in maintaining consistent operation of the laser and the electronics driving the movable OH source could have led to much of this variability. As a result, this comparison exercise probably does not represent the capability of the PSU instrument to measure OH reactivity in forest environments.

Measurements by the FZJ LP-LIF and DWD CIMS instruments in the experiments with terpenes (Figs. 5.9 and 5.11) agree well during the first experiment with monoterpenes (13 April 2016, Fig. 5.4) and only a small underestimation is seen during the second experiment (14 April 2016). Though no obvious explanation can be provided as to why the CIMS underestimated OH reactivity compared to LP-LIF up to 12 s^{-1} on 14 April 2016, the CIMS instrument performance might have been influenced by unidentified internal chemical reactions. This also corresponds to observations in the presence of isoprene, MVK, MACR or a mixture of urban OH reactants (see above). Because NO was present as an impurity in the CIMS sulfur dioxide titration gas mixture (see above and Table 5.4), a NO correction function was also applied in experiments with monoterpenes (13 April 2016) and sesquiterpenes (15 April 2016). This could explain some of the smaller, but systematic differences compared to LP-LIF measurements (Muller et al., 2018).

Similarly to the CIMS instrument, the agreement between CRM and LP-LIF instruments is worse in the presence of monoterpenes and the sesquiterpene compared to other experiments. Lower linear correlation coefficients (R^2) between 0.48 and 0.72 and a higher scatter of data with relative mean absolute residuum values between 0.34 and 0.45 (numbers only for periods without ozone) are observed. The agreement is even worse during the ozonolysis parts of the experiments, when CRM instruments measure values that are up to five times smaller than measurements of the LP-LIF instruments. Similar results are seen in the experiment with the sesquiterpene (Fig. 5.10). In all these cases, the level of agreement varies among the CRM instruments and the specific experiment, but the measurements tend to be significantly smaller than those of the other instruments.

The residence times in the sampling lines of the CRM instruments were generally longer (5 to 6 s) compared to the sampling lines of the other instruments (0.5 to 4 s) and the volume to surface ratio was lower, because CRM instruments used 1/4" OD PFA tubing in 2015. In addition, two CRM instruments (MDOUAI and LSCE) used a sampling pump with Teflon surfaces to introduce the sample into the CRM reactor. Oxygenated and low-volatility (monoterpene and sesquiterpene) species may adsorb on these surfaces and the pump may have therefore played a role in the underestimation seen for these instruments. One instrument (MPI-CRM) used a heated inlet line. Other instruments used up to 1" OD PFA or Silconert-coated stainless steel tubing (Table 5.1). Results (Figs. 5.9 and 5.10) show that MPI measurements are partly significantly higher than those of the LSCE and MDOUAI instruments, suggesting that the underestimation of the LSCE and MDOUAI CRM instruments could be partly due to a loss of OH reactants in the sampling system (unheated inlet line+pump). However, an impact of the monoterpene or sesquiterpene chemistry on the CRM measurements cannot be ruled out.

In the experiments with terpenes in 2016 (Figs. 5.9 and 5.11), a better agreement between measurements by the MPI CRM and FZJS LP-LIF is found, specifically for the experiment with β -caryophyllene, compared to the experiments in 2015. The reason for this improvement is not clear but could be related to the larger diameter inlet tube used in 2016 compared to 2015 (Table 5.1), supporting the potential influence of losses in the inlet system for these compounds.

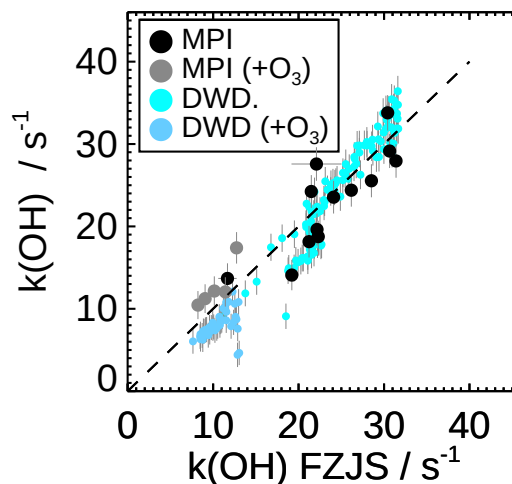


Figure 5.11: Correlation between OH reactivity measurements by the MPI CRM and DWD CIMS instruments and measurements by the FZJS instrument for the part of the experiment on 15 April 2016 when β -caryophyllene was present in the chamber. Times when ozone was also present are coloured differently.

5.4.5 OH reactivity measurements in the presence of NO

The presence of NO can affect measurements of the OH reactivity in all instruments due to the recycling of OH by the reaction of HO_2 with NO that is contained in ambient air (see above). These effects are amplified if OH is produced by water photolysis, because HO_2 is concurrently formed with OH.

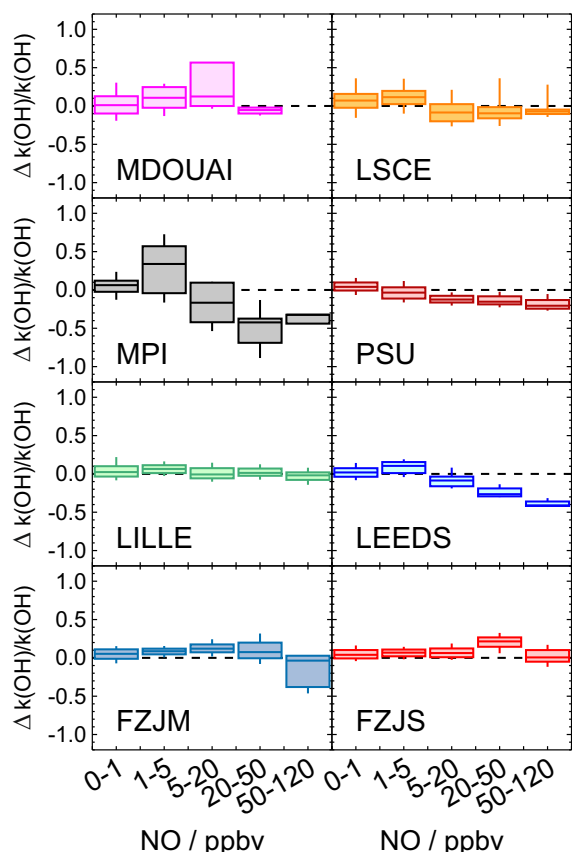


Figure 5.12: Relative difference between measured and calculated OH reactivity depending on the NO mixing ratio in experiments on 7, 12, 13, 15 October 2015. Boxes give median and 25 and 75 percentiles, whiskers give 10 and 90 percentiles. Because the MDUAI CRM instrument did not measure on 7 October 2015, when NO concentrations were systematically changed, limited data are available for this instrument. For the Leeds LP-LIF instrument the OH decays were fitted by a single-exponential decay for all NO, whereas a bi-exponential decay was used for Lille, FZJM and FZJS for $\text{NO} > 20$ ppbv.

In 2015, the NO concentration was increased stepwise (up to 120 ppbv) in the presence of CO on 7 and 15 October 2015 (Fig. 5.1). NO was also present in the two experiments with urban OH reactants (12 and 13 October 2015). Figure 5.12 shows the dependence of the relative difference between measured and calculated reactivity on the NO mixing ratio in these experiments. In 2016, the presence of NO was tested in two experiments in combination with the presence of pentane and in the urban OH reactant mixture (8 and 12 April 2016, Fig. 5.13). Due to the lack of OH reactant concentration measurements on 8 April 2016, measurements performed by the FZJS instrument are taken as the reference with which to analyse the impact of NO on the performance of the other two instruments (Fig. 5.13).

Discrepancies between calculated and measured reactivity are mostly within the range of differences observed in other experiments for LP-LIF instruments. For NO mixing ratios higher than 20 ppbv, median values deviate up to 20% from calculated reactivities. The OH production rate from recycling reactions is within the range of the OH destruction rate in the case of CO at highest NO mixing ratio in the experiment on 7 October 2015. Nearly all the LP-LIF instruments applied a bi-exponential fit function in this case except the Leeds LP-LIF instrument. Only the FZJM/FZJS instruments applied a bi-exponential fit

to measurements on the second experiment with high NO (15 October 2015). However, separating OH reactivity from OH recycling by applying a bi-exponential fit function might still lead to some systematic errors for the experiment with high NO in the presence of only CO because of the OH recycling rate that was higher than for typical atmospheric conditions. Therefore, the faster decay rate could deviate from

the OH reactivity. The scatter in the measurements increases with increasing NO mixing ratio as expected from the lower precision of measurements for high reactivity values.

As with all other LP-LIF instruments, OH reactivity from the Leeds LP-LIF agrees well with calculated OH reactivities below 20 ppbv NO. However, values are increasingly lower for higher NO mixing ratios. The lower values of OH reactivity for NO higher than 20 ppbv are caused by the application of a single-exponential fit to the OH decay data rather than a bi-exponential fit as used by other LP-LIF groups. Similar behaviour is achieved if a mono-exponential fit is applied to measurements by the Lille and FZJS/FZJM LP-LIF instruments during the experiment with CO and NO (7 October 2015). A bi-exponential fit, although it gives an OH reactivity closer to the calculated value for this particular experiment, is not necessarily the correct function to apply to fit atmospheric data, and so was not used by Leeds (even though a bi-exponential fit returns a larger value of OH reactivity). Model simulations under relevant conditions indicate that a bi-exponential fit can return an OH reactivity that is greater than the true value. Fitting the data more rigorously requires a modelling approach, similar to that applied when OH recycling was observed in a laboratory kinetics study (Onel et al., 2014). Hence, although application of a bi-exponential fit improves the agreement with the calculated value for this experiment, caution is needed when applying it to atmospheric data at high NO where conditions could be different.

Measurements by the PSU LIF instrument, which also uses water photolysis as an OH source, show a tendency to underestimate reactivity values with increasing NO mixing ratios. The maximum median of the relative difference is 20 %. This difference was significantly reduced from 70 to 20 % in the final data compared to the data submitted before reactivity measurements from all groups and OH reactant concentrations were made available. The correction procedure for the presence of NO was changed later from a new procedure to the one described in Shirley et al. (2006) (see above).

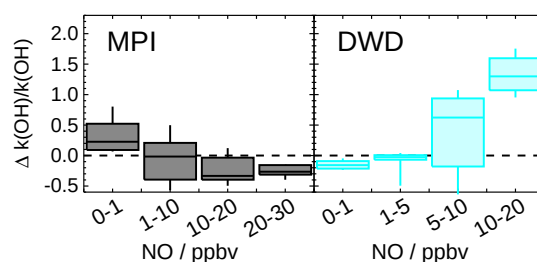


Figure 5.13: Relative difference between measured OH reactivity and measurements by the FZJS instrument depending on the NO mixing ratio for the experiment on 8 and 12 April 2016. Boxes give median and 25 and 75 percentiles, whiskers give 10 and 90 percentiles.

Measurements by the MDOUAI and LSCE CRM instruments do not exhibit a clear trend in the relative difference between measured and calculated reactivity with NO. In contrast, measurements by the MPI CRM instrument give lower reactivity values compared to calculated reactivities with increasing NO mixing ratios in both campaigns in 2015 and 2016 (Figs. 5.12 and 5.13). Measurements by all CRM instruments were corrected by applying an empirical correction function. The magnitude of the correction is of the order of the OH reactivity values (Table 5.4), making results very sensitive to any systematic error in the correction procedure. The differences in the corrections needed for each CRM instrument emphasise the necessity for a careful characterisation of the instrument.

In the campaign in 2016, the relative difference between measured reactivity by the DWD CIMS instrument and the reference (FZJS LP-LIF instrument) is small for NO mixing ratios lower than 5 ppbv but increases with increasing NO mixing ratio (Fig. 5.13) to up to a factor of 1.3 (median value) for 10 to 20 ppbv NO.

This difference demonstrates that the correction applied to the CIMS measurements leads to systematic errors for NO mixing ratios larger than 5 ppbv, in particular for the urban mixture (12 April 2016). The chemical composition does seem to play a role (Table 5.3): the correction in the pentane experiment fits well in contrast to the urban mix experiment, in which it partly produces inaccurate results. The strength of OH recycling by the reaction of HO_2 with NO is also dependent on the CIMS internal abundance of HO_2 which was not measured during the SAPHIR campaign. Also, the correction term can become rather large for high OH reactivity and large NO concentration (up to 30 s^{-1}), which illustrates the limit of the instrument in its current configuration (Fig. 5.4).

5.4.6 Influence of humidity on OH reactivity measurements

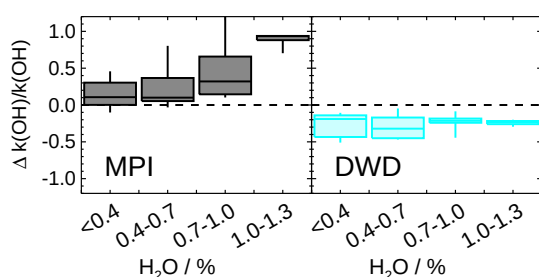


Figure 5.14: Relative difference between measured OH reactivity and measurements by the FZJS instrument depending on water vapour mixing ratio during experiments in April 2016 when only CO, pentane, or a mixture of propene, xylene and toluene were injected (part of the experiments on 7, 8, 11 and 15 April 2016).

In experiments in 2015, humidity was similar in most experiments and only systematically varied in one experiment on 6 October 2015 (Fig. 5.1). In contrast, water vapour concentrations were highly variable in experiments in 2016 because of the high dilution flow that was required. Figure 5.14 shows the dependence of the relative difference of measurements by the instruments (taking measurements by the FZJS instrument as reference) for all experiments, in which an overall good agreement is observed (CO, pentane). A clear trend towards overpredicting OH reactivity with increasing water vapour can be seen for measurements by the MPI

CRM. This trend is consistent with lower measurements at the lowest water mixing ratios observed in the experiment on 6 October 2015 (Figs. 5.1 and S7). In contrast, the results from 6 October 2015 do not indicate that the other CRM instruments are affected in the same way by water vapour. No clear trend with water vapour is observed for the LSCE and MDOUAI instruments.

Some changes in the relationship between the CIMS instrument and the LP-LIF instrument are seen after water vapour additions in some experiments in 2016 (for example 9 and 11 April 2016, Fig. 5.3). On 9 and 11 April 2016, the CIMS instrument showed an instrumental instability before the water addition, which could explain some changes in the relationship (Fig. S2). No systematic trend in the entire data set is observed (Fig. 5.14). Also, on 15 April 2016 CIMS measurements deviate from observations of the LP-LIF instrument, when the humidity was increased after the addition of sesquiterpenes, but deviations could be due to errors in either one of the instruments. The LP-LIF instrument observed an increase in OH reactivity, whereas the decreasing trend of the CIMS measurements does not change. The increase ob-

served by the FZJS LP-LIF instrument could be due to desorption of sesquiterpenes inside the instrument but could also be due to desorption from the chamber wall increasing the reactivity in the chamber. However, the decrease observed by the CIMS instrument would be consistent with the dilution of trace gases in the chamber. Both instruments agree better again after the injection of ozone, when sesquiterpenes have become small.

In the CRM and CIMS instruments, the concentrations of OH and HO₂ depend on the water vapour concentration as they are produced together by water vapour photolysis. In CRM instruments, corrections are applied, when the water vapour concentration changes between the different measurement modes which are required to calculate the OH reactivity (Table 5.4). Also, a humidity dependence in the detection sensitivity of pyrrole is taken into account. Fast changes in the water vapour concentrations, for example during the humidification procedure of the chamber air, can therefore cause systematic errors. However, systematic differences are observed on a longer timescale than the duration of the humidification (< 30 min) in these experiments. Humidity-dependent memory effects in the inlet system could be the reason for this behaviour. Another possibility could be that observations are related to changes in the OH and HO₂ concentrations that depend on the water vapour concentration. OH recycling processes and correction factors depend on the radical concentrations and chemical conditions. For experiments in 2015, the dependence of the correction factor for the deviation from pseudo first-order kinetics was not well characterised for the low OH concentrations at low water vapour concentrations, so that the deviation from calculated OH reactivity might be due to a systematic error in this correction for these conditions.

Further investigations will be necessary to understand the exact influence of the water vapour concentration on the OH reactivity measurements by the MPI CRM instrument and the reason for the instrumental instability of the CIMS instrument. It cannot be fully excluded that the observed effects are related to the experimental procedure of humidifying the chamber air that leads to a relatively fast change in the water vapour concentration.

5.5 Previous comparisons

Two comparisons of OH reactivity instruments were performed in the past. In one campaign, the MDOUAI CRM and the Lille LP-LIF instruments took measurements on the campus of the University of Lille in October 2012 (Hansen et al., 2015). Either a complex mixture of VOCs or oxygenated VOCs or ambient air was sampled. Experiments with synthetic mixtures of hydrocarbons and OVOCs indicated that the CRM instrument was underestimating the reactivity by 39 and 53 %, respectively, while the LP-LIF measurements were in agreement with the calculated reactivity values within their uncertainty. The discrepancy was attributed to the photolysis of aromatic compounds and oxygenated VOCs in the CRM instrument. This effect is expected to be insignificant in this campaign, because the lamp intensity in the MDOUAI instrument was lowered as a result of the campaign in 2012.

In the present study, a good agreement with calculated reactivity is found in experiments with urban OH reactants including aromatic compounds. This confirms that photolysis processes observed in 2012 for the MDOUAI CRM no longer play a role.

The comparison between the two instruments during ambient measurements showed that the CRM measurements were lower than the LP-LIF measurements by 22 % on average. No dependence in the agreement between the MDOUAI CRM and Lille LP-LIF in the presence of NO was observed in 2012, consistent with results in this campaign for these instruments (Fig. 5.12). Similar to the results of this campaign, the accuracy of the determination of the instrument zero of the LP-LIF instrument limited the accuracy of the measurements.

Measurements taken with the MDOUAI CRM were also compared to measurements by the LSCE CRM during a field campaign at a remote site in France in summer 2013 (Zannoni et al., 2015). Both instruments sampled either ambient air or emissions from enclosed plants. Measurements by both instruments agreed well overall in that campaign (the regression yielded a slope of 0.96), but the linear correlation coefficient R^2 was only 0.54 for reactivity values below 50 s^{-1} because of the large scatter in the data at OH reactivity below 50 s^{-1} . This is consistent with results in this campaign, where measurements from these two instruments were often similar but also differed by 20 to 50 % in some experiments (Figs. 5.1 and 5.2).

The MDOUAI instrument was operated under similar conditions to the present study, i.e. with a long sampling line and a pump in the inlet system. The inlet system of the LSCE instrument did not include a pump, unlike in the present study, and consisted of sampling Teflon line with a small diameter (1/8"-OD) and a PTFE filter. It is likely that losses of low-volatility compounds during sampling impacted the previous comparison, similarly to observations in the present study.

5.6 Summary and conclusions

Measurements of OH reactivity were compared in experiments performed in the atmosphere simulation chamber SAPHIR in two campaigns in 2015 and 2016. All instrument types presently used for atmospheric measurements were used in one or both of the campaigns. A few additional instruments exist worldwide (e.g. Yang et al., 2016), but they are similar to the instruments in these campaigns.

5.6.1 Summary of findings

Not only were many measurements successfully performed in these campaigns but also a number of findings already led to an improvement in the data quality during the process from measurements to the final data:

- ♦ an ozone-dependent background signal was found for measurements of the MPI CRM;
- ♦ application of the correction of measurements is recommended due to the deviation from pseudo first-order conditions in CRM instruments by empirical correction factors (Michoud et al., 2015);
- ♦ misalignment of the photolysis laser beam in the LP-LIF instruments can lead to a complication in the data evaluation procedure.

These results will also improve the precision and accuracy of measurements in the future.

The findings of the comparison of the final data set are as follows:

- ◆ Measurement techniques are capable of measuring OH reactivity for a range of chemical conditions that are relevant for ambient air measurements but with different levels of precision and accuracy. Losses of OH reactants in inlet lines could be of importance.
- ◆ Measurements by LIF and CIMS instruments have a higher precision than CRM instruments leading to a limit of detection better than 1 s^{-1} at a time resolution of a few minutes. For chemically complex conditions, the scatter of the data is within the range of 10 % for LP-LIF instruments and 10 to 20 % for the CIMS and the flow-tube LIF instruments. The precision of data from the flow-tube LIF instrument was reduced in this campaign compared to typical operation in the field due to the application of a high dilution flow. Measurements by CRM instruments exhibit a higher limit of detection of approximately 2 s^{-1} at a time resolution of 10 to 15 min. The scatter of the CRM data for chemically complex conditions ranges from 17 to 45 % (mean relative difference between measurements and linear regression with reference values). Additional work is needed on the CRM technique to improve the measurement precision at a level closer to that observed for other instruments.
- ◆ Biases in the measurements by the LP-LIF instruments are lower than their limit of detection with a few exceptions in some experiments for the Lille and Leeds instruments. The instrument zero in the PSU instrument varied by 1.3 s^{-1} , but this value is amplified by the dilution factor of 5 that is not normally used in field measurements. The smaller number of data points for the CRM instruments makes conclusions about a day-to-day variability of a potential bias less accurate. However, the distribution of measurements during zero-air measurements becomes more compact for the LSCE and MPI CRM instruments if an offset is subtracted for each individual experiment (Table 5.5).
- ◆ Maximum absolute deviations of LP-LIF measurements from calculated reactivities or measured reactivities from the instrument taken as the reference (FZJS) are 12 % (mostly less than 5 %). Deviations are smaller than the accuracy of the calculation from measured OH reactant concentrations (Table 5.2). Results from this campaign demonstrate a high accuracy of LP-LIF instruments.
- ◆ The accuracy of CRM instruments varies with chemical conditions. Whereas measurements agree on average with calculated reactivities within 5 % (higher deviations for LSCE CRM 31 %) if only CO, CH₄ or pentane are present, deviation from measurements with the FZJS LP-LIF instrument are up to a factor of 2 for mixtures containing terpenic compounds. Also, the scatter of data is larger in these cases. While the impact of OH recycling in the terpenic chemistry cannot be ruled out, losses of these compounds in inlet systems can explain the observed discrepancies. The transmission of low-volatility compounds such as terpenes and their oxidation products needs to be improved for CRM instruments. Inlet systems used in this campaign partly differed from deployments in previous campaigns (for example the use of the additional pump in the inlet of the LSCE instrument), so that losses could have been different in campaigns in the past.
- ◆ Even in the presence of up to 120 ppbv NO, agreement with calculated reactivity within the accuracy of measurements and calculations is achieved for the MDOUAI and LSCE CRMs, whereas deviations of up to 50 % for the MPI CRM instrument and a factor of 1.8 for the CIMS are observed. All these instruments

applied large corrections to account for OH recycling from the reaction of HO₂ with NO. The variability in the accuracy of the correction emphasises the need for a careful characterisation of the instrument-specific operational conditions.

- ◆ Measurements by LP-LIF instruments are not affected as much as the other instruments by OH recycling reactions even for NO mixing ratios higher than 20 ppbv. In this case, a bi-exponential fit function to the OH decay curve rather than a single-exponential fit improves the agreement with the calculated value of the OH reactivity. A bi-exponential function was not applied to OH decays measured by the Leeds LP-LIF, so larger deviations were observed for NO mixing ratios higher than 20 ppbv. Although a bi-exponential fit to the data generated a closer agreement with the calculated value of the OH reactivity for the conditions of this particular experiment, it should be noted that it may not represent the best function to fit to atmospheric data at high NO (where the composition is different to this experiment), and careful thought needs to be given as to the optimum function to fit to the data.
- ◆ Measurements by the flow-tube LIF instrument give larger deviations ($\pm 20\%$) in the chemically more complex experiments compared to conditions with single, anthropogenic reactants (deviations $\pm 3\%$), although the flow-tube LIF measurements are likely affected by instrument issues related only to the instrument that was assembled for this comparison.
- ◆ Experiments in 2016 reveal a so far unrecognised effect of the water vapour concentration on measurements by the MPI CRM instrument (factor of 2 difference at 1 % water vapour mixing ratio), although changes of the humidity and therefore radical concentrations are taken into account in the evaluation. The water vapour correction procedure might have not been applicable here, because humidity changes were faster than typical in the atmosphere. Water vapour was changed in only one experiment in 2015. Results do not indicate that the other CRM instruments are affected in the same way by water vapour.
- ◆ The accuracy of measurements by the CIMS instrument varied between experiments. Compared to the calculated OH reactivity, an agreement is observed within the accuracy of measurements and calculations for the experiments with CO and pentane (deviation of the regression slope from 1 : 1 line of 13 %). For the isoprene and urban reactant mixture cases, lower accuracy is observed with a deviation of the regression slope from 1 : 1 line of 27 %. In contrast to that, the regression slope is 1.01 for the monoterpene/sesquiterpene cases when measurements are referenced to the FZJS LP-LIF instrument. On some days a change in the relationship between measurements by the CIMS instrument and the LP-LIF instrument is observed with changing water. Overall, the variability in the level of agreement hints to instrumental instabilities.

5.6.2 Conclusions for future instrument operation and measurements in the past

Overall, the comparison demonstrates that OH reactivity measurements by LP-LIF instruments are precise and accurate for a wide range of atmospheric conditions. Instrumental parameters such as laser alignment and instrument zero are recommended to be regularly checked to achieve a high accuracy and to avoid additional complications in the data evaluation.

In this campaign, the flow-tube LIF instrument gives slightly less accurate and precise measurements compared to the LP-LIF instruments, which is related to the different operational conditions compared to previous campaigns. A different laser system was used and a high dilution flow was applied, which reduced the instrument performance. Had it been possible to use the field PSU instrument without dilution, it is likely that its precision and accuracy would have been similar to that of the LP-LIF instruments.

The OH reactivity scheme of the CIMS instrument is relatively new. It has only been deployed at the monitoring station Hohenpeissenberg so far, where OH reactivity values are typically small (2 to 10 s^{-1}). Further improvements of the data quality for high NO conditions ($> 3\text{ ppbv}$) are needed to expand the device ability to measure in more polluted regimes.

The accuracy of the current observations depend on the quality of NO concentration measurements and the assumption that the OH decay obeys single-exponential behaviour. All OH recycling processes need to be well characterised. Any deviation from these assumptions leads to systematic errors, and needs further investigations to capture other unknown complex mixtures of OH reactants under polluted conditions. Additional reaction times (injection points for SO_2 and propane) and concurrent measurements of RO_x and HO_2 concentrations could help characterise the OH recycling processes in unknown mixtures of OH reactants in the future.

While CRM instruments are less precise and accurate than other techniques, a reasonable agreement is usually observed between the CRM instruments and the other techniques for air mixtures containing simple compounds such as CH_4 , CO and isoprene, and for urban air mixtures containing anthropogenic hydrocarbons and NO_x . The correction factors, which depend on the exact instrumental conditions such as the OH, HO_2 and pyrrole concentrations in the reaction volume, are a potential source of systematic errors. In order to minimise these errors, the CRM operating conditions are such that the ratio of pyrrole to OH concentrations ranges from 1.7 to 2, so that corrections for operating under non-pseudo first-order conditions can be within 10 % (1σ) for different air compositions (Michoud et al., 2015). The error associated to this correction needs to be propagated to the measurement uncertainty. The largest correction is for the recycling of OH from $\text{HO}_2 + \text{NO}$, which is only relevant for urban atmospheres. This correction can be of the same order of magnitude as the measured OH reactivity value and needs to be carefully characterised on each CRM instrument. The level of agreement is degraded when low-volatility terpenoid compounds and/or their oxidation products are sampled. Although all CRM instruments use the same detection scheme and the same reaction tube, measurements differ between the three CRM instruments and also significantly differ from other LIF-based techniques. While OH recycling in the CRM reactor cannot be ruled out when these species are sampled, losses of OH reactants in inlet lines and sampling pumps (partly different than typical inlet lines in field campaigns) could have led to additional systematic errors in this campaign. The quality of the measurements depends on both the instrumental technique but also the procedure used to transfer the sample into the instrument. A high flow (short residence time) in the inlet lines and/or the use of inert inlet line materials like Silconert coated steel might help to reduce inlet line effects as indicated by the results of LP-LIF instruments. This improvement is a prerequisite to investigate whether the terpenoid chemistry inside CRM reactors can lead to an underestimation of ambient measurements.

The CRM method is a younger technique compared to the LP-LIF and flow-tube LIF method, but the number of instruments has quickly increased due to the commercial availability of detectors for pyrrole such as the PTR-MS instrument. Results of this campaign emphasise that careful instrument characterisation for the specific operational conditions are required in order to achieve accurate measurements. Future work should focus on improving its performances in terms of precision and limit of detection. In addition, the accuracy of measurements would improve if corrections could be lowered.

The results of this campaign demonstrate that all detection schemes that are currently applied to OH reactivity measurements give reasonable results for a range of chemical conditions which are relevant for ambient air measurements. These first comprehensive comparison campaigns were conducted to assess the current performance of the instruments. The results already led to the implementation of changes in some instruments to achieve better data quality. More work will be done in order to improve the instrument performance for issues that have been identified which currently limit the precision or accuracy of measurements. More comparison campaigns could help to further increase the trustability of measurements by conducting them in a formal, blind way and/or at even more realistic conditions with ambient air.

In the field, OH reactivity measurements are often used to identify unexplained reactivity from OH reactants that were not measured as individual species (Yang et al., 2016). Large unexplained reactivity (several 10 s^{-1}) was found in several field campaigns in biogenic environments, such as the boreal forest in Finland (Nölscher et al., 2012a) and rainforests (Edwards et al., 2013; Nölscher et al., 2016), as well as in urban environments in wintertime (e.g. Dolgorouky et al., 2012; Yoshino et al., 2012). Results here show that measurements by the LIF instruments are accurate. In these comparison campaigns, deviations that are seen mostly for CRM instruments for complex conditions involving large concentrations of terpenic compounds show the tendency for OH reactivity to be underestimated. Therefore, results do not indicate that high, unexplained reactivity values that were measured in previous field campaigns were due to measurement artifacts.

Data availability. Data are available on request from Hendrik Fuchs (h.fuchs@fz-juelich.de) and will be made available in the Eurochamp database (<http://www.eurochamp.org>).

Supplementary. The Supplement related to this article is available online at <https://doi.org/10.5194/amt-10-4023-2017-supplement>.

Competing interests. The authors declare that they have no conflict of interest.

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CHAPTER 6

Conclusions and future perspectives

Conclusions

In this doctoral project, total OH reactivity, the total atmospheric load of OH reactants, was used to study the influence of anthropogenic activity on reactive trace gases in two different contexts: (1) The indirect human impact of anthropogenic climate change and deforestation will lead to an increasing frequency of drought and heat events in the Amazon rainforest. This is thought to influence biogenic trace gas emissions and was investigated with total OH reactivity observations during an extreme El Niño event. (2) Total OH reactivity measured above the seaways around the Arabian Peninsula, dominated by anthropogenically emitted trace gases from ships and petrochemical activities, was used to examine regional ozone formation.

Through this thesis, it was shown that changes in the atmospheric reactivity can be expected by the predicted human-impacted increasing frequency of El Niño drought and heat events in the Amazon rainforest. The diel cycle of total OH reactivity above the pristine rainforest canopy during the abiotic stress conditions of an extreme El Niño event exhibited a striking difference to "normal" diel behavior. After the usual early afternoon OH reactivity maximum, a second, larger peak was observed during the sunset hours. The unattributed fraction of OH reactivity was, with up to 60 %, especially important in this evening peak. The sum of daytime reactivity was not altered compared to a normal dry season despite a larger modeled boundary layer height, indicating potentially enhanced emissions. A possible explanation for the increased sunset reactivity was found in stronger turbulent transport above the canopy caused by the changed meteorological conditions, combined with an additional, stress-related release of monoterpenes and other (unmeasured) BVOCs by plants.

In an environment of obvious human influence through shipping and oil/gas production, OH reactivity investigations helped explain the regional severe photochemical air pollution. Total OH reactivity measured around the Arabian Peninsula showed the dominance of anthropogenic emissions above the seaways in this region. Reactivity levels observed even in 100 km distance to the coasts were comparable to highly polluted urban areas such as Beijing. The extreme regional ozone concentrations could be explained by a favorable mixture of NO_x and VOCs combined with intense solar irradiation, causing rapid photochemical reactions. The latter led to a dominance of OVOC-attributed OH reactivity over other trace gas groups. This study also revealed the importance of quantifying an unusually wide range of OVOCs, including compounds with unidentified structure measured by PTR-ToF-MS, for reducing the unattributed reactivity fraction. Ozone versus OH reactivity correlation plots were found to be a valuable tool in identifying different chemical regimes with regards to ozone formation and loss. The good data coverage during these first shipborne OH reactivity measurements, even in rough sea, demonstrated the robustness of the CRM method.

The method-oriented part of this doctoral project was based on the need of robust, accurate measurements of total OH reactivity for understanding atmospheric photochemistry in the Anthropocene.

When the CRM method for total OH reactivity detection was developed, it was intended to become an accessible, uncomplicated technique that could ultimately be used at stations for standard air chemistry observations. As a part of this thesis, a new CRM instrument for long-term autonomous measurement of total OH reactivity was

successfully characterized and tested in Helsinki. Pseudo-1st-order deviations and interferences could be reproduced reasonably by a model of the reactor chemistry. Ozone and NO_x interferences increased the measurement uncertainty in this urban environment, but will not be relevant during the intended long-term deployment in the boreal forest. The total OH reactivity observed in winter in Helsinki was with an overall median of 7.6 s^{-1} at the lower end of worldwide urban observations. In the aftermath of this study, the tested device has successfully been deployed continuously for four months by the Finnish Meteorological Institute at the Hyytiälä boreal forest station in Finland (Praplan et al., 2019).

In the first comprehensive intercomparison campaign for total OH reactivity measurements, all available instrument types were deployed simultaneously at an atmospheric simulation chamber. Results showed that the CRM device is suited for a range of atmospheric mixtures (from isoprene-dominated to anthropogenic), but large deviations were seen in terpene-dominated and high NO conditions. Overall, the indirect CRM method had higher detection limits, lower accuracy and precision compared to the methods directly detecting OH decay. An ozone interference, which also impacted the size of the NO_2 interference, was discovered for the MPIC CRM. The HO_2 concurrently produced with OH and photolysis inside the reactor were identified as major sources of interferences and uncertainties. OH recycling through carbonyl oxidation and peroxy radical photolysis in the reactor was found to be a possible reason for underestimation of reactivity by CRM. The experiments also showed that inlet losses, especially for compounds with lower volatility, were important. Heating and a larger inlet diameter reduced these losses in the second part of the intercomparison. In conclusion, the intercomparison demonstrated that the CRM method is better suited for pristine than polluted environments, and emphasized the necessity of careful characterization of each CRM instrument and of further refinement of the CRM method.

Atmospheric OH reactivity in the Anthropocene: Future research perspectives

Despite its usefulness in the understanding of atmospheric reactant chemistry, directly measured total OH reactivity has not yet become a standard quantity in atmospheric chemistry studies. This is due to the fact that all available techniques are so far not commercially available and relatively complex to operate. The complexity of the CRM method lies in the number of corrections it requires. Through this doctoral project, it was found that the interfering OH recycling reactions caused by NO_x and ozone influence each other. Therefore, the characterization of a combined correction is recommended.

A reduction in corrections could be achieved by addressing the photolysis and the HO_2 production in the reactor. Attempts to reduce photolysis with a newly designed CRM reactor reduced the sensitivity and increased OH recycling interferences. A promising alternative would therefore be to produce OH via a different reaction, ideally without the need for a UV lamp and without the simultaneous production of HO_2 .

The sensitivity of the CRM method could be improved by measuring the product of reagent oxidation by OH instead of differences in the reagent level. However, endeavors to use reagents with a detectable oxidation product were so far not successful, because the reaction yields were too far below 100 % and the products underwent

further reactions. The search for a suitable reagent with a stable OH oxidation product remains a possible direction for future CRM research.

A prevailing issue of CRM is that, due to the pseudo-1-st-order deviation, knowledge of the relative composition of the air sample increases the accuracy of the results. This counteracts the original idea of delivering total OH reactivity values without the need for individual trace gas characterization. In the Helsinki CRM characterization study which is part of this thesis, a model was used to describe the chemistry inside the CRM reactor. It compared reasonably well with measured data, but relied on input from measurements (e.g. OH levels). A comprehensive CRM chemistry model that includes photolysis reactions would be a possibility to derive reliable corrections for different measurement conditions and reduce uncertainties.

Extreme drought and heat are expected to occur more often in the future in many regions of the world. However, the influence of such abiotic stress events on reactive plant emissions is still not well understood. Studies of the impact of drought, heat or oxidative stress on BVOC emissions are in most cases limited to laboratory conditions with a single stress factor and a single plant species. Therefore, further research about the impact of combined abiotic stress factors at an ecosystem level is necessary. This could be realized by long-term observations that catch natural events, or controlled studies in an enclosed ecosystem.

Studies of VOCs in the Amazon rainforest were so far conducted with PTR-Quadrupole-MS and offline GC sampling, and were therewith limited to relatively few compounds and/or coarse time resolution. The chemical compounds causing unattributed OH reactivity generally, and particularly during drought conditions, could be unraveled by long-term observation of a wide range of VOCs by PTR-ToF-MS. Especially BVOCs other than isoprene or monoterpenes could help explain the thus far unattributed fraction of OH reactivity. Additionally, oxygenated VOCs, possible products of the mono- and sesquiterpene primary emissions, may be important, because of the intense solar irradiation in the tropics, as was the case around the Arabian Peninsula. Flux measurements of a comprehensive range of VOCs and of OH reactivity would also be of great value for understanding the bidirectional emission and deposition rates in the tropical forest and untangle them from the influence of transport or dilution processes on observed concentrations.

The connection of total OH reactivity to ozone formation has been analyzed for some locations, e.g. in the Arabian Basin as part of this thesis, but links to particle formation, as another source of air pollution, have only been included in one study (Mogensen et al., 2011). If secondary organic aerosol formation could be constrained or the production rates defined using total OH reactivity, this would be a promising way to simplify the problem of the multitude of organic compounds contributing to particle formation.

With nearly 20 years of total OH reactivity measurements, the global coverage of such observations has increased rapidly. Still, the southern hemisphere is nearly a white spot on the OH reactivity map. Regarding measurements on moving platforms, only one ship and two airborne campaigns have been conducted to date. The necessity of total OH reactivity observations continues for constraining models and improving the holistic understanding of natural and human-driven reactive emissions and their feedbacks with atmospheric chemistry in the Anthropocene.

Appendices

APPENDIX A

Miscellaneous CRM experiments

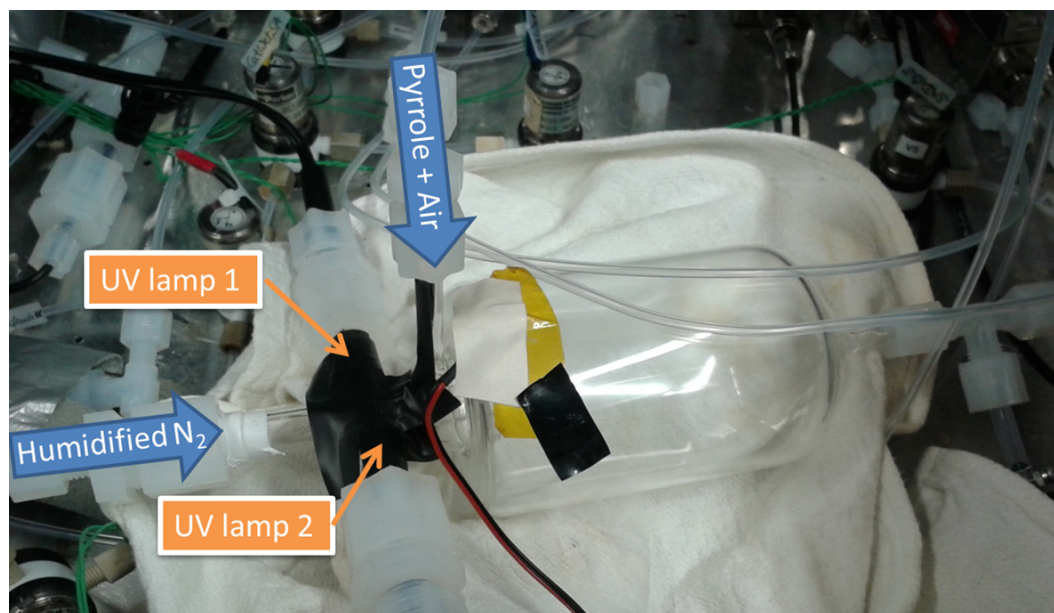


Figure A.1: Changed reactor design for CRM to reduce photolysis inside the reactor.

A.1 Photolysis reduction experiments

The current standard CRM reactor design (Sect. 1.2.3) is such that light from the UV pen-ray lamp enters the reaction volume, which causes photolysis of pyrrole and of ambient reactants. As the OH reactivity intercomparison (Chapter 5) showed, this is a source of inaccuracy, especially when the photolysis yields OH (e.g. from peroxy radicals; Hansen et al. (2017)). Additionally, the UV light entering the reactor causes the dependence of OH levels from ambient humidity and therewith the necessity for a C2 humidity correction (Sect. 1.2.3; Keßel, 2016).

A.1.1 Lamp tip coverage

A preliminary experiment to prevent UV light from entering the reactor was conducted by covering the tip of the pen-ray lamp with aluminum foil (as an inert material). Thereby, the light intensity within the reactor was strongly reduced, while the water vapor still traversed an illuminated pathway inside the nitrogen arm. However, the water photolysis within the nitrogen arm of the reactor was not sufficient to produce the OH radical levels needed for a distinct difference between C2 and C3 levels. Total OH reactivity measurements failed with this configuration. This experiment made clear that the formation of OH radicals inside the reaction volume contributes significantly to the total OH formation.

A.1.2 Low-photolysis reactor design

Based on the results from the abovementioned preliminary experiment, a new reactor design was developed for the CRM system. The main design goal was to decrease photolysis by reducing UV light intensity inside the reactor while producing sufficient levels of OH radicals. Therefore, two UV lamps in the new reactor were positioned vertically towards the nitrogen flow and the ambient air/pyrrole mixture was added in a position where the light scattering from the lamps is expected to be

low (Fig. A.1). Here, the formation of OH radicals is expected to take place before pyrrole and ambient air are added, whereas in the CRM standard reactor, significant amounts of OH are produced after the addition of reagent and ambient air to the flow (see Sect. A.1.1).

Characterization tests with this reactor showed several differences to the standard version:

- ♦ **Reduced photolysis.** Pyrrole photolysis was successfully reduced from 10–12 % (standard reactor) to 0.2–1 % (new reactor).
- ♦ **Decreased sensitivity.** Because of the distance between the locations of OH formation and reaction of OH with pyrrole or VOCs, the OH mixing ratio in the reactor was lower than in the standard reactor (20 ppb vs. 30–40 ppb). This causes less distinct steps between C2 and C3, and therefore degrades sensitivity (Fig. A.2a). On average from all experiments except three outliers, the reactivity necessary to cause a change of 1 ppb in the pyrrole signal was 13.3 s^{-1} for the new reactor and 11.2 s^{-1} for the standard reactor, a 19 % difference.
- ♦ **Lower necessary correction for deviation from pseudo-1st-order conditions** (Fig. A.2b). This may be due to the generally larger pyrrole/OH ratios caused by the decreased OH levels, but also to less interfering photolysis reactions of the reactants.
- ♦ **Larger NO and ozone interferences.** As shown in Figs. A.2c and A.2d, the decrease in C3 levels caused by OH recycling was significantly larger in the new reactor. This would require a larger correction for the NO_x and ozone interferences. The reason for this increased OH recycling may stem from a higher HO_2 concentration in the new reactor (from the slope of the ozone addition experiment, a factor of ≈ 2 can be deduced). HO_2 is not as rapidly lost on surfaces as OH, and so is transmitted more efficiently from the point of formation into the reaction cell than of OH. This could cause larger HO_2/OH ratios in the new reactor.

Attempts were made to reduce the HO_2/OH ratio by adding ozone to the flow of humidified nitrogen. However, the oxygen produced from the reaction of ozone with HO_2 can recycle HO_2 already in the nitrogen arm of the reactor due to the presence of H radicals from water photolysis. The reaction between HO_2 and ozone, yielding OH and oxygen (eq. A.1), is three orders of magnitude slower than the formation of HO_2 (eq. A.2).



with $k_1 = 2.0 \cdot 10^{-15} \text{ molec cm}^{-3} \text{ s}^{-1}$ and $k_2 = 1.0 \cdot 10^{-12} \text{ molec cm}^{-3} \text{ s}^{-1}$ (IUPAC, 2018).

Despite the successfully reduced photolysis in the newly designed reactor, the downsides outweighed its advantages for the currently used CRM OH production chemistry and reagent. The reduced sensitivity and the apparently larger HO_2 concentrations in the reaction volume would cause larger measurement uncertainties than the standard reactor.

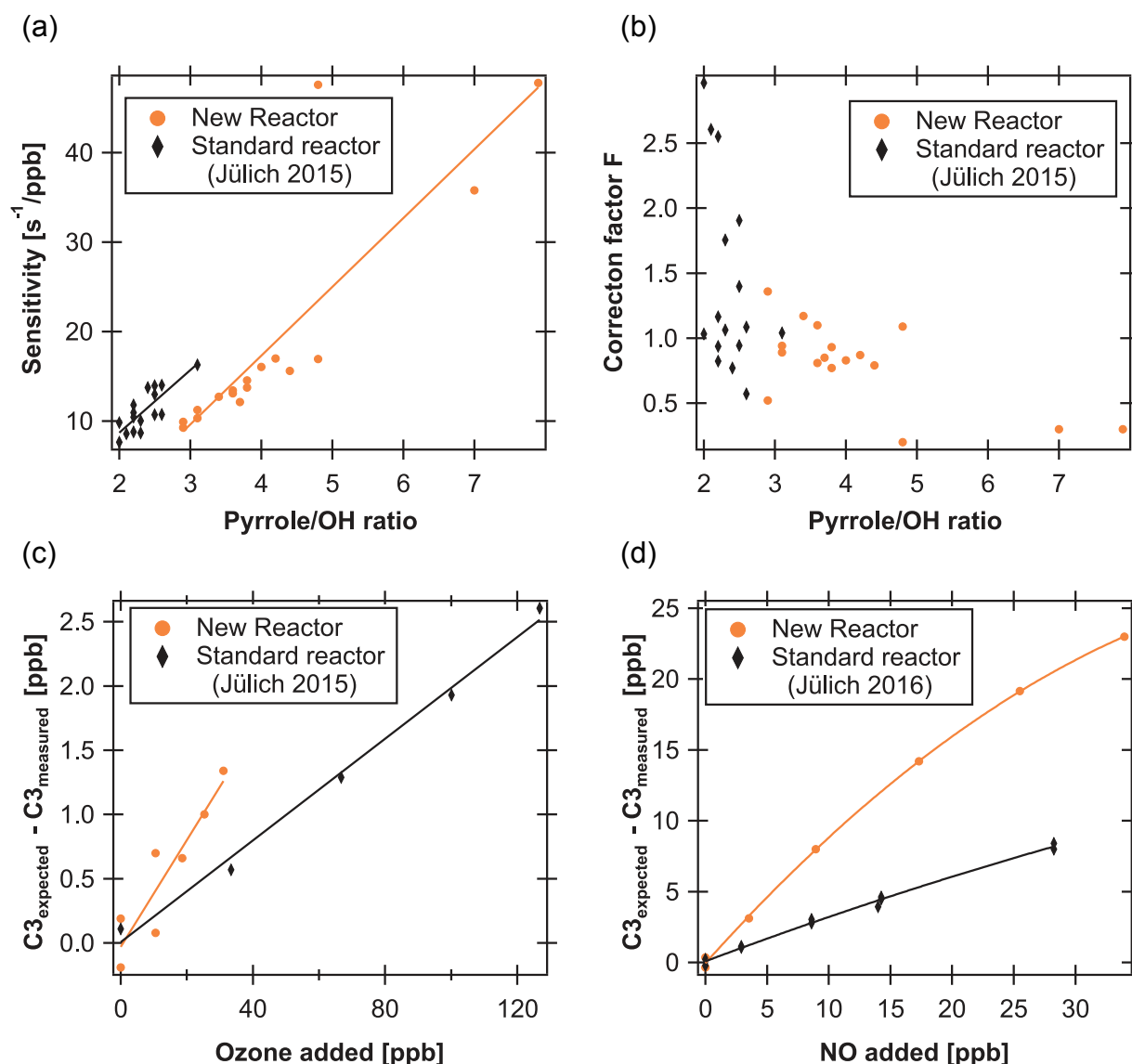


Figure A.2: (a) Sensitivity expressed as reactivity [s^{-1}] per change in pyrrole signal [ppb], shown for the new reactor design and the standard reactor design. Linear regression results: For the new reactor $r^2 = 0.72$ ($y = -13.5 + 7.7x$), for the standard reactor $r^2 = 0.65$ ($y = -5.3 + 7.0x$).

(b) Correction factor F representing expected vs. measured OH reactivity (see Sect. 1.2.3) for deviation from pseudo-1st-order conditions at different pyrrole/OH ratios, shown for the new reactor and the standard CRM reactor. Trace gases used to derive the correction factors were isoprene, propene and propane.

(c) Difference between expected C3 (from calculated OH reactivity) to measured C3 in ppb of pyrrole for addition of different mixing ratios of ozone, shown for the new and the standard reactor. Linear regression: For the new reactor $r^2 = 0.84$ ($y = -0.03 + 0.04x$), for the standard reactor $r^2 = 0.99$ ($y = 0.007 + 0.02x$).

(d) Difference between expected C3 (from calculated OH reactivity) to measured C3 in ppb of pyrrole for addition of different mixing ratios of nitrogen oxide, shown for the new and the standard reactor. Polynomial regression: For the new reactor $y = 1.0x - 0.009x^2$, for the standard reactor $y = 0.3x - 0.001x^2$.

A.2 CRM product detection

Currently, the CRM method relies on the detection of reagent (pyrrole) concentration changes. The detection of a change in an already high signal decreases precision. This causes the relatively high detection limit and low sensitivity of the method compared to others (see Chapter 5). Therefore it would be advantageous to detect a product of the reaction $\text{OH} + \text{reagent}$. The OH oxidation of pyrrole does not yield a single, measurable product. PTR-ToF-MS measurements showed that pyrrole rather seems to be broken down to a multitude of unidentified small fragments. Two candidate molecules for product detection, acetylacetone and cyclohexane, were tested.

Acetylacetone (pentane-2,4-dione) was quickly found to not yield the expected product (3-hydroxy-2,4-pentanedione). Instead, methyl glyoxal ($m/z = 73$) and acetic acid ($m/z = 61$) could be observed as OH oxidation products (Fig. A.3). In addition to these two compounds, literature suggests 63 % of "other" products (Zhou et al., 2008). For a successful CRM product detection approach, a reproducible, close to unity yield of one product would be necessary. Therefore, acetylacetone was rejected as a CRM reagent.

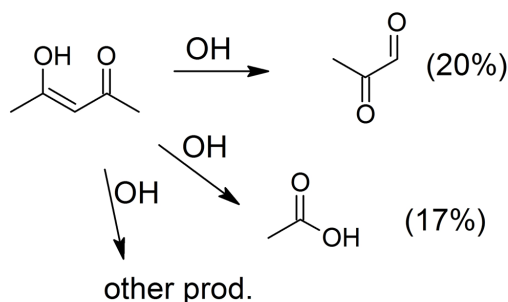


Figure A.3: Reaction products of acetylacetone with OH (Zhou et al., 2008). The reaction rate coefficient is $k = 1.12 \cdot 10^{-12} \text{ molec cm}^{-3} \text{ s}^{-1}$ (acetylacetone + OH $\longrightarrow$ products; Dagaut et al. (1988)).

Cyclohexane is oxidized to cyclohexanone by OH (Fig. A.4). When cyclohexane from a standard gas cylinder (Westfalen AG, Münster, Germany) reacted with OH in the CRM reactor, cyclohexanone was detected by PTR-MS at $m/z = 99$. However, the yield was low, likely due to the further reaction of cyclohexanone with OH ($k = 6.39 \cdot 10^{-12} \text{ molec cm}^{-3} \text{ s}^{-1}$; Dagaut et al., 1988). In order to apply the CRM equation, the condition $[\text{cyclohexanone}] = [\text{OH}]$ would have to be met. A large surplus of cyclohexane was required to reach this concentration equality. The surplus resulted in failure of the competition with other VOCs, leading to an underestimated OH reactivity. If cyclohexane were to be used as a CRM reagent, the yield had to be known, but would cause the necessity of an additional correction factor, which increases uncertainty.

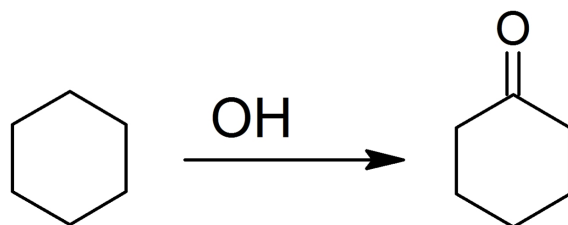


Figure A.4: Reaction of cyclohexane with OH. The reaction rate coefficient is $k = 6.97 \cdot 10^{-12} \text{ molec cm}^{-3} \text{ s}^{-1}$ (Atkinson, 2003).

The CRM product detection experiments showed that a suitable OH oxidation product would need to have a near-unity yield and should be stable instead of reacting further with OH. An alternative way for increasing the CRM precision would be using a reagent with a slower reaction rate coefficient with OH than pyrrole. With acetaldehyde, this has been shown to improve the detection limit, but was not further pursued due to its occurrence in ambient air and OH recycling (Keßel, 2016).

A.3 Combined NO₂ and ozone correction

The OH recycling interference during C3 mode caused by the reaction of ambient NO or ozone with HO₂ has been discussed in Sect. 1.2.3. The usual approach to quantifying the necessary corrections for NO₂, NO or ozone is the individual addition of one of these compounds to the CRM reactor. In real-world ambient air, all three compounds usually occur as a mixture. As a first step towards a more realistic interference test, NO₂ (from a calibrated gas cylinder, Westfalen AG, Münster, Germany) and ozone (generated by a Sonimix 6000 Modular Calibration System, LN Industries, Geneva, Switzerland) were added to the CRM reactor simultaneously. Because ozone levels are usually higher than NO₂ levels in ambient air, the aim of the experiment was to find an NO₂ correction on an ozone background.*

It was found that it is possible to use the ozone correction derived from an ozone-only test and apply it to calculate the deviation from expected C3 pyrrole levels when NO₂ is added. The resulting NO₂ correction is smaller than the NO₂-only correction (Fig. A.5). This is an important finding because applying an NO₂-only correction to data from ambient, ozone-containing air could lead to an overestimated total OH reactivity. The reason for the decreased effect of NO₂ may be the reaction of NO₂ with ozone:



This reaction, although it is relatively slow ($k = 3.5 \cdot 10^{-17}$ molec cm⁻³; IUPAC, 2018) could leave less NO₂ available for photolysis, leading to lower amounts of NO available to recycle OH.

With the findings from this experiment, the NO_x corrections for CRM could be improved. They were applied to the data from the 2016 Jülich intercomparison. More work is necessary to understand the combined effect of OH-recycling ambient reactants in the complex chemical situation of the CRM reactor.

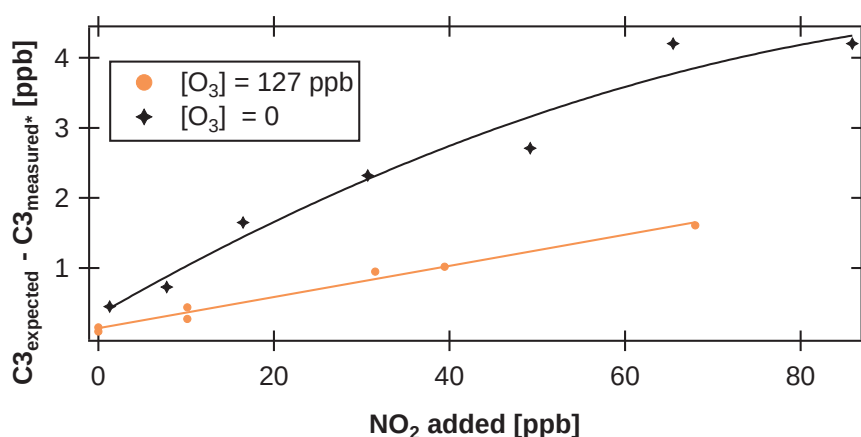


Figure A.5: NO₂ interference with an added background of [O₃] = 127 ppb and without ozone added. C3_{expected} is the calculated pyrrole level from the combined OH reactivity of ozone and NO₂. C3_{measured}* represents the pyrrole level measured in C3 mode, corrected for the ozone background. Linear regression for [O₃] = 127 ppb: $y = 0.02x + 0.14$, $r^2 = 0.98$. Polynomial regression for [O₃] = 0: $y = 0.33 + 0.07x - 0.0003x^2$.

*Note that this ozone background is in addition to the ozone produced constantly inside the reactor. The constantly produced ozone does not interfere with the measurements because it stays unchanged over C2 and C3 modes.

Abbreviations and Acronyms

AQABA	Air Quality and Climate Change in the Arabian Basin campaign
ATTO	Amazon Tall Tower Observatory (Brazil)
BVOC	Biogenic volatile organic compound
CIMS	Chemical Ionization Mass Spectrometer
cps	counts per second
CRM	Comparative Reactivity Method
DWD	German Weather Service
ENSO	El Niño Southern Oscillation
GC-FID	Gas Chromatography-Flame Ionization Detector
GC-PID	Gas Chromatography-Photo-Ionization Detector
HO ₂	Hydroperoxyl radical
HO _x	Sum of HO ₂ and OH
ISOPOOH	Isoprene hydroxy hydroperoxides
FEP	Fluorinated ethylene propylene
FMI	Finnish Meteorological Institute (Helsinki, Finland)
FZJ	Forschungszentrum Jülich
k	Reaction rate coefficient
k _{OH}	OH reactivity
LIF	Laser-Induced Fluorescence
LOD	Limit of detection
LP-LIF	Laser-photolysis-Laser Induced Fluorescence
LSCE	Laboratoire des Sciences du Climat et de l'Environnement (Paris)
LT	Local time
MACR	Methacrolein (2-methylprop-2-enal)
MDOUAI	École nationale supérieure des Mines-Télécom de Lille-Douai
MFC	Mass flow controller
MPIC	Max Planck Institute for Chemistry
MVK	Methyl vinyl ketone (but-3-en-2-one)
ncps	normalized counts per second
NO _x	Sum of nitrogen oxide (NO) and nitrogen dioxide (NO ₂)
NMHC	Non-methane hydrocarbon
OD	Outer diameter
OH	Hydroxyl radical
OVOC	Oxygenated volatile organic compound
PAR	Photosynthetically active radiation
ppb	parts per billion (= nmol mol ⁻¹ = 10 ⁻⁹ mol mol ⁻¹)
ppt	parts per trillion (= pmol mol ⁻¹ = 10 ⁻¹² mol mol ⁻¹)
PSU	Pennsylvania State University (USA)

PTFE	Polytetrafluoroethylene
PTR–MS	Proton Transfer Reaction–Mass Spectrometry
PTR–ToF–MS	Proton Transfer Reaction–Time of Flight–Mass Spectrometry
UTC	Universal Coordinated Time
UV	Ultraviolet (wavelength: 10–380 nm)
RH	Relative humidity
R_{total}	Total OH reactivity
SAPHIR	Simulation of Atmospheric Photochemistry in a Large Reaction Chamber
SOA	Secondary Organic Aerosol
VOC	Volatile organic compound

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