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Impact of COVID-19 Lockdown on HOx Chemistry in the Upper Troposphere

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Abstract

The hydroxyl radical (OH) is the primary oxidizing agent in the atmosphere and plays a crucial role in initiating the removal of pollutants like carbon monoxide (CO), greenhouse gases like methane (CH_4) and volatile organic compounds (VOCs), which serve as a precursor to tropospheric ozone. In the spring of 2020, the COVID-19 pandemic and lockdowns caused a drastic reduction in emissions from transportation and industry. This provided a unique opportunity for the airborne BLUESKY campaign to investigate these reductions and their impact on atmospheric chemistry, particularly changes in the oxidation capacity in the upper troposphere. High Altitude Long Range (HALO) aircraft equipped with 14 different instruments measured trace gases, aerosols, and meteorological parameters. OH and HO_2 concentrations were measured using the Laser-Induced Fluorescence – Fluorescence Assay by Gas Expansion (LIF-FAGE) based HORUS instrument.

The instrument was calibrated using the All Pressure Altitude-based Calibrator for HOx Experimentation (APACHE) with improvements from the previous version. The total measurement uncertainty for OH and HO_2 at 1σ interval is 30% and 32%, respectively. The measured OH and HO_2 data, compared with the steady-state CAABA MECCA box model, showed a high correlation of more than 90% and 80% respectively. In the upper troposphere, the average OH mixing ratio was recorded at 0.042 \pm 0.02 (1 σ) pptv, while the HO₂ mixing ratio stood at 21 ± 5 (1 σ) pptv. The measured data from the BLUESKY campaign was compared against another campaign named HOOVER II in order to study the effect of the COVID-19 lockdown on the atmosphere. The comparison indicated a 2-6 fold reduction in OH production during the BLUESKY period in the upper troposphere above 7 km. This significant decline primarily stemmed from decreased NO levels resulting from reduced air traffic and also due to metrological effects. This decline in OH production during BLUESKY compared to HOOVER II affected OH recycling efficiency by 30 - 60% and reduced the methane oxidation rates in the upper troposphere by 50 - 60%. These findings point to a possible future scenario where lowering NOx concentrations in the upper troposphere as part of climate action plans.

Zusammenfassung

Das Hydroxylradikal (OH) ist das primäre Oxidationsmittel in der Atmosphäre und spielt eine entscheidende Rolle bei der Beseitigung von Schadstoffen wie Kohlenmonoxid (CO), Treibhausgasen wie Methan (CH_4) und flüchtigen organischen Verbindungen (VOC), die als Vorläufer des troposphärischen Ozons dienen. Im Frühjahr 2020 führten die COVID-19-Pandemie und die anschließenden Abriegelungen zu einer erheblichen Verringerung der Emissionen aus dem boden- und luftgestützten Verkehr und aus der Industrie. Dies ergab die einzigartige Gelegenheit die resultierenden Veränderungen in der atmosphärischen Zusammensetzung zu untersuchen. Im Rahmen der BLUESKY Kampagne wurde auf dem Forschungsflugzeug HALO mit 14 verschiedenen Messinstrumenten Spurengase, Aerosole und meteorologische Parameter gemessen. Die OH- und HO_2 -Konzentrationen wurden mit dem auf LIF-FAGE (Laser-Induced Fluorescence - Fluorescence Assay by Gas Expansion) basierenden HORUS-Instrument gemessen.

Das Instrument wurde mit dem All Pressure Altitude-based Calibrator for HOx Experimentation (APACHE) kalibriert, der gegenüber der vorherigen Version verbessert wurde. Die Gesamtmessunsicherheit für OH und HO2 im 1σ -Intervall beträgt 30% bzw. 32%.Die gemessenen OH- und HO2-Daten, konnten dem Box Modell CAABA/MECCA mit einer hohen Konsistenz und Übereinstimmung von 80-90% reproduziert werden. In der oberen Troposphäre wurde ein durchschnittliches OH-Mischungsverhältnis von $0,042\pm0,02$ (1 σ) pptv gemessen, während das HO_2 -Mischungsverhältnis bei 21 ± 5 (1 σ) pptv lag. Die Messdaten der BLUESKY-Kampagne wurden mit einer anderen Kampagne namens HOOVER II verglichen, um die Auswirkungen der COVID-19-Abriegelung auf die Atmosphäre zu untersuchen. Der Vergleich ergab, dass die OH-Produktion während des BLUESKY-Zeitraums in der oberen Troposphäre oberhalb von 7 km um das 2-6 fache abnahm. Dieser signifikante Rückgang war in erster Linie auf verringerte NO-Konzentrationen zurückzuführen, die sich aus dem verringerten Flugverkehr ergaben, aber auch auf meteorologische Effekte. Dieser Rückgang der OH-Produktion während BLUESKY im Vergleich zu HOOVER II beeinträchtigte die OH-Recycling-Effizienz um 30 - 60% und verringerte die Methanoxidationsraten in der oberen Troposphäre um 50 - 60%. Diese Ergebnisse deuten auf ein mögliches zukünftiges Szenario hin, in dem die Senkung der NOx-Konzentrationen in der oberen Troposphäre als Teil von Klimaschutzplänen vorgesehen ist.

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Chapter 1

The Atmosphere, the COVID-19 Pandemic and the Global Air Quality

1.1 The Earth's Atmosphere

The Earth's atmosphere, despite its relatively small vertical extent ($\approx 1\%$) compared to the planet's radius, plays a vital role in supporting life. It is structured into various layers, each characterized by distinct thermal properties, ionization levels, and underlying physical processes. These factors also influence the composition of the atmosphere at different altitudes. A schematic representation of the vertical profile of Earth's atmosphere is shown in Figure 1.1.

The vertical arrangement of the atmosphere is primarily defined by its temperature profile, marked by distinct boundaries known as "pauses." The lowest layer, the troposphere, is where the temperature decreases with altitude due to adiabatic expansion and compression of air masses driven by solar radiation. This leads to the formation of the tropopause, typically around 16 km in the tropics and 10 km at higher latitudes. Additionally, infrared radiation emitted by water vapour causes cooling in the upper troposphere (Marshall & Plumb, 2008).

Within the troposphere, there are two main regions: the free troposphere and the atmospheric boundary layer. The boundary layer, spanning approximately 1-3 km above the surface, experiences direct influences from surface friction and momentum exchange. It comprises layers such as the molecular viscous layer, the Prandtl layer dominated by turbulent diffusion, and the Ekman layer, where wind direction transitions from surface winds to geostrophic winds due to pressure gradient and Coriolis force interactions (Marshall & Plumb, 2008).

The next layer, the stratosphere, exhibits contrasting thermal conditions compared to the troposphere. While the lower stratosphere is cooled by water vapour at the tropopause, the upper layers are heated by solar radiation absorbed by ozone, resulting in a temperature increase with altitude peaking around 50 km. Beyond the stratosphere lies the mesosphere, extending up to 85 km, where temperature decreases with altitude similar to the troposphere, culminating in the coldest point, the mesopause. Above the mesopause lies the thermosphere, where temperatures rise significantly, reaching up to 1500 K due to the absorption of solar UV radiation by oxygen (Marshall & Plumb, 2008).



Figure 1.1: Schematic representation of the vertical structure of Earth's atmosphere. Taken from (Marshall & Plumb, 2008).

1.2 The COVID-19 Pandemic and the Global Air Quality

The onset of COVID-19 in late 2019 swiftly evolved into a worldwide health crisis, prompting governments to enact unprecedented measures. Among these measures, lockdowns became a primary strategy to mitigate the spread of the virus, impacting numerous sectors, including the aviation industry. However, an unexpected consequence of these lockdowns was the notable improvement in global air quality, offering a glimmer of hope amid the challenging circumstances (Saha et al., 2022; Venter, Aunan, Chowdhury, & Lelieveld, 2020).

COVID-19, stemming from the SARS-CoV-2 virus, was officially declared a pandemic by the WHO in March 2020, prompting governments worldwide to implement varying degrees of lockdowns. These measures aimed to limit virus transmission by enforcing social distancing, implementing travel restrictions, and mandating remote work, among other strategies.



Figure 1.2: Seven days averaged air traffic and COVID-19 cases in EUROPE from 2019 to 2021. The red box indicates the period when the BLUESKY campaign took place. Taken from (E. C. Report, 2021)

1.2.1 Silent Skies and Empty Roads: A World on Pause

The aviation industry, vital for global connectivity, faced unprecedented challenges due to lockdowns. With plummeting passenger demand and safety concerns, airlines were forced to cancel flights, and ground fleets, and implement cost-saving measures. Moreover, the aviation supply chain, including manufacturers and airports, felt the ripple effects of reduced demand, resulting in scaled-back production and operational disruptions. The IATA estimated a 66% decline in global air passenger demand in 2020, leading to substantial revenue losses. Figure 1.2 shows the reduction in air traffic during the first COVID-19 lockdown in 2020 March-April as per European Commission report 2021 (E. C. Report, 2021). As per the report, in Europe, the number of flights decreased by 55.2% in 2020 compared to pre-COVID times. During the peak of the initial nationwide lockdowns in various countries around the world, a comparable decrease in road traffic of up to 90% was observed, primarily occurring towards the end of March and the beginning of April 2020. The magnitude of this reduction in road traffic was influenced by the respective government's measures in place.

1.2.2 Clearing the Air: The surprise benefits and the rare opportunities

Despite disruptions, COVID-19 lockdowns brought about significant improvements in global air quality. Reduced industrial activity, traffic, and aviation emissions led to declines in pollutants like *NO*₂, *SO*₂, CO, and particulate matter (PM). Satellite data and ground monitoring stations confirmed substantial reductions in pollution levels worldwide. These

improvements translated into better air quality metrics, particularly in megacities notorious for poor air quality. From the end of March 2020 to the beginning of June 2020, this specific timeframe presented a distinct opportunity for scientists globally to examine the changes and consequential effects of reduced emissions on local and global atmospheric properties.

Guevara et al. (2021) studied the reductions in primary emissions due to the COVID-19 lockdowns in Europe using the reduction factors based on open-access and near-realtime measured activity data from a wide range of information sources. The study from Guevara et al. (2021) showed that during the strictest phase of lockdown measures (end of March till the end of May 2020), it's estimated that NOx emissions decreased by an average of 33%, Non-Methane Volatile Organic Compounds (NMVOCs) by 8%, SOx by 7%, and $PM_{2.5}$ by 7% across the EU-30 region (EU-28 plus Norway and Switzerland). Road transport accounted for over 85% of the reductions in all pollutants except SOx. In countries like Italy, France, and Spain, where lockdown measures were particularly stringent, reductions were even more pronounced, reaching 50% for NOx, 14% for NMVOCs, 12% for SOx, and 15% for $PM_{2.5}$.

Another study conducted by Voigt et al. (2022) using measurement data from two onboard aircraft campaigns named BLUESKY and satellite data between May 16 to June 9 2020, also revealed similar results. According to Voigt et al. (2022), during the initial phase of lockdown, significant reductions (ranging from 10% to 50%) in tropospheric NO₂ were observed over industrialized continental and urban areas, as well as in major city outflow regions, as indicated by data from TROPOMI and GOME satellites. Analysis of tropospheric NOy and CO profiles over Frankfurt on May 28, 2020, compared to climatological data from 2004 to 2015, revealed notable reductions (30% to 40%), confirming the impact of decreased emissions on these pollutants. Additionally, measurements of sulfur species, including DMS (Dimethyl Sulphate $(CH_3)_2S$), SO2, H_2SO_4 , and sulfate aerosols, enabled investigation into the sulfur budget in the upper troposphere and lower stratosphere, which was still affected by the aftermath of the Raikoke volcanic eruption in June 2019 and subsequent smaller eruptions. Observations also showed substantial reductions in aerosol fine mode number concentrations and mass, particularly below 5 km, compared to previous European summer campaigns and the MOZAIC dataset. Decreased organic aerosol particulates aloft suggested that lower emissions of volatile organic compounds (VOCs) from the surface may have contributed to reduced production of secondary organic aerosols in the free troposphere. Furthermore, the dramatic 80% decline in air traffic resulted in significant reductions in contrail cover and associated radiative forcing compared to air traffic levels in 2019.

Some of the similar studies conducted locally and globally can be found in (Nussbaumer et al., 2022; Hamryszczak et al., 2022; Zauner-Wieczorek et al., 2022; Zhang et al., 2022;

Mertens et al., 2021; Tavella & da Silva Júnior, 2021; Reifenberg et al., 2022; Peng et al., 2022; Qu et al., 2022; Stevenson, Derwent, Wild, & Collins, 2021).

The current study aims to find out the effect of the COVID-19 lockdown on HOx chemistry in the upper troposphere by comparing the data obtained from the airborne atmospheric measurement campaign called BLUESKY which was during the first national-wide lockdown period (May 20-June 9 2020) with another airborne campaign along the similar location named HOOVER II during summer 2007. The thesis describes the basics of HOx chemistry and the measurement technique in chapter 2 and chapter 3 respectively. Chapter 4 describes the calibration procedure for the HOx measurement instrument HydrOxyl Radical Measurement Unit based on fluorescence Spectroscopy or in short "HORUS". Chapter 5 describes the HOx data obtained during the BLUESKY campaign and its comparison with a steady state box model calculation. This chapter also describes the different HOx production and loss channels. Chapter 6 will give an insight into the effect of reduced emissions during the COVID-19 lockdown on the HOx chemistry and the Earth's atmosphere's oxidation capacity, followed by a conclusion and outlook.

Chapter 2

HOx Chemistry

2.1 HOx sources, recycling and sinks

Each year, megatons of trace gases from natural and anthropogenic sources are emitted into the atmosphere. These trace gases go through various oxidation processes to produce products that can be easily removed by wet or dry depositions. The hydroxyl (OH) radicals, also known as the "detergent of the atmosphere," are the main daytime oxidising agent in our atmosphere and serve as the primary purifying agent (Lelieveld, Dentener, Peters, & Krol, 2004; Levy, 1971).

The solar ultraviolet (UV) radiation, the O_3 and water vapour (H₂O) concentrations control the primary formation of OH in the troposphere. When O_3 is photolysed at UV wavelengths, electronically excited O(¹D) atoms are produced and quenched by air molecules O(³P) ground state, which subsequently combines with O_2 to produce ozone. A small amount of O(¹D) reacts with water vapour to form OH. The photolysis of peroxides represents, typically, a secondary source of OH since they are formed during the oxidation process of volatile organic compounds VOCs and radical recombination. A comprehensive chemical pathway of HOx production and losses is shown in figure 2.1 and table 2.1.

$$O_3 + hv(\lambda < 320nm) \to O_2 + O(^1D)$$
 (2.1)

$$O(^{1}D) + M \to O(^{3}P) + M$$
 (2.2)

$$O(^{3}P) + O_{2} + M \to O(^{3}P) + M$$
 (2.3)

$$O(^{1}D) + H_{2}O \to 2OH \tag{2.4}$$

In the lower troposphere (below < 4km), where water vapour mixing ratios are high ($\approx 10^3 molmol^{-1}$), the primary production channel for OH is dominant. However, in regions of high pollution, rich in NOx, and in the upper troposphere above 8 km altitude where water vapour mixing ratios drop to around $10^{-5}molmol^{-1}$, this primary production channel for OH likely diminishes in significance. In such conditions of the upper troposphere, other sources of OH and HO_2 , like the photolysis of peroxides and aldehydes (e.g., formaldehyde, HCHO), often assume a more prominent role in the initial production of HOx.



Figure 2.1: Simplified illustration of HOx chemistry. The green represents the primary OH and HO_2 production, the black represents the cycling reaction and the red represents the HOx loss channel. Figure taken from(Marno, 2021).

Through catalytic cyclic reactions with nitric oxide (NO), the hydroperoxyl radical (HO₂) can create OH (table 2.1, reaction 7). HO₂ has a background atmospheric concentration roughly in the order 10^8 molecules/ cm^3 compared to 10^6 molecules / cm^3 of OH. Besides that HO₂ also has a much longer atmospheric lifetime, which can last for several minutes compared to the very short lifetime of OH about a second. Due to the lifetime of OH and HO_2 and their strong chemical coupling, a fast equilibrium is reached, and as a result, they act as one another's buffer, which is crucial for the oxidation capacity of the atmosphere (Lelieveld, Gromov, Pozzer, & Taraborrelli, 2016).

The fate of radical recycling depends on whether the reaction channel shown in Figure 2.1 propagates or terminates. One of the most significant processes in HO_X cycling is the OH-initialized oxidation of CO. OH can form HO₂ by a fast reaction with CO and O₃ (table 2.2, reaction 9-10). The reaction with CO involves the loss of the OH radical, which results in the formation of CO₂ and a hydrogen atom (H). The H atom then quickly interacts with O₂ to make HO₂. Other reactions that produce HO₂ from OH are given in table 2.2. The HO₂ that formed from the above-mentioned reactions can either recycle back OH by reaction with O₃ or NO or cease the HOx recycling by radical-radical reactions or by direct formation of acids such as HONO, HNO₃, and HNO₄.

The reaction of NO with HO_2 is of larger importance since it produces NO_2 , which rapidly photodissociates, releasing an oxygen atom in its ground state that goes on to generate ozone which aids in maintaining the HOx cycle. This implies that the presence of NOx (NO+ NO_2) becomes the limiting factor of OH recycling and O_3 formation in the troposphere.

The oxidation of volatile organic compounds (VOCs) by the hydroxyl radical (OH) is a significant pathway for HO_2 recycling in the atmosphere. One of the most abundant VOCs in the atmosphere is methane (CH_4), which has a relatively long lifetime of around 9 years. In the process of CH_4 oxidation by OH, the methane molecule reacts with an OH radical to form a methylperoxy radical (CH_3O_2). This methylperoxy radical can further react with nitrogen oxides (NO) to produce a methoxy radical (CH_3O). The methoxy radical then rapidly reacts with oxygen (O_2) to produce hydroperoxyl radical (HO_2) and formaldehyde (HCHO). Interestingly, this pathway involving HCHO can lead to an increase in the overall production of HOx radicals by a median factor of 1.7 (Logan, Prather, Wofsy, & Mcelroy, 1981). Finally, the completion of the HOx cycle occurs when OH is formed back from reactions 7 and 8. Other channels of HOx production and loss due to VOC oxidations and peroxy nitrate (PAN) can be found in (Jenkin, Young, & Rickard, 2015) and (E. V. Fischer et al., 2014) respectively.

No:	Reactions	Remark
1	O_3 +h ν (λ <340nm) \rightarrow O(¹ D)+O ₂	
2	$O(^{1}D)$ + $H_{2}O \rightarrow 2OH$	
3	H_2O_2 + $h\nu$ (λ <557nm) \rightarrow 2OH	OH primary production
4	ROOH+ $h\nu$ (λ <360nm) \rightarrow OH + RO	
5	HONO+ $h\nu(\lambda < 380nm) \rightarrow OH + NO$	
6	Alkene + $O_3 \rightarrow \alpha OH$ + products	
7	$NO\text{+}HO_2 \rightarrow NO_2\text{+}OH$	
8	$O_3\text{+}HO_2 \rightarrow 2O_2\text{+}OH$	Cycling reactions (HO ₂ into OH)
9	$OH{+}CO \rightarrow HO_2{+}CO_2$	
10	$OH{+}O_3 \rightarrow HO_2{+}O_2$	
11	$OH\text{+}HCHO \rightarrow HO_2\text{+}H_2O\text{+}CO$	Cycling reactions (OH into HO_2)
12	$OH\text{+}H_2SO_4 \rightarrow HO_2\text{+}H_2O\text{+}SO_4^-$	
13	$OH{+}SO_2 \rightarrow HO_2{+}H_2SO_4$	
14	$H{+}O_2{+}M \to HO_2{+}M$	
15	$HO_2\text{+}HO_2 \rightarrow H_2O_2\text{+}O_2$	
16	$HO_2 \text{+}RO_2 \rightarrow ROOH \text{+}O_2$	
17	$HO_2\text{+}NO_2 \rightarrow HNO_4$	
18	$OH+NO_2 \rightarrow HNO_3$	HO_x sink
19	$OH+NO \rightarrow HONO$	
20	$OH+OH \rightarrow H_2O + O^3P$	
21	$OH\text{+}CH_4 + O_2 \rightarrow CH_3 + H_2O$	

Table 2.1: Important atmospheric sources, sinks and the recycling reactions of OH and *HO*₂.

Chapter 3

The HORUS

Due to its short lifetime (< 1 second for OH) and high reactivity, hydroxyl radicals are extremely difficult to measure and require instruments with fast detection and minimal wall losses. Moreover, during daytime, OH concentrations can often be relatively low, typically averaging around 10^5 to 10^6 molecules per cubic centimetre. In contrast, the HO_2 radical normally exhibits concentrations about 100 times higher than OH and has a lifespan in the atmosphere ranging from seconds to minutes. Given the atmospheric behaviour of HOx, a highly sensitive instrument is needed for measuring HOx species. A brief description of some of the already existing measurement techniques is given below:

3.1 HOx Measurement Techniques

Chemical Ionization Mass Spectroscopy (CIMS) serves as an indirect method for determining atmospheric OH and HO_2 mixing ratios. In this technique, atmospheric OH is measured by titrating sampled air using ${}^{34}SO_2$, leading to the generation of $H_2^{34}SO_4$, which is subsequently measured. The produced H_2SO_4 is then ionized through a charge transfer reaction with nitrate ions (NO_3^-). Typically, NO_3^- ions exist primarily as a chemical complex with HNO_3 or H_2O . The resulting $H_2^{34}SO_4^- \bullet HNO_3$ chemical complex undergoes fragmentation within a collision chamber, and the subsequent fragments are detected using mass spectrometry. The concentration of measured $H_2^{34}SO_4^-$ ions correlates directly with the concentration of atmospheric OH that took part in the titration reactions. Because of the relatively low natural occurrence of ${}^{34}S$ isotopes, they can be readily distinguished from atmospheric H_2SO_4 and the $H_2^{34}SO_4$ generated from OH titrations. Furthermore, propane (C_3H_8) is added before sampling to eliminate atmospheric OH for accounting chemical background (Eisele et al., 1997; Kukui, Ancellet, & Bras, 2009; Petäjä et al., 2009).

Similarly, the HO_2 and RO_2 radicals are measured via chemical conversion to OH by adding NO. HO_2 react with NO to form OH and NO_2 and similarly, the reaction of RO_2 with NO also creates HO_2 . The key distinction between the atmospheric OH detection and the detection of HO_2/RO_2 using CIMS is the absence of the need for isotopically labelled

 SO_2 when measuring HO_2 and RO_2 . Due to the atmospheric concentrations of HO_2 and RO_2 being approximately 100 times higher than that of OH, the background interference from atmospheric H_2SO_4 is minimal. Similar to other multi-tier chemical reaction-based approaches for trace gas detection, the primary uncertainties in this technique come from the reaction rate constants. For OH and HO_2 measurements, the standard detection limits range from $1 - 2 \cdot 10^5$ molecules cm^{-3} , with a time resolution of 5 minutes and $\approx 7 \cdot 10^5$ molecules cm^{-3} with an integration time of 1 minute respectively (Heard & Pilling, 2003).

Differential optical absorption spectroscopy - DOAS works on the principle that every molecule absorbs light of different wavelengths and the concentration of that particular species is obtained by measuring the intensity before ($I_0(\lambda)$) and after ($I(\lambda)$) transmission through a known length L and absorption crosssection ($\sigma_{OH}(\lambda)$) :

$$I(\lambda) = I_o(\lambda) \cdot \exp\left[\int_0^L -\sigma_{OH}(\lambda) \cdot [OH] \cdot dL\right]$$
(3.1)

Various chemical species can be measured by extracting their corresponding absorption spectra. For OH measurements, to attain a detection limit of $7.3 \cdot 10^5$ molecules cm^{-3} , integration times of 100 seconds and light path lengths of 2240 m are necessary (Fuchs et al., 2012). However, DOAS is no longer utilized for in-situ atmospheric OH detection due to elevated detection limits caused by light scattering from aerosols along the light path (Fuchs et al., 2012).

¹⁴**CO Tracer method** relies on the assumption that CO is predominantly oxidized by OH radicals. Atmospheric OH concentrations can be determined by introducing isotopically labelled ¹⁴*CO* and subsequently analyzing the resulting ¹⁴*CO*₂ through freeze desalination. By simultaneously measuring the concentrations of ¹⁴*CO* and ¹⁴*CO*₂ and applying the known rate constant of OH with CO, OH concentrations can be calculated. However, despite the ¹⁴*CO* method offering a detection limit of $2 \cdot 10^5$ molecules cm^{-3} and requiring integration times of only a few minutes, the complex sampling procedure may make this technique less suitable for in-field atmospheric OH detection (Felton, 1988).

Electron Spin Resonance (ESR) Spectroscopy is a method employed to detect chemical species possessing unpaired electrons. EPR entails the resonant absorption of microwaves (electromagnetic radiation) by a sample within a magnetic field. However, this approach alone is too slow to detect species like OH which has only less than 1 second lifetime. The integration of EPR with spin trapping enables OH detection but only at the expense of higher time resolution (Watanabe et al., 1982).

3.1.1 Laser Induced Fluorescence - Fluorescence Assay by Gas Expansion (LIF -FAGE)

The Laser-Induced Fluorescence (LIF) technique relies on exciting electronic transitions and detecting emitted photons when molecules return to their ground state. The first atmospheric measurement of OH radicals using this method was conducted by (C. C. Wang & Davis, 1974) using a tunable UV laser to excite OH radicals at 282.6 nm, near the P1(2) transition line, with subsequent detection of emitted fluorescence at 308 nm using a spectrometer positioned perpendicular to the excitation beam.

In atmospheric conditions, molecules collide roughly every nanosecond, causing collision quenching where excited radicals lose energy to collision partners, resulting in no fluorescence emission. The natural lifetime($A2\sum +v' = 0$) of the excited OH state is 700 nanoseconds (Bailey, Heard, Henderson, & Paul, 1999). Therefore, only a fraction of excited OH radicals emit photons under these conditions. The measurement technique by (C. C. Wang & Davis, 1974) used a continuously operated laser, leading to elevated background signals due to scattered light. Additionally, the use of 282 nm wavelength also caused ozone photolysis, generating artificial OH radicals, thus compromising atmospheric measurements.

One of the most important further developments in the LIF technique is obtaining fluorescence in the low-pressure range, first described in (Hard, O'Brien, Cook, & Tsongas, 1979) and later first used to measure atmospheric air in (T.M.Hard, R.J.O'Brien, Chan, & Mehrabzadeh, 1984). In this approach, atmospheric gas is introduced into a low-pressure (approximately 5 mbar) measuring cell, reducing collision frequency and enhancing photon yield by minimizing collision quenching and scattering interference. Despite the risk of increased wall losses due to a higher mean free path, the benefits of reduced pressure outweigh the drawbacks, leading to modern OH-LIF instruments operating in low-pressure regimes.

Further refinement involved the adoption of pulsed lasers, minimizing artificial radical detection by ensuring complete air exchange between pulses. Changing the excitation wavelength to 308 nm ((Chan, Hard, Mehrabzadeh, George, & O'Brien, 1990)) reduced interference from artificially generated OH due to the smaller O_3 absorption cross-section and at the same time the electromagnetic OH excitation is improved, as the absorption cross-section for OH at 308 nm is larger (Dorn, Neuroth, & Hofzumahaus, 1995). However, the overlap between excitation and fluorescence wavelengths necessitated detectors capable of collecting fluorescence between laser pulses. To ensure accurate measurements, it is crucial that the excitation laser pulse has dissipated before collecting the fluorescence light. This is accomplished by employing detectors that capture fluorescence signals between laser pulses (Stevens, Mather, & Brune, 1994). To achieve this, the detector signal is recorded and subsequently amplified once the excitation laser pulse has ceased.



Figure 3.1

(a) A schematic of the different branches in the rotational structure of OH and the $A^2\Sigma^+ \rightarrow X^2\Pi\nu' = 1 \leftarrow \nu''$ transitions used during laser excitation. K stands for the quantum number of angular momentum (rotation+orbit), and J stands for the quantum number of the total angular momentum (rotation+orbit+spin). Figure and caption taken from (Marno, 2021; Kubistin, 2009).



(b) Figure taken from (Chan et al., 1990) showing the absorption spectrum of OH radicals at wavelength \approx 308 nm at pressures of \approx 5 mbar.

3.2 HydrOxyl Radical Measurement Unit based on fluorescence Spectroscopy (HORUS)

For the current scientific work discussed in this thesis, the HydrOxyl Radical measurement Unit based on fluorescence Spectroscopy (HORUS) of the Max Planck Institute for Chemistry is used for measuring OH and HO_2 species during the airborne field experiment 'BLUESKY'. The main objective of the BLUESKY campaign was to understand the effect of the COVID-19 lockdown and the subsequent effect on atmospheric composition (Voigt et al., 2022). More details about the campaign will be discussed in Chapter 5.

The measurement technique used by HORUS is based on LIF-FAGE as mentioned previously. The design of the instrument is based on the 'Airborne/Ground Tropospheric Hydrogen Oxide Sensor' (ATHOS/GTHOS) as described in (Faloona et al., 2004) with further modification for airborne, shipborne and ground-based campaigns (Martinez et al., 2010; Marno et al., 2020; Rohloff, 2022; Kubistin, 2009; Regelin et al., 2013; Mallik et al., 2018; Novelli, 2015). The current design of the airborne HORUS instrument was specially modified for High Altitude Long Range (HALO) research aircraft and was previously deployed for OMO - Asia 2015 (Marno, 2021) and CAFE Africa (Rohloff, 2022) airborne field campaigns.

Figure 3.2 shows the overall instrument configuration for HALO airborne measurement campaigns. The setup consists of an external inlet shroud, laser system, inlet pre-injector (IPI), detection unit and a vacuum system.

The inlet shroud serves multiple purposes, including facilitating in-flight calibrations, monitoring instrument sensitivity, and improving sampling conditions for HOx radicals. In-flight calibrations are essential for tracking instrument performance changes during flight, such as HO_2 conversion efficiency, interference levels, detector degradation, and reflectivity changes of White Cell mirrors. Within the shroud, a shutter-able UV Pen-Ray lamp is utilized to maintain a thermal steady state and emit consistent UV radiation intensity. During normal measurements, the shutter blocks UV radiation, but it is opened during in-flight calibrations to photolyze atmospheric water vapour and produce stable OH and HO_2 concentrations.

To optimize sampling conditions for HOx radicals during flight, the inlet shroud system is designed with three progressively smaller shrouds to ensure central air flow sampling and parallelize airflow to the inlet pre-injector (IPI) nozzle. To prevent excessive collisions of OH and HO_2 with the IPI nozzle and internal walls, a choke is installed behind the IPI to overcome airflow momentum inertia and promote airflow direction into the IPI. This choke effectively limits airflow speeds in the shroud to prevent OH variability from exceeding detection limits, even with aircraft pitch, roll, and yaw adjustments (Marno, 2021).



Figure 3.2: Overview of the airborne HORUS system as installed in the HALO aircraft. An Inlet Pre-Injector (IPI) is mounted inside the inlet shroud and is designed to allow for chemical background detection within HORUS. Post critical orifice, the OH radicals are excited by laser light at around 308 nm within the detection cells. The fluorescence of these molecules is detected using a multi-channel plate detector (MCP) that forms part of one of the detection cell arms. The MCPs look towards the centre of the detection cells through a series of focal optics, perpendicular to the incoming laser beam from the fibres. In a second detection axis, HO_2 is detected indirectly through the addition of NO that quantitatively converts HO_2 into OH. The NO injection occurs via a stainless steel 1/8 inch line, shaped into a ring perpendicular to the airflow with several unidirectional apertures of 0.25 mm diameter creating essentially a NO shower. Figure and caption taken from (Marno et al., 2020; Marno, 2021) The **laser system** comprises a specialized dye laser setup, featuring a Nd(¹¹¹)-doped yttrium aluminium garnet (YAG) pulsed tunable dye laser operating at a pulse repetition rate of 3 kHz. This system is used to generate 308 nm UV light for the excitation of OH radicals. A schematic representation of the dye laser system is shown in figure 3.3. A diode-pumped Nd:YAG laser at 532 nm is employed to optically pump the dye laser system. The pump laser beam is precisely focused onto the dye cell using a combination of optics and piezoactuated mirrors to ensure accurate alignment. The laser dye used is Pyrromethane-597 dissolved in high-purity isopropanol, circulated to prevent dye saturation within the cell. Light emitted from the dye cell is amplified within the laser cavity, with selective amplification of 616 nm wavelength achieved using SF10 dispersion prisms and a rotatable intracavity etalon optic. Frequency doubling in a BBO crystal generates the desired 308 nm UV light, which is then directed to detection cells via angle-polished optical fibres to minimize signal interference. A detailed description of the laser setup can be found in (Hens, 2014).



Figure 3.3: A schematic of the dye laser system. The incoming 532 nm wavelength Nd:YAG laser beam is focused onto the dye cell. The pyrromethane-597 laser dye fluoresces at λ = 616 nm which is amplified within an optical resonator (the telescope, dispersion prisms, etalon mirror and back reflection (end) mirror). 308 nm wavelength UV light is generated by amplifying selectively 616 nm sufficiently to allow frequency doubling to occur within a nonlinear doubling crystal (β -barium borate, BBO). Figure and caption taken from (Hens, 2014; Marno, 2021)

The Inlet Pre-Injector (IPI) was a first-of-its-kind dedicated inlet pre-injector system that was designed to eliminate atmospheric OH, allowing for real-time measurement and quantification of potential chemical background OH interferences (OH_{CHEM}) (Marno, 2021). The pressure within the IPI is maintained at approximately 30 to 80 mbar lower than the ambient pressure, which typically ranges from 250 to 1130 mbar for an airborne measurement.

This pressure regulation is accomplished by connecting a blower to the end of the IPI section. In the HORUS IPI setup, propane (C_3H_8) is added every 2 minutes for 30 seconds and serves as a scavenger to remove atmospheric OH before reaching the critical orifice, positioned before the low-pressure section where OH detection takes place and thus residual OH chemical background signal ($S_{OH_{CHEM}}$) is measured. A comprehensive examination of the performance of IPI, and the scavenging efficiency will be discussed in Chapter 4, section 4.5.2.

The HORUS instrument features a critical orifice situated at the end of the Inlet Pre Injector (IPI), positioned at the centre of the IPI cross-section. This allows the instrument to sample airflow ranging from 3 to 17 standard litres per minute (SLPM) from the central flow within the IPI. This setup minimizes the impact of wall losses within the IPI on the measured signal in the cells. To remove excess flow within the IPI, a perforated ring surrounding the base of the critical orifice cone is utilized, and the excess airflow is evacuated by a blower.

In the **low-pressure detection unit**, air sampled after passing through the IPI is directed through a critical orifice with a diameter of approximately 1.4 mm with a flow rate of approximately 3 - 17 litres per minute. All internal surfaces, including those of the IPI, are coated with black anodized aluminium. The critical orifice generates an internal cell pressure of around 18 mbar at ground level and \approx 3 mbar at 13 km. This rapid change in pressure from IPI to the detection unit induces rapid adiabatic expansion of the measuring gas. This exchange rate of sample air is essential to prevent the excitation of the same sample air from two consecutive laser pulses, thus minimizing the production and interference of laser-generated OH.

Located approximately 77.5 mm upstream from the critical orifice, in the direction of airflow, is the centre of the first detection block, where atmospheric OH excitation, fluorescence, and detection take place. To enhance the excitation of atmospheric OH and maximize HORUS sensitivity, a White Cell (White, 1942) setup is employed within the detection cells. In this setup, reflection mirrors are aligned to create 32 light paths, enhancing the interaction with the detection volume.

Similar to other LIF-FAGE instruments, HORUS operates on the principle of resonant absorption of laser light by OH molecules, specifically targeting the Q1(2) transition from the ground state $X^2\Pi_{3/2}$ to the excited state $A^2\Sigma^+$ (Figure 3.1). The resulting return to the ground state induces detectable fluorescence of OH (Dorn et al., 1995; Holland, Hessling, & Hofzumahaus, 1995) in the low-pressure regime (< 18 mbar) within the detection cells. The ground state electron configuration of OH is $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (\pi^+)^2 (\pi^-)^1$ with an unpaired electron in the π orbital (Freeman, 1958). In the electronically excited state $A^2\Sigma^+$, the electron configuration becomes $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (\pi^+)^2 (\pi^-)^2$. There is a separation in the rotational ground states for OH due to spin-orbit coupling, forming two electronic substrates $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$. The excited state $A^2\Sigma^+$ has no angular momentum and therefore no spin-orbit coupling. More details about the molecular structure and fluorescence property at 308 nm can be found in (Kubistin, 2009; Marno, 2021; Rohloff, 2022; Hens, 2014)

To quantify the signal generated by OH fluorescence (S_{OH}), LIF-FAGE HOx instruments utilize a cycling process where the laser tuning is alternated between on-resonance and off-resonance states. The on-resonance state captures the total signal including OH fluorescence and other sources, termed OHF_{on} , while the off-resonance state measures all sources except OH fluorescence, termed OHF_{off} . The net OH signal (S_{OH}) is then computed as the difference between the on-resonance and off-resonance signals (Mao et al., 2012), as expressed by the equation:

$$S_{OH} = OHF_{on} - OHF_{off} \tag{3.2}$$

During the BLUESKY airborne campaign, the HORUS dye laser was cycled between on-resonance and off-resonance states in intervals of 5 seconds each. Off-resonance measurements were alternated by adjusting the etalon mirror \pm 500 steps (37 GHz) around the Q1(2) transition line. This methodology is detailed in(Kubistin, 2009)

To determine the interference signal $S_{OH-CHEM}$, a controlled amount of propane (C_3H_8) is introduced into the system at a rate of 200 sccm (standard cubic centimetres per minute) into the Inlet Pre Injector (IPI). This effectively removes atmospheric OH from the sampled air. Propane injection lasts for 30 seconds, equivalent to one on-resonance measurement period. Afterwards, the propane injection system is purged by shutting off the injection valve and mass flow controller and introducing 1 SLPM (Standard Liters per minute) of pure synthetic air for approximately 1 second to clear any residual propane from the IPI. The propane injection system is then isolated from the IPI for 120 seconds, which corresponds to 24 on-resonance and off-resonance cycles. During this time, both atmospheric OH and OH_{CHEM} (referred to as OH(tot) in this context) are measured (Marno, 2021). The absolute interval for the addition of propane and NO (which will be discussed in the upcoming section) will vary from campaign to campaign as part of optimizing its performance.

 HO_2 is indirectly measured in the second detection axis by quantitatively converting atmospheric HO_2 to OH through the injection of NO into the low-pressure conditions within HORUS, as described by reaction 7, table 2.1. The detection of the subsequently produced OH (from atmospheric HO_2) and atmospheric OH occurs in the second detection axis, effectively measuring atmospheric HOx. The net HO_2 signal (S_{HO2}) is calculated by subtracting the net OH signal from the first detection axis, normalized by the ratio of the OH sensitivities in the two detection axes ($C_{OH}(2)/C_{OH}$), from the net HOx signal (S_{HOx}). Then S_{HO2} is corrected by the second detection cell sensitivity towards HO_2 (C_{HO2}) and laser power ($W_{z2 \text{ pwr}}$) to determine the absolute HO_2 mixing ratio:

$$[OH] = \frac{S_{\rm OH}}{C_{\rm OH} \cdot W_{\rm z1}} \tag{3.3}$$

$$[HO_2] = \frac{1}{\left(C_{HO_2} \cdot Wz_2\right)} \cdot \left\{S_{HO_X} - \frac{\left(C_{OH(2)} \cdot\right)}{\left(C_{OH} \cdot Wz_1\right)}S_{OH}\right\}$$
(3.4)

Where W_{z1} is the laser power in the first detection axis, W_{z2} is the laser power in the second detection axis, and C_{OH} and C_{HO_2} are the calibrated sensitivity factors for OH and HO_2 (cts s⁻¹ pptv⁻¹ mW⁻¹) respectively. The subscript 2 is used to distinguish variables in the second detection axis from those in the first detection axis (Marno, 2021; Rohloff, 2022).

Vacuum System

To maintain stable pressures at 16 mbar and below within the HORUS detection cells, the air is drawn in through a critical orifice via a two-tier vacuum system. This system consists of a compressor (Type M90 roots blower, Eaton) and a vacuum pump (ESDP-30 scroll pump, Edwards). The M90 roots blower compresses and elevates the pressure of the sampled air ahead of the scroll pump, thereby improving the pumping efficiency of the ESDP-30 (Marno, 2021; Rohloff, 2022).

Chapter 4

HORUS Calibration

As mentioned in the previous chapter, HORUS uses a low-pressure LIF measurement technique to measure the HOx radicals. To convert the measured signal into a corresponding concentration, the sensitivity of the cell detectors must be determined. To get an accurate hold on the sensitivity, a known amount of OH and HO_2 has to be produced and the corresponding fluorescence signal needs to be measured. Since the pressure inside the airborne HORUS detector cell changes (2-13 mbar) as the flying altitude changes, the sensitivity needs to be quantified for a similar pressure range inside the detection cell while performing the calibration. This is accomplished by using the 'All Pressure Altitude based Calibrator for HOx Experimentation' system (APACHE; see (Marno et al., 2020)). Figure 4.1 shows APACHE calibration set up and figure 4.2 depicts the steps involved in the HORUS calibration. A detailed description of the calibration set-up can be found in (Marno et al., 2020).

OH radicals are produced inside APACHE by photolysis of water molecules at 184.9 nm using a UV mercury ring lamp(see Appendix figureA.1) as given in equation 4.1 . This photolysis method has the advantage that an equal amount of OH and HO_2 are generated (Marno et al., 2020; Creasey, Halford-Maw, Heard, Pilling, & Whitaker, 1997).

$$H_2O + hv \xrightarrow{\lambda = 184.9nm} OH + H*$$
 (4.1)

$$H^* + O_2 \xrightarrow{O_2} OH + O_3 \tag{4.2}$$

$$H^* \xrightarrow{M} H$$
 (4.3)

$$H + O_2 \xrightarrow{M} HO_2$$
 (4.4)

The photolysis of H_2O at 184.9 nm has only one energetically favourable dissociation channel, which makes an equal amount of OH and H* (Engel et al., 1992). Even though the reaction 4.2 is possible ((Dong H. Zhang, 2000)), the fast energy loss of H* via reaction 4.3 allows all the H atoms produced in reaction 4.3 to react with O_2 to form HO_2 via reaction



Figure 4.1: Schematic representation of APACHE - HOURUS calibration set-up. The section to which the HORUS instrument is attached is called the APACHE chamber.

4.4 (Fuchs et al., 2011). Similar calibration methods used for HOx instruments can be found in (Faloona et al., 2004; Martinez et al., 2010; Mallik et al., 2018; Marno et al., 2020; Rohloff, 2022).

To quantify the OH and HO_2 concentration that is produced during the calibration, the photon flux of the mercury UV ring lamp needs to be determined. With known water mixing ratio and photon flux, the produced OH and HO_2 concentration by the UV lamp inside the APACHE system can be calculated using equation 4.5

$$[OH] = [HO_2] = [H_2O] \cdot F_{184.9 \text{ nm}} \cdot \sigma_{H_2O} \cdot \phi_{H_2O} \cdot t_{lamp}$$
(4.5)

where $[H_2O]$ is the known concentration of water vapour added, t_{lamp} is the residence time of the sampling air under the lamp, σ_{H_2O} is the absorption cross-section of H_2O molecules and ϕ_{H_20} is the quantum yield of reaction 4.1 which is 1 (Creasey, Heard, & Lee, 2000). The absorption cross-section of water vapour (σ_{H_2O}) at 184.9 nm is $7.22(\pm 0.22) \cdot 10^{-20} cm^2$ per molecules (Creasey et al., 2000). The t_{lamp} in equation 4.5 is calculated using the flow speed of the sample air as mentioned in the previous section and the beam width of the UV lamp. The $F_{184.9nm}$ is the UV ring lamp's actinic flux (units in *photons* cm^{-2} s^{-1}) as it passes through the column amount of the sample air which depends on the initial actinic flux of the UV lamp (ϕ_0) and its attenuation by water vapour and O_2 molecules as described in equation below (equation 4.6) :



Figure 4.2: Different steps involved in the HORUS calibration using the APACHE system.

$$F_{184.9nm} = \phi_0 \cdot e^{-(\sigma_{H_2O} \cdot [H_2O] + \gamma_{O_2} \cdot [O_2])}$$
(4.6)

where γ_{O_2} is the absorption cross-section of O_2 molecules at 184.9 nm which is described in section 4.3.1

4.1 APACHE Calibration Set Up

Figure 4.1 shows the APACHE calibration set up. The system consists of the APACHE chamber, three sets of scroll pumps to maintain pressure in the three sections of the system and a series of mixing blocks in which dry synthetic air is mixed with a quantified volume of humidified air. The mixing block consists of mainly two mass flow controllers (MFC), one with a maximum flow capacity of 750 standard litres per minute (SLPM) which controls the dry airflow and the other one with a maximum flow capacity of 300 standard litres per minute (SLPM) which controls the humid air. The air through the 300 SLPM mass flow controller is heated to a higher temperature (120 - 150 C) before the air enters the MFC and a controlled amount of water is added using a peristaltic pump (model 'Chem-Ad-VPP-E'; see Appendix A.8). The sample air from both MFCs is later mixed in a mixing chamber, thereafter the humidity is measured and finally fed into one end of the APACHE system via another mass flow controller with a maximum flow rate of 2000 SLPM. The total flow entering the APACHE depends on the pressure that is needed to simulate the in-flight condition and typically varies from 300 SLPM up to 1000 SLPM.

The sampled air entering the APACHE passes through a 2 mm thick sintered filter (bronze alloy, filter class 10) with a pore size of 35 μm which helps to create a homogeneous flow. The sampled air is later exposed to the 184.9 nm UV mercury lamp before it enters the HORUS inlet. The UV ring lamp is separated from the main chamber by a quartz window. An aluminium ring with thirty 4 mm (30 x 4mm) aperture is used to limit the UV light entering the chamber and thus reducing the illuminated area. The flow velocity and residence time of the sample air under the lamp and the residence time between the lamp and the HORUS inlet also need to be determined properly to quantify the produced radicals and also to minimize any major physical or chemical losses of these radicals inside the APACHE chamber. This is achieved by electronically controlling the speed of the exhaust pump. This procedure will be discussed in the next section. The HORUS inlet nozzle protrudes 51 mm into the APACHE chamber, as it does when fitted in the aircraft shroud system. The IPI section is connected to an external pump (Edwards XDS 35) via an electronically controlled butterfly valve. The pressure inside the IPI section is matched with the pressure during the aircraft measurement by controlling the position of this butterfly valve. Following the IPI section, the sample air moves into the detection units, as indicated in section 3.2, where the OH fluorescence is measured. By regulating the sample airflow with the pumps, the pressures inside the APACHE chamber, IPI section, and detecting unit are matched to the inlet (280 - 1000 mbar), IPI (200 - 920 mbar) and detection cell pressure (3 - 13 mbar) respectively during the aircraft measurement.

Once the fluorescence signal is measured, the calibrated sensitivity can be calculated as shown in the equation

$$C_{OH}(P,T) = \frac{S_{OH}}{[OH].W_{Z1}}$$
 (4.7)

$$C_{HO_2}(P,T) = \frac{S_{HO_2}}{[HO_2].W_{Z2}}$$
(4.8)

where S_{OH} is the fluorescence signal from the first axis, [OH] is the OH concentration calculated using equation 4.5 and W_{z1} and W_{z2} are the laser power in the first and second detection cells respectively. S_{HO_2} is the corrected HO_2 signal since both OH and HO_2 are measured in the second cell as mentioned in section 3.2. The fluorescence signal S_{OH} and S_{HO_2} is dependent on several factors such as pressure, collisional quenching of molecules, diffusion and transmission loss inside the HORUS instrument etc. The influence of these parameters will be discussed in detail in section 4.4.

To obtain the corrected HO_2 signal from the total $HOx (OH + HO_2)$ signal, the corresponding OH contribution needs to be subtracted. This OH contribution in the second axis is determined by considering the ratio of OH sensitivity in the second axis ($C_{OH(2)}$) to that in the first axis (C_{OH}). Subtracting this contribution allows for the correction of the HO_2 signal in the second axis, as outlined in Equation 4.1.

$$S_{HO_2} = \left(S_{HO_x} - \frac{C_{OH(2)} \cdot W_{Z2}}{C_{OH} \cdot W_{Z1}} \cdot S_{OH}\right)$$
(4.9)

where $(C_{OH(2)})$ is the sensitivity of OH in the second axis which can be determined when NO addition is off.

4.2 Characterizing the flow speed

In order to assess the extent of OH loss inside the APACHE chamber, the flow speed of the sampled air and thereby the residence time inside the APACHE chamber needs to be quantified. If the flow speed inside the APACHE is too fast, then the sample air doesn't have enough residence time under the lamp thereby not producing the required amount of radicals. Similarly, if the flow speed is too slow, the residence time inside the APACHE becomes too high and the produced radical can be lost easily by either chemical reactions such as radical-radical recombination or by physical loss such as wall loss inside the chamber and end up with concentrations below the HORUS detection limit. Thus it is essential to find the flow velocity in which there is enough residence time to produce the radical but at the same time not too slow to lose those radicals inside the chamber. This is achieved by finding out the appropriate pump frequency of the exhaust pump (Edwards GSX 150). The experiment was conducted by changing the pump speed (or frequency) from 60 Hz to 110 Hz (maximum possible) for different pressures and the corresponding OH signal was measured. Figure 4.3 shows the residence time of the sample air inside the APACHE against the OH signal for different pump speeds and different pressures. The residence time of the sampled air inside the chamber was calculated by assuming a plug (or piston) flow and considering the measured volume flow rate (units in *meter³/second*) and the physical area of the APACHE (in *meter*²). For pressures below 550 mbar, observations indicate that beyond 90 Hz, the normalized OH signal (referenced in Figure 4.3) maintains a steady plateau. This suggests that at this flow velocity, velocity-dependent (or residence time-dependent) factors such as wall losses or self-reactions do not significantly affect radical concentration and make the flow speed within APACHE the dominant controlling parameter. The pump speed was set to 95 Hz for pressures below 550 mbar for the rest of the experiments with a sample air speed of 1.6 ($\pm \approx 3\%(1\sigma)$) m/s. The uncertainty in the flow speed predominantly arises from the 1σ statistical deviation in the measurement fluctuation.

For pressures exceeding 550 mbar and at a frequency of 95 Hz, the flow rate surpasses 1000 SLPM. This exceeds the operational range of the smaller mass flow controller (300 SLPM and 750 SLPM) used in the calibration setup and potentially affects the accuracy and



Figure 4.3: The recorded normalized OH signal plotted against the sample air residence time within the APACHE for different APACHE pressures. The number in Hz units represents the blower speed of the pump.

stability of the flow. To account for this and also to save the excess use of dry synthetic air, the pump speed was further decreased. For pressures above 550 mbar, the pump speed was set to 75 Hz with a sample air speed of 1.2 ($\pm \approx 3\%$) m/s.

4.3 Characterising the 184.9 nm UV ring lamp

Oxygen absorption at 185 nm is a significant phenomenon with implications across various scientific disciplines. At this specific wavelength, oxygen molecules demonstrate strong absorption characteristics owing to the electronic transitions arising from their molecular structure. This absorption band, commonly known as the Schumann – Runge band, arises from the excitation of molecular oxygen from its ground state to higher electronic states (Yoshino, Freeman, & Parkinson, 1984; Blake, 1979). This band describes a series of overlapping absorption bands exhibited by oxygen molecules in the UV range, typically spanning wavelengths between approximately 175 nm and 200 nm. The continuum arises from electronic transitions within molecular oxygen (O_2) molecules, involving the excitation of electrons from lower to higher energy states. Specifically, the absorption bands in the Schumann–Runge continuum are attributed to the transition of oxygen molecules from the ground state ($X^3 \Sigma_g^-$) to excited electronic states, such as the $B^3 \Sigma_u^-$ state.

To accurately calculate the concentration of OH and HO_2 radicals using Equation 4.5, a sequence of procedural steps is necessary:

- 1. Assess the UV lamp's line width to determine the O_2 absorption cross-section.
- 2. Determine the sampling area within the APACHE chamber.
- 3. Quantify the photon flux of the UV ring lamp at 184.9 nm.
- 4. Determine the water vapour concentration in the sample air.
- 5. Estimate the exposure time of the sample air under the ring lamp.

4.3.1 Determining the linewidth of the lamp and the corresponding O₂ absorption cross-section

To determine the photon flux at 184.9 nm using Equation 4.6, and subsequently calculate the total OH production using Equation 4.5, it is essential to first ascertain the oxygen absorption at this specific wavelength. Due to a highly discrete Schumann–Runge band, the O_2 absorption cross-section decreases by a factor of 10^4 (from 10^{-20} to $10^{-24}cm^2$) between 175 nm and 195 nm while at around 185 nm the O_2 absorption cross-section varies by a factor of 10 (Blake, 1979; Yoshino et al., 1984; Price & Collinss, 1935). Determining the linewidth of the UV lamp is crucial for the precise calculation of the O_2 absorption cross-section and thereby the absorption factor due to oxygen.

Figure 4.4 shows the experiment set up for finding the linewidth and the O_2 absorption cross-section. For the experiment, all 4 mm aperture holes in the aluminium ring below the UV ring lamp are closed except one in the top centre as shown in the figure. This will ensure that the light is coming only from one direction. A UV cuvette tube (Type 34, cylindrical cell, UV Quartz, 100mm LP, 2 PTFE stoppers) with a length of 10 cm and 2 PTFE stoppers was kept right below the light path. A 193 nm band pass filter (Edmund optics, 195 nm x 15 nm; Appendix A.2) with full width at half maximum (FWHM) of 15 nm is kept on the top (or the entrance) of the cuvette in order to prevent any other UV light from entering the cuvette. A UV power meter (Hamamatsu H8025 -185) with a sensor that can measure the optical power at 185 nm is attached at the bottom of the cuvette. The cuvette was supplied with pure oxygen with a flow rate ranging from 0 to 1000 standard cubic centimetres per minute (sccm) via a mass flow controller. For each flow, the corresponding intensity was measured at the other end of the cuvette.

$$I = I_0 e^{-\gamma \cdot n \cdot l} \tag{4.10}$$

$$\gamma = \log(\frac{I}{I_0}) \cdot \frac{1}{n \cdot l} \tag{4.11}$$

Using Beer -Lambert's theory (equation 4.10), the absorption cross-section can be calculated using equation 4.11, where I_0 is the intensity when no O_2 is present, I represents



Figure 4.4: Schematic representation of the experimental set-up to find the line width and the O_2 absorption cross-section.

the measured intensities at different O_2 column density, *n* is the corresponding O_2 concentrations and l is the path length of the light inside the cuvette (10 cm). The O_2 column density was calculated using the measured internal pressure and temperature and the accuracy of the pressure and temperature sensor was 1% (Appendix A.5 and A.6) and the statistical uncertainty of the pressure reading during the experiment was less than 2%. The calculated absorption cross-section from equation 4.11 is fitted against the measured values from (Yoshino, Esmond, Cheung, Freeman, & Parkinson, 1992) by iteratively adjusting the wavelength at intervals of 0.01 nm (corresponds to the assumed linewidth of the lamp) between 184.85 and 185.1 nm. The (Yoshino et al., 1992) contains measured O₂ absorption cross-section for wavelength between 180-195 nm for different O₂ pressures ranging from 3 to 1013 mbar with a wavelength interval of $2 \cdot 10^{-4}$ nm. The UV photolysis of O_2 at 184.9 nm also results in the formation of ozone, which subsequently influences the absorption intensity. The amount of ozone that was produced inside the cuvette was calculated using a steady-state assumption and the corresponding impact on the absorption intensity was found to be at least a factor of 10 less than O_2 absorption alone depending on the O_2 concentration.

Figure 4.5 shows the O_2 absorption cross-section obtained from the experiment (blue) using equation 4.11 and (Yoshino et al., 1992) measured O_2 absorption cross-section (green) for at 184.9 nm wavelength for a given linewidth of $0.045 \pm 4\%$ nm. Figure 4.6 represents the ab-
sorption intensity of the UV lamp at $184.9 \pm 0.045(\pm 4\%)$ nm. A typical value of O_2 column density inside the APACHE chamber is between $0 - 50 \cdot 10^{18}$ molecules cm^{-2} and the corresponding O_2 absorption cross-section was found to be between $14 - 10 \cdot 10^{-21} cm^{-2}(\pm 4\%)$ and the UV ring lamp with emission line of $184.9 \pm 0.045(\pm 4\%)$ nm. The total uncertainty is calculated by combining the quadratic sum of individual uncertainties at the 1σ level. These uncertainties include variations in measurements due to statistical factors, alongside systematic uncertainties originating from calibrations of pressure and temperature sensors, and the uncertainty from the numerical fit. The systematic deviation in the measured O_2 absorption from that reported by Yoshino et al. (1992) may arise due to differences in spectral resolution, uncertainties in the pressure or temperature sensors, or inaccuracies in estimating the ozone formation and its influence on UV intensity.



Figure 4.5: The calculated O_2 absorption cross-section using equation 4.11 (blue) and Yoshino1992 measured (green) O_2 absorption cross-sections at 184.9 ± 0.045 nm. The red line indicates the fit obtained as a function of O_2 column density. The error bars represent the statistical measurement variation at 1σ . The 1σ uncertainty of the mean value is less than 3%. A comprehensive trend of O_2 absorption at this wavelength for a wider range of O_2 column densities is provided in Appendix B.1.



Figure 4.6: The emission line and its absorption intensity of the UV mercury ring lamp at 184.9 ± 0.045 nm that was used for APACHE calibration.

4.3.2 Estimating the sampling area inside the APACHE chamber

As described in Marno et al. (2020), when moving away from the UV ring lamp or towards the centre of the APACHE chamber from the wall, the amount of OH produced inside the chamber decreases due to the strong absorption of UV light by O_2 molecules at 184.9 nm and also due to the attenuation of the light as described in section 4.3.3 . From equation 4.5, it is evident that the OH production is directly proportional to the UV intensity. This implies that the air entering the HORUS inlet from the chamber exhibits varying concentrations of OH depending on the specific section of the chamber from which the air travels. An experiment was conducted to estimate the area inside the APACHE from which the air enters the HORUS instrument.

Figure 4.7 shows a schematic diagram of the experiment set up. A 1/16-inch insertion was made right after the sintered plate in the APACHE chamber and a 1/16-inch metal tubing was inserted perpendicular to the flow through this point. One end of the tube was connected to a 20% *NO* bottle using a Mass Flow Controller (MFC). The opposite end of the metal tube was then inserted through the new insertion and positioned at varying distances from the chamber wall, ranging from 0 to 9 cm. The portion after the HORUS inlet was replaced by a 24-inch metal tube which is connected to a scroll pump. The pressure inside the 24-inch metal tube section remains consistent with that in the IPI during calibration, ensuring equivalence between the air drawn from the APACHE chamber during the experiment and the actual calibration process. The exhaust of the pump is connected to a TEI NO monitor (TECO 42C, Thermo Environmental Instrument Inc). The UV lamp was turned off completely during this experiment to avoid any effect due to photolysis.

The APACHE chamber was fed with a dry nitrogen flow of 365 SLPM ($\pm < 2\%$) and 612 SLPM corresponding to 250 mbar and 450 mbar APACHE chamber pressure. The pressure inside the 24-inch metal section was adjusted to 200 mbar and 380 mbar, with a corresponding mass flow of 77 SLPM and 130 SLPM, mirroring that of the actual calibration procedure. The actual mass flow rate during a typical APACHE ground calibration is given in figure 4.8. For each flow, 1 standard cubic centimetre per minute (sccm) of 20% *NO* ($2 \cdot 10^5$ ppm) was injected perpendicular to the flow direction from different distances relative to the chamber wall, ranging from 0-9 cm and the final NO concentration that entered the HORUS inlet was measured using the TEI NO monitor. The final concentration of measured NO with respect to the distance from the chamber wall will indicate the section where the most air enters the HORUS.

The graph depicted in Figure 4.9 illustrates the concentration of NO measured within the HORUS inlet, plotted against the distance of the NO injection point from the APACHE wall. If the air inside of the chamber is fully mixed and the HOURS samples this fully mixed air, the measured NO concentration should be uniform for all injection points. However, the experiment reveals that most of the NO that were added entered the HORUS inlet only after 2 cm from the APACHE wall. Until 2 cm from the chamber wall, the NO concentration was at least a factor of 5 -10 (lower limit) less than that after 2 cm. This implies the majority of the air that HORUS samples during the calibration period comes 2.5 cm away from the wall. A small fraction (about a factor of 5 - 10 less) also enters the HORUS from the wall.

4.3.3 Determining the Intensity profile of the Hg UV ring lamp

The intensity of a light source diminishes as it propagates through a medium or space due to various factors such as absorption, scattering, and as well as divergence. To understand the intensity profile due to the divergence of the light source, the UV intensity was measured at different distances from the source. For this purpose, all the 4 mm holes in the aluminium rod were covered except the one hole in the top as described in section 4.3.1. A UV photometer (Hamamatsu H8025 -185) was used to measure the intensity of the light at different distances from the source. To safeguard the light path from potential interference by stray light, a non-reflective black tube with a diameter of 5mm was utilized, spanning from the lamp to the UV photometer sensor, thereby covering the distance between the UV photometer and the light source. The tube was continuously flushed with dry N_2 to avoid any other absorption from external influence.

Figure 4.10 shows the reduction of the UV intensity of the ring lamp as the UV photometer's sensor moves away from the source. The experiment revealed that the intensity



Figure 4.7: Schematic representation of the experimental set-up to find the sampling area inside the APACHE chamber.



Figure 4.8: A comparison of the total mass flow inside the APACHE and the total flow inside the IPI section of HORUS during calibration is illustrated in the left panel. The ratio between the total flow inside APACHE and that of the IPI section (fractional flow) is presented in the left panel. The error bars denote the 1σ measurement variations.



Figure 4.9: The measured NO concentration in the HORUS inlet versus the distance of the NO injection point from the APACHE wall for two APACHE chamber pressure levels. The error bar indicates the 1σ measurement variation. The uncertainty in measuring the distance from the wall is less than 5%. The calibration standard of the NO bottle and calibration of the NO monitor that was used in the experiment is given in Appendix A.4 and B.2.

of the lamp has a square dependency as it moves away from the APACHE wall. As the light travels towards the centre of the APACHE chamber, its intensity diminishes by nearly 80%. The previous experiment described in section 4.3.2 aimed at determining the sampling area revealed that the majority of the sample air entering the HORUS inlet originates from a region approximately 2 cm away from the wall. The total volume of air sampled by HORUS during calibration constitutes approximately $20\% \pm 3\%$ of the total flow within the APACHE chamber, regardless of the varying pressures within the APACHE chamber as shown in the figure 4.8. The effective area of the sampling will be discussed in section 4.3.4. Combining these findings, it can be concluded that the air sampled at the HORUS inlet was exposed to photons exhibiting a reduction in intensity ranging from 30% to 70% due to different pressure conditions compared to those emitted at the source when no absorption is considered. During APACHE ground calibration, the photon intensity is further reduced due to the presence of additional absorbing species in the sample air, which will be discussed in the next section.



Figure 4.10: The measured UV lamp intensity profile (in percentage) as a function of distance from the APACHE chamber wall. The error bar indicates the 1σ measurement variation.

4.3.4 Determining the photon flux of the UV ring lamp

The photon flux of the UV ring lamp was determined by using the N_2O actinometry measurement as described in (Edwards et al., 2003). At 184.9 nm , N_2O photodissociate to form an excited $O(^1D)$

$$N_2O + hv \to O\left(^1D\right) + N_2 \tag{4.12}$$

which in turn react with N_2 or N_2O itself (R. Sander, Kerkweg, Jöckel, & Lelieveld, 2005; Martinez et al., 2010; Marno et al., 2020) leading to the following reactions

$$O(^{1}D) + N_{2} + M \to N_{2}O$$
 $k_{a} = 2.8 \cdot 10^{-36}$ (a) (4.13)

$$O(^{1}D) + N_{2}O \rightarrow N_{2} + O_{2}$$
 $k_{b} = 4.4 \cdot 10^{-11}$ (b) (4.14)

$$O(^{1}D) + N_{2}O \rightarrow 2NO$$
 $k_{c} = 7.2 \cdot 10^{-11}$ (c) (4.15)

$$O(^{1}D) + N_{2} \rightarrow O(^{3}P) + N_{2}$$
 $k_{a} = 2.6 \cdot 10^{-11}$ (d) (4.16)

$$O(^{1}D) + N_{2}O \rightarrow O(^{3}P) + N_{2}O \qquad k_{a} = 1 \cdot 10^{-12} \qquad (e) \qquad (4.17)$$

The photon flux of the lamp can be calculated by measuring the NO concentration at the centre of the chamber (7.5 cm) that is produced by the photodissociation of N_2O in a carrier gas as given in equation 4.19:

$$\Phi_{7.5} = \frac{(k_{\rm a} [N_2] [M] + k_{\rm d} [N_2] + k_{\rm b} [N_2O] + k_{\rm c} [N_2O]) [NO]}{2k_{\rm c} [N_2O]^2 \sigma_{\rm N2O} \cdot t}$$
(4.18)

and at the wall

$$\Phi_{0} = \frac{\left(k_{a} \left[N_{2}\right] \left[M\right] + k_{d} \left[N_{2}\right] + k_{b} \left[N_{2}O\right] + k_{c} \left[N_{2}O\right]\right) \left[NO\right]}{2k_{c} \left[N_{2}O\right]^{2} \sigma_{N2O} \cdot f_{N2O} \cdot t}$$
(4.19)

where ϕ_0 is the photon flux of the lamp, k_a , k_b , k_c , k_d are the rate coefficients of the corresponding reactions, σ_{N_2O} is the absorption cross-section of N_2O at 184.9 nm, f_{N_2O} is the absorption factor of N_2O along the pathlength of the light and t is the exposure time of the sampled air under the lamp. f_{N_2O} is calculated as $f_{N_2O} = exp^{-\sigma_{N_2O} \cdot n \cdot l}$, where the σ_{N_2O} is the absorption cross-section of N_2O (1.42 \cdot 10⁻¹⁹ \pm 2%), n is the N_2O density (1.8 – 5.5 \cdot 10¹⁷ molec per cm^3) and 1 is the absorption path length which is 7.5 cm. The contribution from the reaction 4.17 is neglected since its rate is ten times slower than the other reactions.

In order to calculate the photon flux using this method, a known amount of N_2O (1.8 – $5.5 \cdot 10^{17}$ molec per *cm*³) is added into a 100 SLPM dry N_2 carrier gas and fed into the APACHE chamber. The produced NO from equation 4.12 is measured from the centre of the chamber using a calibrated NO monitor (TECO 42C, Thermo Environmental Instrument Inc). The NO monitor calibration and the NPL (National Physical Laboratory) standard NO bottle used for calibration can be found in Appendix B.2 and A.4 respectively. The N_2O bottle also contains a trace amount of NO_2 which can also in turn undergo photolysis and produce NO. This effect is negligible since the concentration of NO_2 was less than 5 ppt. The typical flow profile inside the APACHE for flows above 250 SLPM can be found in the reference provided (Marno et al., 2020). To determine the exposure time 't', the flow velocity needs to be calculated using the volume flow and the physical area of the chamber. Firstly, the volume flow is calculated from the measured mass flows as:

$$Q = (\frac{100}{60}) \cdot standard fraction = 1.9 \times 10^{-3} \text{ m}^3/\text{s}$$

where standard fraction is the ratio of standard pressure (1013 mbar) to pressure inside the chamber (980 mbar) multiplied by chamber temperature (298 K) to standard temperature (273k). The cross-sectional area of the APACHE chamber is calculated as:

$$A = \pi r^2 = \pi (0.075 \text{ m})^2 \approx 0.0177 \text{ m}^2$$

Considering a 1 σ uncertainty in the mass flow controller of 2% and a < 1% uncertainty in the physical dimensions (see (Marno et al., 2020) and appendix A.3), the average velocity is estimated as $v_{avg} = Q/A$, resulting in 0.106 m/s.

For the given conditions, the calculated Reynolds number is:

$$\operatorname{Re} = \frac{\rho \cdot v_{avg} \cdot D}{\mu} \approx 1000$$

Where ρ , μ , and D are the density inside the APACHE chamber (2 · 10¹⁹ molec per *cm*³), the dynamic viscosity of dry nitrogen ($\mu = 1.76 \cdot 10^{-5} Pa \cdot s$), and the diameter of the chamber respectively (15*cm* ± 1%).

Given that the Reynolds number is less than 2300, the flow regime is generally considered laminar. However, due to the presence of a sintered plate at the beginning of the APACHE system, the flow initially demonstrates a plug or piston flow, characterized by a uniform velocity across the cross-section. The hydrodynamic entry length (X), which is the minimum length required for a plug flow to develop into a fully laminar profile, can be defined by the equation:

$$X = 0.05 \cdot Re \cdot D$$

where *D* is the diameter of the tube system (Incropera, DeWitt, Bergman, & Lavine, 2011). For the APACHE system, with a diameter of 15 cm, the calculated hydrodynamic entry length is 750 cm. The UV ring lamp, where the photon flux is measured, is located 13.3 cm from the sintered plate, which is significantly shorter than the calculated hydrodynamic entry length. This indicates that the flow remains in the plug flow regime at the point of measurement. Therefore, the velocity can be approximated as $V_{avg} = 0.106$ m/s, with a corresponding residence time *t* of 0.3 seconds.

Figure 4.11 shows the photon flux $\phi_{7.5}$ and ϕ_0 calculated using the equation 4.18 and 4.19 as a function of N_2O mixing ratios and table 4.1 lists the uncertainties for this calculation. The calculated ϕ_0 using the N_2O actinometrical method using equation 4.19 was $3.2(\pm 0.5) \cdot 10^{13}$ photons per cm^2 second and at the centre of the chamber the $\phi_{7.5}$ was $3(\pm 0.5) \cdot 10^{12}$. This decrease is mainly due to the absorption from N_2O (35% on average) and the rest due to the intensity profile of the UV beam.

To map the photon flux and consequently the OH production within the circular APACHE chamber below the UV ring lamp, a ray tracing simulation was developed. This simulation calculates the intensity profile over the circular spatial domain using the equation 4.10. At first, a rough estimate of initial photon flux, Φ_0 , is derived from equation 4.19 .The absorption cross-section of O_2 for various column amounts is sourced from the data presented in figure 4.5. The beam divergence as the ray propagates was assessed visually using a card ruler, as described in appendix B.3. By using this divergence and the volume flow, the exposure time inside the chamber at different sections was calculated. The absorption factor as the ray propagates is calculated using the Beer-Lamberts (equation 4.10) at a step size of 0.1mm from one end of the chamber wall to the other end of the wall and finally, the



Figure 4.11: Calculated photon fluxes from the measured NO concentrations using equation 4.19 as a function of different N_2O mixing ratios at the centre (7.5 cm) of the APACHE chamber (figure a) and at the wall (figure b). The data shown in the figure illustrates the outcomes of three consecutive experiments. The error bar represents the statistical measurement variability at 1σ interval. The data sheet of N_2O bottle (99.9% N_2O) can be found in Appendix A.7.

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Parameters	Uncertainty (1 σ)	Remark	
NO monitor	4 %	Calibration uncertainty	
		(Appendix B.2)	
NO standard (NPL)	1%	Purity and concentration of the gas	
		(Appendix A.4)	
Kinetic rate coefficients	12%	JPL recommendation	
		(Burkholder et al., 2015)	
N_2O standard	2%	Purity and concentration of the gas	
		(Appendix A.7)	
N_2O cross-section	2%	JPL recommendation	
		(Burkholder et al., 2015)	
Mass flow controller	< 2%	Industrial Calibration	
		(Appendix A.3)	
Pressure and temperature sensor	< 2%	Validated with NIST standard	
		(AppendixA.5,A.6)	
Experimental stability	15%	measurement variability	
Total Uncertainty	19%		

Table 4.1: Parameters and uncertainties for determining the photon flux using the N_2O photolysis method. The total uncertainty is the sum of the quadrature of the individual uncertainty listed above.

corresponding OH concentration at each point is calculated using equation 4.5. The initial I_0 value used to initialize this simulation might be inaccurate since the photon flux was determined by NO measurement at the centre of the chamber, which is an integral value of photon flux from the 30 pinholes of the flux reducer ring. To correct this in the simulation, the intensity profile was scaled such that at the centre of the chamber (7.5 cm), the photon flux value should match the measured one as shown in figure 4.14 A.

The simulation iterates over the angles surrounding the lamp and the rays emitted from each point, calculating the intensity and OH production at each step of the UV beam's path. This estimation has a drawback since, in contrast to the actual scenario, this represents the UV lamp as a continuum rather than rays coming from 30 pin-holes. Nevertheless, this assumption will have more impact only if most of the sample air comes directly from the wall which is in contrast to what was observed in figure 4.9. The simulation was repeated for three different O_2 mixing ratios (0%, 10%, 20%) to evaluate the impact of O_2 absorption within the APACHE chamber. Since the values used for this simulation are the same as those of the measurements, the total 1 σ uncertainty of the simulation is similar to that of the measurement as listed in table 4.2. Figure 4.12 and Figure 4.13 shows the integrated photon flux distribution and the corresponding OH produced along the flow direction under the UV ring lamp for different O_2 column densities at different APACHE pressures calculated from the simulation.

In order to check the reliability of the result, an experiment was conducted with different O_2 mixing ratios in a pure nitrogen carrier gas, with a known amount of water vapour (1800 ppm), which was fed into the APACHE chamber at different pressures and exposed to the UV ring lamp and the corresponding fluorescence signal was measured in the OH detection cell. Figure 4.17, panel A shows the measured OH fluorescence normalized to laser power as a function of different O_2 mixing ratios for different APACHE pressures. It is evident that, as the O_2 mixing ratio increases in the carrier gas, the fluorescence signal decreases as the collisional quenching due to O_2 molecules increases as given in panel B. A more detailed study about collisional quenching due to O_2 is described in section 4.4. Once this effect (quenching) is normalized (see panel C), the impact of O_2 in the OH signal (or the OH measured) varies only less than 15 % as the O_2 mixing ratios change. This implies that the produced OH molecules inside the APACHE chamber from the simulation should also show similar O₂ dependency after considering radical losses inside the chamber. Furthermore, from section 4.3.2 (figure 4.9), it was found that the majority of the sampled air comes from 2.5 cm away from the chamber wall. Similarly, figure 4.8 indicates that only about 20% of the total flow in the APACHE chamber is sampled. By combining these three findings (O_2 dependency, sampling area, and fractional flow), a robust estimate of OH production is obtained, represented as a white circle in figure 4.13.

Parameter	Value	Uncertainty(1 σ)
ϕ_0	3.10^{13}	19% (table 4.1)
σ_{H_2O}	$7.22 . 10^{-20}$	2% (Creasey et al., 2000)
γ_{O_2}	$13.8 - 12 \cdot 10^{-21}$	4%(from section4.3.1)
$[O_2](molec.cm^{-3})$	$1-4.10^{18}$	2% *
$[H_2O](molec.cm^{-3})$	$1-3.5 . 10^{16}$	3% *
Pressure Sensor	200-1013 mbar	< 2% (AppendixA.5)
Temperature Sensor	290-300 (K)	< 2% (AppendixA.5)
Mass flow controller (SLPM)	222-1125	< 4% (Appendix A.3)
Uncertainty in residence time		20%
Total Uncertainty		28%

Table 4.2: Parameters and overall uncertainty for calculating OH concentration as described in section 4.3.4. The total uncertainty is the sum of the quadrature of the individual uncertainties.

 * The uncertainty arises from calculating their respective concentration using measured pressure and temperature inside the APACHE chamber.

Figure 4.15 shows the OH production profile as a function of distance from the APACHE chamber wall for two different APACHE pressures. The highlighted area represents the HORUS sampling area. Since the flow regime inside the APACHE chamber is turbulent (Reynolds number > 2000, see (Marno et al., 2020)), causing mixing, the integral value along the sampling area is used to calculate the total OH production, as shown in figure 4.16. The calculated OH production under these findings also shows a similar dependency on O_2 when compared to the measurement shown in panel C of figure 4.17. This agreement regarding O_2 dependency between the measurement and the model suggests that the aforementioned calculation is a good representation of the real scenario. The disparity in absolute values observed in Figure 4.17 (panel C) and Figure 4.16 can be attributed to factors such as absolute sensitivity of the detectors and the chemical loss of radicals, which are not yet accounted for in the calculation. A more detailed discussion about absolute sensitivity will be provided in section 4.4. The primary chemical loss of radicals inside the APACHE chamber occurs due to radical-radical recombination (OH + OH and HO_2 + HO_2) and the HOx reaction with O₃, which is formed by the photolysis of the UV light at 253 nm (the UV ring lamp has different emission peaks, see Appendix A.1). The loss rates were calculated by accounting for the reaction rate coefficients from (Burkholder et al., 2020) and the sample residence time inside the chamber after the UV lamp (≈ 0.1 seconds) and the combined loss rate was less than 5%.



Figure 4.12: Calculated photon flux (in log scale) under the UV ring lamp for different O_2 column densities and different APACHE pressures. The section inside the white circle represents the sampling area as obtained from 4.3.2



Figure 4.13: Calculated OH production (in log scale) under the UV ring lamp for different O_2 column densities and different APACHE pressures. The section inside the white circle represents the sampling area as obtained from 4.3.2.





Figure 4.14: Figure A shows the model-calculated photon flux distribution for 1% N_2O in 100 SLPM of N_2 as mentioned in figure 4.11. Figure B shows integrated photon flux along the flow direction as a function of distance from the APACHE wall for different O_2 mixing ratios at 251 mBar and 680 mBar APACHE pressure. The grey-shaded region represented the sampling area. The blue arrow indicates the position of the IPI inlet (\approx 5.1cm) from the APACHE chamber wall.



Figure 4.15: Overview of integrated OH production along the flow direction as a function of distance from the APACHE wall for different O_2 mixing ratios at 251 mBar and 680 mBar APACHE pressure. The grey-shaded region represented the sampling area. The blue arrow indicates the position of the IPI inlet (≈ 5.1 cm) from the APACHE chamber wall.



Figure 4.16: The calculated mean OH productions under the UV lamp for different O_2 mixing ratios for different APACHE pressures. The mean OH is calculated according to the shaded area shown in figure 4.15. An additional figure illustrating OH production as a function of mixing ratio (pptv) can be found in the Appendix B.4. The error bar indicates the total 1 σ measurement uncertainty of the parameters used for the model calculation.



Figure 4.17: The figure depicts the calibration procedure done with different O_2 mixing ratios. Panel A displays the recorded signal of OH fluorescence (SOHF) normalized against laser power for different mixing ratios of O_2 under various APACHE pressures. Panel B exhibits the derived quenching factors. Panel C illustrates the signal (SOHF) normalized against quenching. The error bar indicates the total 1σ measurement uncertainty.

4.4 Determining sensitivity at different pressure

The sensitivity of the LIF-FAGE instrument as derived from equations 4.7 and 4.1, is contingent upon factors such as fluorescence signal strength and the concentrations of OH and HO_2 . Given that the airborne HORUS instrument collects air samples across diverse altitudes, temperatures, and pressures, its detection cell parameters including pressure, internal residence time, etc. fluctuate accordingly. Consequently, the instrument's sensitivity is influenced by changes in cell densities, collisional quenching of fluorescence molecules, and wall losses, which are subject to variations in temperature and pressure. To understand the sensitivity more accurately, it's crucial to thoroughly quantify the parameters affecting fluorescence signals under various pressure conditions, such as those encountered during airborne operations. The pressure-temperature-dependent sensitivity is formulated in the equation 4.20, 4.21, 4.22. The subscript (2) identifies the second detection cell where the HO_2 is measured by converting HO_2 to OH by adding NO.

$$C_{\rm OH}(P,T) = Q_{\rm IF}(P,T,[M]) \cdot b_c(T) \cdot \alpha_{IPI_{\rm OH}}(P,T) \cdot \alpha_{\rm detection \ cell \ _{OH(2)}}(P,T) \cdot \left[c_{(0)OH} \cdot \rho_{\rm Int}(P,T)\right]$$

$$(4.20)$$

$$C_{OH(2)}(P,T) = Q_{IF(2)}(P,T,[M]) \cdot b_{c}(T) \cdot \alpha_{IPI_{OH}}(P,T) \cdot \alpha_{detection \ cell_{OH(2)}}(P,T) \cdot \left[c_{(0)OH(2)} \cdot \rho_{Int(2)}(P,T)\right]$$

$$(4.21)$$

$$C_{\text{HO}_{2}}(P,T) = Q_{\text{IF}(2)}(P,T,[M]) \cdot b_{c}(T) \cdot \alpha_{IPI_{\text{OH}}}(P,T) \cdot \alpha_{\text{detection cell}_{\text{HO}_{2}}}(P,T) \cdot \left[c_{(0)HO_{2}(2)} \cdot \rho_{\text{Int}(2)}(P,T)\right]$$

$$(4.22)$$

where $\rho_{Int}(P, T)$ denotes the internal density of the detection cell. $c_{(0)OH}$, $c_{(0)OH(2)}$, and $c_{(0)HO_2(2)}$ encompass all pressure-independent or unspecified sensitivities. $b_c(T)$ represents the temperature-dependent Boltzmann correction. The α_{IPI} and $\alpha_{detectioncell}$ signify the pressure-dependent transmission within the IPI section and along the detection axis, respectively, while Q_{IF} denotes the collisional quenching of the excited molecules within the detection axis. Furthermore, during in-flight measurements, the final sensitivity of HO_2 is affected by chemical interference resulting from the NO addition. This addition of NO can potentially react with OH thereby creating HONO or it can react with peroxy radicals (RO_2) present in the sampled atmospheric air, leading to either a decrease or increase in the HO_2 signal respectively. Detailed discussion on the chemical interference is given in section 4.5.

Pressure-dependent diffusion loss (*α***)**

Since the IPI operates between 200 - 980 mbar pressure while the detection cell operates at 2.5-13 mbar pressure ranges, the pressure-dependent diffusion transmission (here it is

represented as transmission ie, 1-loss) can be quantified separately as given in the equation 4.23.

$$\alpha_{IPI_{OH}} = 1 - \left\lceil \frac{OH_D(P, T) \cdot t_{IPI}(P, T) \cdot \pi}{IPI_A \cdot P_{IPI}} \right\rceil$$
(4.23)

$$\alpha_{IPI_{HO_2}} = 1 - \left\lceil \frac{HO_{2D}(P,T) \cdot t_{IPI}(P,T) \cdot \pi}{IPI_A \cdot P_{IPI}} \right\rceil$$
(4.24)

where the terms OH_D and HO_{2D} represent the diffusion coefficients of OH and HO_2 . The temperature-dependent diffusion coefficient is taken from (Liu, Ivanov, & Molina, 2009). t_{IPI} denotes the transit time within the IPI, indicating how long it takes for air to flow from the IPI nozzle to the critical orifice of HORUS. IPI_A refers to the internal cross-sectional area of the IPI, while P_{IPI} represents the measured pressure inside the IPI. Within the operational pressure range of the IPI (200 - 800 mbar), the residence time inside the IPI ranged from 50 to 80 milliseconds, resulting in transmission rates for α_{OH} and α_{HO_2} ranging from 0.98 to 0.99. Since the operating pressure and the residence time inside the OH and HO_2 detection cell are different, the diffusion-driven transmission factor $\alpha_{HORUSOH}$, $\alpha_{HORUSOH(2)}$, $\alpha_{HORUSHO_2(2)}$ needs to be calculated separately as given in equation

$$\alpha_{HORUS_{OH}} = 1 - \left[\frac{OH_D(P, T) \cdot t_{cell(1)}(P, T) \cdot \pi}{HORUS_A \cdot P_{int}} \right]$$
(4.25)

$$\alpha_{HORUS_{OH(2)}} = 1 - \left[\frac{OH_D(P, T) \cdot t_{cell(2)}(P, T) \cdot \pi}{HORUS_A \cdot P_{int}} \right]$$
(4.26)

$$\alpha_{HORUS_{HO_2}} = 1 - \left[\frac{HO_{2D}(P,T) \cdot t_{cell(2)}(P,T) \cdot \pi}{HORUS_A \cdot P_{int}} \right]$$
(4.27)

where $t_{cell(1)}$ and $t_{cell(2)}$ represent the transit times calculated from the critical orifice to the 1st and 2nd detection axes, respectively. $HORUS_A$ denotes the internal cross-sectional area of HORUS, while P_{int} signifies the measured internal pressure within the HORUS detection unit. For the specified operating pressure range of the HORUS detection cell (3 -13 mbar), the corresponding residence times were 8 milliseconds for the first detection axis and 51 milliseconds for the second detection axis. Under these conditions, the transmission rates ($\alpha_{HORUSOH}$, $\alpha_{HORUSOH(2)}$, $\alpha_{HORUSHO_2(2)}$) ranged from 0.92 to 0.94, 0.7 to 0.84, and 0.8 to 0.88, respectively and illustrated in figure Appendix B.5. The larger transmission loss in the second axis is due to the higher residence time between 1st and 2nd detection units. **Boltzmann Correction** (b_c) In order to account for the thermally excited OH molecules present in the HORUS cell the Boltzman correction factor is applied. The mathematical formulation, correction coefficient and procedures were taken directly from (Dieke & Cross-white, 1962).

Quenching (Q_{IF})

Collisional quenching refers to a process in which the excited state of an atom or molecule loses its energy due to collisions with other atoms or molecules. This collisional de-excitation prevents the excited species from emitting light or undergoing further chemical reactions. The Q_{IF} represents the quenching rate in seconds, encompassing various factors such as the natural decay frequency of OH, the decay of excited OH caused by collisional quenching influenced by pressure, temperature, and the concentrations of N_2 , O_2 , and water vapour, as well as the gating times of the detector's opening and closing after the initial excitation of the laser pulse. The calculation of Q_{IF} follows the methodology outlined in (Faloona et al., 2004; Martinez et al., 2010; Marno et al., 2020) and is shown in the equation

$$Q_{IF}(P, T, H_2O) = \frac{e^{-\Gamma \cdot t_1} - e^{-\Gamma \cdot t_2}}{\Gamma}$$
(4.28)

Here, t_1 and t_2 represent the times at which the detector gate opens and closes following the initial excitation laser pulse as shown in the figure Appendix B.6. Γ denotes the frequency of decay in the excited state, encompassing both the natural decay frequency (γ) and the deactivation of the excited state caused by collisional quenching with other molecules, primarily N_2 , O_2 , and water vapour, indicated as [X] in the below equation.

$$\Gamma = \gamma + \Sigma(k_X(T) \cdot [X]) \tag{4.29}$$

where

$$k_x(T) = aT^{\frac{1}{2}} - bT^{\frac{3}{2}} + c \tag{4.30}$$

and the coefficients a, b, c for N_2 , O_2 and H_2O are experimentally determined and can be found in (Bailey et al., 1999), (Heard & Henderson, 2000).

The IPI system operates within a pressure range of 200 - 900 mbar, while the detection cell functions at a lower pressure of 2 - 13 mbar. The transition from the high-pressure IPI section to the low-pressure detection cell via free jet expansion induces a cooling in temperature due to adiabatic expansion. This cooling effect is present during both the calibration and inflight measurement phases. This impacts the lifetime of electronically excited OH molecules and consequently affects the quenching (Creasey, Heard, et al., 1997).

To evaluate the impact of free jet expansion on quenching within the HORUS detection axis, we compare the measured fluorescence decay against the calculated fluorescence decay using Equation 4.28 across various detection cell pressures and humidity levels. Figures

4.18A and B display the outcomes of this comparison for different detection cell pressures and temperature and water mixing ratios. The temperature employed for quenching calculations is derived from the measured temperature sensor readings situated at the end of the second detection axis, as depicted in figure 3.2. The calculated and measured quenching decay showed a larger deviation for OH detection cells especially in the lower pressure and this deviation becomes less prominent at higher pressures. However, this deviation was comparatively less while comparing the fluorescence decay in the second detection axis. Since the OH detection axis is positioned right after the jet expansion zone, the sampled air has very little time to heat up compared to the second detection cell $(HO_2 \text{ detection cell})$, which is located 50 cm away from the expansion zone, allowing the sample air to gradually approach the surrounding temperature. Consequently, the OH detection cell encounters cooler sampled air in contrast to the HO₂ detection cell. Additionally, as previously discussed, the temperature sensor's location enables it to measure the sample air temperature near the second detection axis (HO₂ detection cell). Thus a correction for temperature in the first axis (OH) must be applied. The correction temperature is found iteratively until the measurement matches with the calculated temperature as shown in figure 4.19.

Figures 4.20 and 4.21 illustrate a comparable scenario under inflight conditions. A fitting relationship between pressure and temperature difference, as depicted in the figure 4.22, has been established to incorporate this effect into the final quenching calculations for both ground calibration and inflight scenarios.



(A)

Figure 4.18: Figure A represents the calculated (blue) and measured (red) OH fluorescence decay (counts in log scale) in the OH detection axis during ground APACHE calibration. The actual temperature sensor reading is used for calculating the quenching. The abbreviation '*P*' stands for pressure inside the detection cell, '*H*' stands for humidity and $Temp_{off}$ stands for the calculated offset in measured temperature.



(B)

Figure 4.18: Figure B represents the calculated (blue) and measured (red) OH fluorescence decay (counts in log scale) in the HO_2 detection unit during ground APACHE calibration. Here, the actual temperature sensor reading is used for calculating the quenching. The abbreviation '*P*' stands for pressure inside the detection cell, '*H*' stands for humidity and $Temp_{off}$ stands for the calculated offset in measured temperature.



Figure 4.19: The figure represents the calculated (blue) and measured (red) OH fluorescence decay (counts in log scale) in the OH detection cell after correcting the OH detection cell temperature with a given temperature offset. The abbreviation 'P' stands for pressure inside the detection cell, 'H' stands for humidity, and T_{off} stands for the calculated offset in measured temperature.

(A)



Figure 4.20: Figure A and Figure B represent the calculated (blue) and measured (red) OH fluorescence decay (counts in log scale) in the OH (top panel) and HO_2 (bottom panel) detection cell respectively during an inflight measurement scenario. The abbreviation 'P' stands for pressure inside the detection cell,'H' stands for humidity and T_{off} stands for the calculated offset in measured temperature. In Figure A, the black points indicate the excluded data, as they fall below the detection limit.



Figure 4.21: The figure represents the calculated (blue) and measured (red) OH fluorescence decay (counts in log scale) in the first detection cell with a given temperature offset during an inflight measurement scenario. The abbreviation 'P' stands for pressure inside the detection cell,'H' stands for humidity and T_{off} stands for the calculated offset in measured temperature.



Figure 4.22: Correlation plot between the detection cell pressure and offset in the measured temperature in the first detection cell (OH detection unit) for ground calibration scenario (red) and Inflight scenario (blue).

Pressure-dependent airborne HORUS sensitivity

Following the procedures outlined above for APACHE system characterization, the airborne HORUS system's pressure-dependent sensitivity is assessed by the procedure mentioned in sections 4 and 4.1 and is calculated using the equations 4.31, 4.32, 4.33. Figure 4.23 shows the final HORUS calibration. Plotted as a function of the HORUS internal density is the HORUS sensitivity curve (panel A), the quenching effect (panel B), the linear fits to quantify the pressure-dependent sensitivity coefficients (panel C), and the remaining pressure-independent sensitivities (panel D). The overall uncertainty is described in the table 4.3

$$c_{(0)OH} \cdot \rho_{\text{Int}\,(1)}(P,T) = \frac{C_{\text{OH}}(P,T)}{Q_{IF}(P,T) \cdot b_c(T) \cdot \left[\alpha_{IPI\,\text{OH}}(P,T) \cdot \alpha_{detectioncell_{OH}}(P,T)\right]}$$
(4.31)

$$c_{(0)OH(2)} \cdot \rho_{\text{Int}(2)}(P,T) = \frac{C_{\text{OH}(2)}(P,T)}{Q_{IF(2)}(P,T) \cdot b_c(T) \cdot \left[\alpha_{IPI \text{ OH}}(P,T) \cdot \alpha_{detectioncell_{OH}(2)}(P,T)\right]}$$
(4.32)

$$c_{(0)HO_{2}(2)} \cdot \rho_{\text{Int}(2)}(P,T) = \frac{C_{\text{HO}_{2}(2)}(P,T)}{Q_{IF(2)}(P,T) \cdot b_{c}(T) \cdot \left[\alpha_{IPI \text{ OH }}(P,T) \cdot \alpha_{detectioncell_{OH}(2)}(P,T)\right]}$$
(4.33)

As HO_2 is indirectly measured through conversion to OH by introducing NO, the sensitivity is influenced by the efficiency of this conversion reaction. The final sensitivity of HO_2 is adjusted to account for this factor, as described in section 4.5.

Unspecified Sensitivity (*c*₀**)**

The unspecified sensitivity (c_0) consists of all the parameters such as the transmissivity efficiency of the White cell, the photon collection efficiency of the optical setup, and pressure-independent wall loss, among others. The unit of unspecified sensitivity (c_0) sensitivity is (cts ppt⁻¹ s⁻² molec⁻¹ cm³ mW⁻¹). It is calculated by rearranging the equation 4.20, 4.21 and 4.22 as given below.

$$c_{(0)OH} = \frac{C_{OH}(P,T)}{Q_{IF}(P,T) \cdot b_{c}(T) \cdot \left[\alpha_{IPI OH}(P,T) \cdot \alpha_{detectioncell_{OH}}(P,T)\right] \cdot \rho_{Int\,(1)}(P,T)}$$
(4.34)

$$c_{(0)OH(2)} = \frac{C_{OH(2)}(P,T)}{Q_{IF(2)}(P,T) \cdot b_{c}(T) \cdot \left[\alpha_{IPI OH}(P,T) \cdot \alpha_{detectioncell_{OH}(2)}(P,T)\right] \cdot \rho_{Int(2)}(P,T)}$$
(4.35)

$$c_{(0)HO_{2}(2)} = \frac{C_{HO_{2}(2)}(P,T)}{Q_{IF(2)}(P,T) \cdot b_{c}(T) \cdot \left[\alpha_{IPI OH}(P,T) \cdot \alpha_{detectioncell_{OH}(2)}(P,T)\right] \cdot \rho_{Int(2)}(P,T)}$$

$$(4.36)$$

The unspecified sensitivity (c_0) as defined in equation 4.34, remains unchanged and is seamlessly integrated into the inflight sensitivity assessment process. The (c_0) terms in equations 4.31, 4.32, and 4.33 are calculated using the inflight measured temperature and pressure. This enables us to determine the airborne HORUS instrument sensitivity in real airborne measurement scenarios.

Figure 4.24 shows the inflight sensitivity (figure A) and detection limit (figure B) during a typical inflight measurement (flight number 2 during BLUESKY campaign). The OH sensitivity ranged from 4 (±0.8) cts s ⁻¹pptv⁻¹ mW⁻¹ on the ground to 5.8 (±1.1) cts s ⁻¹pptv⁻¹ mW⁻¹ at 13 km while the *HO*₂ sensitivity ranged from 50 (±10)

cts s $^{-1}$ pptv $^{-1}$ mW $^{-1}$ to 60(±12) cts s $^{-1}$ pptv $^{-1}$ mW $^{-1}$ from the ground to 13 km altitude. The alteration in the sensitivity trend of the HO_2 axis compared to OH is mainly due to the changes in diffusion and wall loss due to the larger residence time inside the HORUS instrument. The total uncertainty, precision of the calibration are listed in table 4.3.

Parameter	Range [cts s $^{-1}$ pptv $^{-1}$ mW $^{-1}$]	Uncertainty (1 σ)
$C_{OH}(m cts~s^{-1}pptv^{-1}~mW^{-1})$	4 - 5	30 %
$C_{OH(2)}$ (cts s ⁻¹ pptv ⁻¹ mW ⁻¹)	10-16	32%
$C_{HO_2}($ cts s $^{-1}$ pptv $^{-1}$ mW $^{-1})$	50 - 65	32 %

Table 4.3: Pressure-dependent HORUS sensitivity and its corresponding uncertainty of OH and HO_2 during APACHE calibration. The total uncertainty is the sum of the quadrature of the individual uncertainties which mainly arises from calculating the OH concentration inside the APACHE chamber as described in 4.3.4 and table 4.2.



Figure 4.23: The calibrated sensitivity parameters of HORUS for OH in the 1st axis (depicted in the left four panels), OH in the 2nd axis (displayed in the middle four panels), and HO_2 in the 2nd axis (shown in the right four panels). The error bar shows the 1 σ uncertainty in the measurement. Panel B, Panel C and Panel D are calculated using the equation 4.28, 4.31 and 4.34 respectively. The black point indicates the data that has been excluded.



Figure 4.24: As a function of altitude, inflight sensitivity (Figure a) and detection limit (Figure b) for OH (blue) and HO_2 (red) for a typical flight (Flight number 2) during the BLUESKY campaign.

4.5 Chemical Interference and Characterization

4.5.1 Conversion efficiency, HONO and RO₂ interference in HO₂ measurement

As described in section 3.2, the HO_2 is measured indirectly by adding NO and converting HO_2 to OH and subsequently measuring the OH fluorescence. This process results in both atmospheric OH and OH converted from HO_2 reaching the second detection unit. To quantify the HO_2 contribution explicitly, the HOx signal needs to be correct as mentioned in section 4.1 and equation 4.37.

$$S_{HO_2(corrected)} = \left(S_{HOx} - \frac{C_{OH(2)} \cdot W_{Z2}}{C_{OH \cdot W_{Z1}}} \cdot S_{OH}\right)$$
(4.37)

where S_{HOx} is the total detected fluorescence signal, $C_{OH(2)}$ and C_{OH} are the sensitivity of OH in the second and first detection units. S_{OH} is the total detected OH fluorescence signal in the first axis and W_{z1} and W_{z2} are the corresponding laser power in the first and second detection unit.

The introduction of NO can lead to the formation of nitrous acid (HONO), which decreases the OH concentration. Conversely, NO can also react with peroxy radicals (RO_2) to generate OH, thereby increasing the OH concentration within the sampled air. Equation 4.37 should be further improved to account for this chemical interference as shown below:

$$HO_{2 \text{ corrected}} = \left[\frac{S_{HO_{2}(\text{corrected})}}{\eta_{\text{conv}}(P,T) \cdot SL_{[HONO]}(P,T)}\right] \cdot \left[1 - \alpha_{RO_{2}}(P,T)\right]$$
(4.38)

 αRO_2 symbolizes the relative impact of RO_2 interference on the HO_2 signal. $HO_{2(corrected)}$ represents the corrected HO_2 signal derived from equation 4.37. $\eta_{conv}(P, T)$ and $SL_{[HONO]}(P, T)$ denote the pressure-temperature-dependent conversion efficiency of NO addition and the reduction in OH signal due to HONO formation, respectively.

In order to determine the chemical residence time and subsequently $\eta_{\text{conv}}(P, T)$ to rectify the HO_2 data, NO titrations were carried out during the flight.

$$\eta_{\rm conv}(P,T) = \left[1 - e^{(-k_{\rm NO}(T)[{\rm NO}]t_{\rm NO}(P,T))}\right]$$
(4.39)

where [NO] is the concentration of NO in the sample flow between the injection point and the second detection axis, t_{NO} is the chemical residence time, and k_{NO} is the rate constant for HO_2 interacting with NO (Burkholder et al., 2020).

Figure 4.25 depicts the calculated NO conversion efficiency ($\eta_{\text{conv}}(P, T)$) and corresponding chemical residence time (t_{NO}) using data collected during the BLUESKY 2020 campaign. As detailed in the HORUS section, the NO injection alternates between 2 sccm ($1 \cdot 10^{13} \pm 0.3$ molecules .*cm*³) and 15 sccm ($7.65 \cdot 10^{13} \pm 0.4$ molecules . *cm*³) during standard in-flight operation. In the low NO injection mode, approximately 40% of HO_2 is converted into OH, whereas with high NO addition, nearly 100% efficiency is achieved across all altitudes. Chemical residence time during NO addition ranged from 13 milliseconds at ground level to 6 ms above 12 km.

With a high NO addition, the reaction of NO with OH can produce HONO, resulting in a decrease in OH radicals and reducing the signal in the second axis, as demonstrated in equation 4.40.

$$OH + NO + M \rightarrow HONO + M$$
 (4.40)

To assess the influence of HONO in the HO_2 signal, the CAABA-MECCA(Chemistry As A Box Model Application –Module Efficiently Calculating the Chemistry of the Atmosphere) is used. A more detailed description of the model can be seen in section 5.2. The model was initialized with the measured internal pressure and temperature during the standard inflight operation while the OH and HO_2 were initialized with zero pptv and 40 pptv respectively. A broad range of NO concentrations, including the standard in-flight operation $(1 - 7.65 \cdot 10^{13} \text{ molecules } cm^{-3})$ was used to initialize NO concentration. The model run time was set to the calculated chemical residence time as shown in figure 4.25. The ratio between the calculated HONO concentrations $([HONO]_{NO+OH+M})$ by the CAABA-MECCA model and the initial HO_2 concentrations within HORUS $([HO_2]_{int})$ is used to derive the correction factor for signal interference due to HONO formation $(SI_{[HONO]})$:

$$SI_{[HONO]} = 1 - \frac{[HONO]_{NO+OH+M}}{[HO_2]_{int}}$$
 (4.41)

Figure 4.26 shows the calculated signal interference of HONO using equation 4.40. During the standard in-flight NO concentration of $1 \cdot 10^{13} \pm 0.3$ molecules cm^{-3} and $7.65 \cdot 10^{13} \pm 0.4$ molecules cm^{-3} is injected into the incoming ambient air. At altitudes ranging above 10 km, 6 - 8 km, and 4 km, the corresponding average signal reductions are approximately on average 1%, 2 - 4%, and 7 - 9%, respectively.



Figure 4.25: Figure A illustrates the calculated conversion efficiency, using equation 4.39, plotted against NO concentration across various altitudes. In Figure B, the left panel, the chemical residence is depicted relative to altitude, while right panel displays the conversion efficiency as a function of attitude for both low and high NO additions.



Figure 4.26: The calculated signal interference due to HONO formation as a function of altitude and colour-coded to various possible injection modes of NO concentration. During standard in-flight conditions, the NO concentration varies between $1 \cdot 10^{13} \pm 0.3$ and $7.65 \cdot 10^{13} \pm 0.4$ molecules .*cm*³.

Apart from the reaction between HO_2 and NO, RO_2 radicals can also react with NO along the measuring axis, initiating the formation of HO_2 initially. Subsequently, if this HO_2 , generated in the measuring axis, further reacts with NO, it produces OH. This OH produced from RO_2 , results in 'the overestimation of the atmospheric HO_2 signal.

$$RO_2 + NO \rightarrow RO + NO_2$$
 (4.42)

$$RO + O_2 \rightarrow RCHO + HO_2$$
 (4.43)

In order to estimate the possible interference from RO_2 , the CAABA-MECCA box model was used. More details about the RO_2 species in the CAABA MECCA model are given in the section 5.4.2. First, a CAABA-MECCA simulation was conducted, wherein the model was constrained by atmospheric pressure, temperature, and available measurement data, except for HOx. These simulations offered a foundational chemical representation of the diversity and concentrations of various atmospheric RO_2 species that entered HORUS during the in-flight measurement. To quantify αRO_2 , two additional simulations (A and B) were carried out using output data from the prior atmospheric simulation to initialize the model's chemistry. In both simulations, the model was set to the in-flight internal conditions of pressure, temperature, and humidity within HORUS. OH was initialized based on measured OH values, and adjusted for internal wall losses to reproduce OH levels observed at the second detection axis. NO was initialized using internally injected NO concentration. The sole difference between the two simulations was that simulation A involved initializing the model with measured HO_2 concentrations (adjusted for wall losses), while simulation B initialized HO_2 levels at zero. Consequently, the increase in OH within simulation B could be directly attributed to RO_2 species generating HO_2 , which subsequently converted into OH. This approach allows us to differentiate between the RO_2 contribution and atmospheric HO_2 contribution in the detected OH signal. The output of the two simulations is as follows:

$$A: OH_A = (OH_{2ndaxis} + OH_{HO_2} + OH_{RO_2})$$

$$(4.44)$$

$$B:OH_B = (OH_{2ndaxis} + OH_{RO_2}) \tag{4.45}$$

where $OH_{2ndaxis}$ is the atmospheric OH in the second detection axis, OH_{HO_2} is the OH produced by atmospheric HO_2 reacting with known NO concentrations from different infflight injection modes and OH_{RO_2} is the OH produced from the computed RO_2 . The total fraction of RO_2 interference α_{RO_2} is calculated by

$$\alpha_{RO_2} = 1 - \left[\frac{OH_A - OH_B}{OH_A - OH_{2ndaxis}}\right]$$
(4.46)

The left panel of Figure 4.27 illustrates the computed contribution of RO_2 to the HO_2 signal, as determined by Equation 4.46. On average, this contribution shows an increase in signal ranging from 1% to 5% across altitudes spanning from 2 to 14 km. The right panel of Figure 4.27 displays the resultant HO_2 concentration (depicted in blue) after accounting for chemical interferences.



Figure 4.27: The percentage contribution of RO_2 interference to HO_2 signal calculated using the CAABA MECCA model by considering CH_4 as the main VOC is shown in the left panel. The right panel shows the measured atmospheric HO_2 (blue) and model calculated total RO_2 (green) concentrations.

4.5.2 OH chemical background and IPI performance

The OH chemical background (OH_{chem}) is measured by adding propane (1.7% or $3 \cdot 10^{14}$ molecules cm^{-3}) at every 2-minute interval and thus removing the atmospheric OH. The ambient OH concentration (OH_{atm}) is calculated by subtracting the OH chemical background (OH_{chem}) from the total OH signal (OH_{total}) which represents the OH signal when no propane is added. Since the reaction of propane with OH is a pressure-temperature-dependent process, the OH_{chem} should be corrected for this dependency for each altitude as described in equation 4.47.

$$OH_{atm} = (OH_{total} - (OH_{CHEM} \cdot \eta_{scav} (P, T)))$$
(4.47)

where $\eta_{\text{scav}}(P, T)$ is the pressure-temperature-dependent scavenging efficiency.

$$\eta_{\text{scav}}(P,T) = 1 - e^{(-k_{\text{C3H8}}(T)[C_3H_8]t_{\text{C3H8}})}$$
(4.48)

 $[C_3H_8]$ is the propane concentration in IPI, and $t_{C_3H_8}$ is the chemical residence time. $k_{C_3H_8}$ is the temperature-dependent rate constant for OH reacting with propane (Burkholder et al., 2020). The chemical residence time denotes the effective duration during which propane is introduced into the sampled air, thereby eliminating atmospheric OH. This was quantified by introducing varying amounts of propane into the IPI system at different altitudes. However, technical and software issues in the IPI system prevented this procedure from being carried out during the BLUESKY campaign. Nonetheless, the IPI cycling, which involved adding propane every 2 minutes, was maintained as in previous campaigns. Since the concentration of added propane, as well as the temperature, pressure, and consequently, the molecule concentration inside the IPI, remained consistent during the BLUESKY campaign compared to the previous CAFE Africa campaign, the $\eta_{\text{scav}}(P,T)$ is directly adopted from the CAFE Africa dataset. More details about the IPI scavenging efficiency during the CAFE AFRICA campaign can be seen in (Rohloff, 2022). The calculated IPI titration efficiency for the BLUESKY data set during IPI cycling was above 99% across all altitude ranges. Figure 4.28 shows the chemical residence time (left panel) adapted from the CAFE Africa data set and the right panel shows the total OH mixing ratio (OH_{total} , red) and the OH chemical background (OH_{chem} , blue) after applying the scavenging efficiency.


Figure 4.28: The chemical residence time $\eta_{scav}(P, T)$ taken from the CAFE Africa data set (right panel) and the corresponding total OH mixing ratio (red) and the OH chemical background sub-tracted (blue) during the BLUESKY campaign. The dark blue and red line represents the corresponding 500 m median values.

Chapter 5

The BLUESKY Campaign 2020

5.1 Measurement campaign

5.1.1 BLUESKY 2020 campaign

The COVID-19 epidemic and the ensuing lockdown in the spring of 2020 resulted in a significant decrease in anthropogenic emissions from industry and all forms of transportation, including aircraft. The main objective of the BLUESKY campaign was to understand the effect of this lockdown on atmospheric composition such as trace gases, aerosols, and cloud properties. The decrease in air pollution and aircraft emissions provided a unique opportunity to analyse the resulting changes in the atmosphere. The reduced pollution levels gave rise to anomalous blue skies, hence the name "BLUESKY" (Voigt et al., 2022). The campaign consists of eight measurement scientific flights with the German High Altitude and LOngrange research aircraft (HALO) from May 23 to June 9, 2020, covering an area from the Mediterranean region in southern Europe ($\approx 35^{\circ}$ N) up to the North Atlantic flight corridor $(\approx 60^{\circ} \text{N})$ ranged in altitude from few meters above the ground up to approximately 14 km into the lower stratosphere. All flights has its origin from the flight base of DLR (Deutsches Zentrum für Luft- und Raum- fahrt), in Oberpfaffenhofen, Germany. The complete flight track during the campaign is shown in 5.1. Vertical profiles were usually obtained during flybys around major airports and metropolitan centres in Europe to sample the air from emission sources on the earth's surface up to the lower stratosphere. A more detailed description of the BLUESKY campaign and distribution of trace gases and aerosols can be found in (Voigt et al., 2022).

During the BLUESKY campaign, a total of 14 different instruments were on board to measure different trace gases, aerosols, and meteorological parameters. More details can be found in (Voigt et al., 2022). Table 5.1 provides a list of campaign instruments, and their measuring technique, which were used for this study. NO was measured using a modified commercially available chemiluminescent detector NOAH (Tadic et al., 2021). TRISTAR, a multichannel spectrometer, was used to detect CO and CH_4 using mid-infrared quantum cascade laser absorption spectroscopy (QCLAS) (Schiller et al., 2008). A wet chemical mon-



Figure 5.1: All measurement flight paths during the BLUESKY 2020 campaign.

itoring device called the HYdrogen Peroxide and Higher Organic Peroxide monitor (HY-PHOP) was used to measure hydrogen peroxide and the total amount of organic hydroperoxides (Hamryszczak et al., 2022). The Fast Alrborne Ozone device, FAIRO, was used to monitor ozone using a chemiluminescence detector that was calibrated by a UV photometer (Zahn et al., 2012). Two spectroradiometers were used to capture the upward and downward spectrum actinic flux density (Bohn & Lohse, 2017). The Sophisticated Hygrometer for Atmospheric ResearchCh (SHARC), which is based on a tunable diode laser (TDL) configuration, was used to assess water vapour mixing ratios and humidity (Krautstrunk & Giez, 2012). Using the BAsic HALO Measurement and Sensor System (BAHAMAS), GPS data as well as measurements of temperature, pressure, wind speed, and actual airspeed were gathered. Further findings from the campaign regarding specific trace gases such as H_2O_2 , NOx, and gaseous H_2SO_4 , can be found in (Hamryszczak et al., 2022; Nussbaumer et al., 2022; Zauner-Wieczorek et al., 2022) respectively. Similarly, a global chemistry model simulation study related to the effect of the COVID-19 lockdown on the atmosphere during the BLUESKY measurement period can be found in Reifenberg et al. (2022)

Figure 5.2 shows the HOx and other relevant measurements during a typical flight during the BLUESKY campaign (flight 8). Sections A and B show the low approaches towards Bordeaux and Madrid respectively. Section C represents a convective outflow measurement where increased OH concentration is measured due to the reaction of HO_2 with elevated NO, while a similar reaction is represented in Section D but the spike in NO is due to lighting. See Appendix B for all time series data that HORUS and other instruments measured during the BLUESKY 2020 campaign.



Figure 5.2: Measured time series data during flight number 8. Sections A and B show the low approaches towards Bordeaux and Madrid respectively. Section C represents a convective outflow measurement where increased OH concentration is measured due to the reaction of HO_2 with elevated NO, while a similar reaction is represented in Section D but the spike in NO is due to lighting. All data shown are interpolated and averaged over the HORUS time resolution (15 s).

Measurement	Measurement Method	TMU [%]	Precision [1σ]	Time resolution	Reference
OH	IPI -LIF-FAGE	28 - 30%	0.01 - 0.2 pptv	15 s	(Marno, 2021)
HO ₂	IPI-LIF-FAGE	30% - 32%	0.01 - 0.4 pptv	15 s	(Marno, 2021)
NO	Chemiluminescence	15%	< 1 pptv	1 s	(Tadic et al., 2021)
H_2O_2 /ROOH	Wet chemical monitoring	28% / 40%	0.2% - 2%	1 min	(Hamryszczak et al., 2022)
<i>O</i> ₃	UVphotometry/Chemiluminescence	2.5%	0.1 ppb	10 Hz	(Zahn et al., 2012)
Photolysis Frequency	Spectral radiometer	7% - 8%	< 3%	2 s	(Bohn & Lohse, 2017)
СО	QCLAS	3%	\approx 3 ppb	1 s	(Schiller et al., 2008)
H ₂ O	TDLAS	5%	1 ppm	1 s	(Krautstrunk & Giez, 2012)

Table 5.1: List of measured species, the instrument, its working principle, and Total Uncertainty Measurement (TMU) that was used during the campaign and for this study. A complete list of instruments onboard HALO during BLUESKY can be seen in (Voigt et al., 2022).

5.1.2 ECHAM/MESSy Atmospheric Chemistry (EMAC) model.

EMAC is a 3-D global general circulation, atmospheric chemistry-climate model which comprises the fifth generation of the European Center Hamburg (ECHAM5) circulation model (Roeckner et al., 2006) and for standard data exchange between sub-models and base models the Modular Earth Submodel System (MESSy) (Jöckel et al., 2010) has been used. The horizontal resolution of the model in this study is T63 (i.e., roughly 1.8° ×1.8°) and the vertical resolution consists of 47 levels up to 1Pa. The dynamics of the EMAC model have been weakly nudged in the troposphere (Jeuken, Siegmund, Heijboer, Feichter, & Bengtsson, 1996; Jöckel et al., 2010; Löffler, Brinkop, & Jöckel, 2016)) towards the ERA5 meteorological reanalysis data (Hersbach et al., 2020) of the European Centre for Medium-Range Weather Forecasts (ECMWF) to represent the actual day to day meteorology in the troposphere. Initial conditions for the meteorology were also taken from the ERA-Interim reanalysis data, while the ones for the chemical composition were from previous EMAC simulations (Pozzer et al., 2022). The Module for Efficiently Calculating the Chemistry of the Atmosphere (MECCA) sub-model was used to simulate stratospheric and tropospheric gaseous and heterogeneous chemistry (R. Sander et al., 2005, 2011; R. Sander, 2015). In addition, the anthropogenic emissions used are based on CAMS-GLOB- ANTv4.2 (Granier et al., 2019) which uses emission data provided by the EDGARv4.3.3 inventory developed by the European Joint Research Centre (JRC; Crippa et al., 2018) and CEDS emissions (Hoesly et al., 2018). The current model study also focuses on the effect of the COVID-19 lockdown on the emission scenario by adopting the reduction coefficient for Europe as in Guevara et al. (2021) (see also section 1.2.2) for the sectors of energy production (ENE), road transport (TRO), and industrial processes (IND). The reduced emissions were averaged for the period 19 to 26 April (i.e., the last available week in the data set), and applied (for each country) for March, April, May, and June. For aviation (AVI) the model adopted the same method, although it applied the estimated factor to the entire aviation emissions, without any country distinction. More details regarding this model study can be found in (Reifenberg et al., 2022; Nussbaumer et al., 2022).

Figure 5.5 shows the vertical profile comparison of OH (left) and HO_2 (right) with HORUS measurement (blue) and EMAC global chemistry model (red) along with the result from CAABA MECCA box model (green) which will be discussed in detail in this chapter.

Data coverage The first two flights of the campaign lacked NO measurements due to instrument issues and the corresponding NOx data for those 2 flights were taken from the EMAC model. The comparison of NOx data with the EMAC model results is discussed in (Nussbaumer et al., 2022). Flight number 7 is completely excluded due to issues with the HORUS instrument. During the BLUESKY campaign, methane (CH_4), a significant sink

for OH, was also not measured and this was taken from the ECHAM/MESSy Atmospheric Chemistry (EMAC) model. A detailed description of the methane chemistry mechanism in the model can be found in (Winterstein & Jöckel, 2021). Several studies showed that, in general, CH_4 from the EMAC model align closely with the real-world observations made from satellite, ground-based and aircraft-based observations. One such study is presented in (Zimmermann et al., 2020) in which the EMAC modelled CH_4 is compared to observations from a long-term aircraft measurement campaign CARIBIC-2 (see Appendix FigureB.13). The rest of the measured species mentioned in 5.1 had complete coverage for the flights considered for this study. All data used in the current studies are interpolated and averaged over the HORUS measurement time resolution of 15 seconds.

5.2 CAABA MECCA Box Model

Real-time observations have frequently been utilized to parameterize and ratify chemical models in the quest of verifying and/or increasing our understanding of HOx chemistry happening at various geographical and temporal scales within our environment. This has led to various advancements in chemical mechanisms and their incorporation into models over time. For this study, the CAABA MECCA (Chemistry As A Box Model Application – Module Efficiently Calculating the Chemistry of the Atmosphere) has been used to calculate the steady-state chemistry mechanism. The Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell, Kirchner, Kuhn, & Seefeld, 1997), the Master Chemical Mechanism (MCM) (Jenkin et al., 2015), and the Mainz Isoprene Mechanism (MIM) (Taraborrelli, Lawrence, Butler, Sander, & Lelieveld, 2009) are mechanisms that exist inside CAABA-MECCA. The MECCA mechanism employed in this investigation is the Mainz Organic mechanism (MOM) (Sander et al., 2019), which consists of 1670 reactions involving CH_4 , HOx, O₃, NOx, non-methane hydrocarbon (NMHC), sulfur chemistry and 2664 chemical species (including 40 dummy species simulating deposition processes). Based on MCM, the original MIM was improved, and MIM2 was created to evaluate a larger variety of NOx regimes with a focus on NOx and organic species that contain nitrogen (Taraborrelli et al., 2009; Mallik et al., 2018).

5.2.1 Box model initialization

All measured values were interpolated on the time intervals of OH and HO_2 measurements (HORUS time) and the model simulations were constrained by fixing the measured species (NO, CO, O_3 , H_2O , H_2O_2 , sum of ROOH as CH_3OOH) to their observed values. Air density, pressure, temperature, humidity, and the photolysis frequencies such as $j(O^1D)$, $j(H_2O_2)$, $j(NO_2)$ were also taken from the relevant measurements. A few more significant species

were extracted, such as CH_4 , and HCHO from the corresponding EMAC model output. All the parameters mentioned above were considered fixed parameters for that given time and the corresponding steady-state OH and HO_2 concentration were calculated. The comprehensive mechanism (S. P. Sander et al., 2011) used in the box model consists of HOx, NOx, CH_4 , O_3 chemistry for the upper troposphere and stratosphere scenarios. Reactions involving halogens, sulphur compounds and higher-order hydrocarbons were switched off in the box model simulations. The complete chemical scheme of the model, its reaction rate coefficients etc can be found in Appendix C. The nomenclature used for defining chemical reactions and rate coefficients for this study is also taken from the given CAABA MECCA chemical scheme as seen in Appendix C.

5.2.2 Monte-Carlo simulation

The uncertainties of the simulated OH and HO_2 in the model caused by the uncertainty of the chemical rate coefficient were determined using the Monte Carlo simulation. Each Monte Carlo simulation consists of 9000 individual simulations in which all reaction rate coefficients were randomly varied within the rate coefficient uncertainties as per JPL and IUPAC recommendations, (Atkinson et al., 2007; R. Sander et al., 2005).



Figure 5.3: Histogram distribution of OH and HO_2 mixing ratios (in ppt) derived from Monte Carlo simulation for a single point in the upper troposphere (Altitude = 11 km, pressure = 238 mbar and temperature = 218 K). The histogram is averaged to nBins=50 with each bin width corresponding to 0.01 pptv and 0.1 pptv for OH and HO_2 respectively. The modelled value (red point) designates the mixing ratio obtained when no Monte Carlo variations were applied.

Figure 5.3 shows the Monte Carlo simulation result for a single point in the upper troposphere. The 1 σ uncertainty is estimated at the 31% and 68.7% percentiles and the calculated median value for the above simulation is 0.32±0.06 pptv and 6.5±0.8 pptv for OH and HO_2 respectively.

Figure 5.4 shows the comparison of measured and modelled OH and HO_2 during the BLUESKY campaign. The x-axis shows the final number of data points available after interpolating all the measured species on the time intervals of OH and HO_2 measurements as mentioned in the previous section. In general, the model was able to reproduce the measured OH and HO_2 and showed no significant deviations except in the red-shaded area. The large discrepancy in the red-shaded area can arise due to two possibilities. The first and more likely possibility is due to a major malfunction of the dye laser that happened before this section during the flight which might have affected the data quality of measured OH and HO_2 afterwards. At the same time, this section also encountered a large convective outflow event which may have affected the model calculations. This combined effect might be the most probable reason for this discrepancy.



Figure 5.4: The figure represents the point-to-point comparison of measured OH and HO_2 with the CAABA MECCA box model output during the BLUESKY campaign. The shaded area represents the total 1 σ uncertainty of the corresponding measurements and model calculations. The initialisation of the model, averaging time etc is mentioned in section 5.2.

5.3 HOx vertical profile during BLUESKY and comparison with EMAC and CAABA MECCA box model

Figure 5.5 shows the vertical profile comparison of OH (left) and HO₂ (right) with HORUS measurement (blue), CAABA-MECCA box model (green), and EMAC global model (red). The comparison with the models shows generally good agreement for both OH and HO_2 . The 1σ uncertainty for the measurement is 30% and 32% for OH and HO_2 respectively. The measured OH vertical profile (Figure 5.5) shows a maximum median mixing ratio of $0.37\pm0.1(1 \sigma, \text{ statistical})$ pptv at 12 km compared to 0.38 ± 0.15 (1 $\sigma, \text{ statistical})$ pptv from the box model. Between 3 and 8 km the OH mixing ratio stays with less variation around 0.14±0.07 (1 σ , statistical) pptv. After 7 km, the OH mixing ratio increases from 0.16±06 to 0.37 ± 0.1 (1 σ , statistical) pptv at 12 km. The average median deviation of the measured OH mixing ratio from the CAABA MECCA box model is less than 10 % with a maximum deviation of 13.5% at 6 km while the EMAC model in general overpredicting slightly by 20 -25% or 0.04 - 0.08 pptv with a maximum deviation of 40% at 8 km. Figure 5.6 shows the correlation plot between OH (left) and HO₂ (right) with the CAABA MECCA box model. On average the OH measurement agrees with 90% and the HO_2 measurement agrees with 80% with the CABBA –MECCA box model. The measured HO₂ vertical profile shows a maximum median mixing ratio of 21 ± 6 (1 σ , statistical) pptv in the mid-altitude (at 6 km) and decreases towards the upper troposphere with a minimum mixing ratio of 5 ± 2 (1 σ , statistical) pptv at 12 km. In general, HO₂ measurement shows a larger mixing ratio (on average 15-20% higher) compared to that of the box model calculation in the low altitude (2 - 7km) with a maximum deviation of 32% at 6 km. This deviation is within the 1 σ measurement uncertainty (32%) of HO₂. Besides that, most of the data in the mid-low altitudes (between 2 and 7 km) are measured while the aircraft is either ascending or descending, which induces rapid temperature changes. As mentioned in the section 3.2, the HO₂ is measured indirectly by converting HO₂ to OH by adding NO (table 2.1, reaction 5). Considering the temperature dependence of the reaction, the discrepancy observed between the measured HO_2 and model predictions at these altitude ranges could potentially be influenced by temperature variations during the rapid ascent and descent of the aircraft. This rapid movement also results in fewer data points at a constant altitude in this altitude range, potentially affecting the overall data quality (appendix B, table1). It is important to acknowledge these factors as possible contributors to the observed deviations, rather than concluding definitively.



Figure 5.5: Box whisker plot of 1km averaged vertical profile comparison of OH (left panel) and *HO*₂ (right panel) with HORUS measurement (blue), CAABA-MECCA box model (green), EMAC global model(red). Lower and upper box boundaries represent the 25th and 75th percentiles, respectively of the 1 km averaged HORUS measurement (15 seconds average). The line inside the box shows the median value and the lower and upper error lines represent the 10th and 90th percentiles respectively of the same 1km averaged data. The number of data points averaged per altitude bin is given in Appendix C, table 1.

5.4 HOx budget calculation

To understand the impact of individual trace gas species on HOx chemistry, it is crucial to assess the production and loss reactions of OH and HO_2 in relation to these trace gases. The following section of this chapter will present an analysis of the OH budget based on measurements (except for CH_4) and later additional discussion in the section by incorporating species data derived from the CAABA-MECCA model.

5.4.1 OH budget calculation using observations

NOTE:

For calculating the HOx budget during the BLUESKY campaign, trace gase species such as OH, HO_2 , NO, CO, H_2O , H_2O_2 , ROOH, O_3 , pressure, temperature, photolysis rates (*j* values) are taken from the corresponding observations. Since the CH_4 was not measured during the campaign, this was taken from the EMAC global chemistry model as mentioned in the previous section. The organic peroxide (ROOH) photolysis rate (*j*_{ROOH}) is taken from



Figure 5.6: The overall correlation plot between HORUS measurement and CAABA –MECCA box model colour-coded as a function of altitude. The error bar (grey) shows the 1σ total measurement uncertainty. The red line shows the linear regression fit and the black dotted line represents 1:1 line.

the measured photolysis frequency of methyl hydroperoxide (j_{MHP}) since MHP is the most predominant organic hydroperoxide (Hamryszczak et al., 2022) which is formed by the reaction of HO_2 with methyl peroxy radical (CH_3OO) which mainly formed by the oxidation of methane (CH_4) by OH (Levy, 1971). Since 90% of the total available data (see Appendix, table 1), is from above 7 km, the rest of the data evaluation will be focusing only above 7 km altitude range.

The primary production of OH ($P_{(OH)}$) is by the photolysis of ozone leading to the formation of O^1D and the subsequent reaction with water molecules as described in equation 5.1. The reaction rate constants (k) and photolysis frequency (j) nomenclature are described according to the CABBA–MECCA model scheme (R. Sander, 2015) and see Appendix C.

$$P_{(OH)} = \varphi_{OH} \cdot j_{O^{1}D} \cdot [O_{3}] = 2 \cdot \left(\frac{k_{2111} [H_{2}O]}{k_{2111} [H_{2}O] + k_{1000} [O_{2}] + k_{3101} [N_{2}]} \right) \cdot j_{O^{1}D} \cdot [O_{3}]$$
(5.1)

where ϕ_{OH} is the branching ratio describing the yield of OH when O^1D reacts with H_2O , which is in direct competition with deactivation collisions of O^1D with N_2 and O_2 molecules. k_{2111}, k_{1000} , and k_{3101} are the reaction rate constants of O^1D collisions with H_2O , O_2 , and N_2 respectively and j_{O^1D} is the corresponding photolysis frequency.

Ozonolysis of alkenes is also considered as a primary source of OH production. However, alkene species were not measured during the BLUESKY campaign. Studies conducted by (Rohloff, 2022) and (Marno, 2021) using similar airborne measurements showed that the contribution of ethene (C_2H_4) which is the most abundant alkene in the atmosphere (Herbin et al., 2009) is an order of magnitude 3 less than other OH sources. Besides this, the strong negative temperature dependence of ozonolysis of alkenes ((Burkholder et al., 2020)) also suggests that their contribution can be neglected in the upper troposphere. Hence the ozonolysis of alkenes as an OH production source is not discussed in this study.

Secondary production of OH ($S_{(OH)}$) consist of the production of OH from the peroxide photolysis and from the reaction of NO and O_3 with HO_2 as mentioned in **Table 1** and is described by the equation 5.2.

$$S_{(OH)} = j_{H_2O_2} [H_2O_2] + j_{MHP} [ROOH] + k_{G2107} [O_3] [HO_2] + k_{G3201} [NO] [HO_2]$$
(5.2)

Where k_{2107} and k_{3201} are the rate constants of reactions 5 and 6 mentioned in **Table 1**.

The loss rate of OH (L_{OH}) can be calculated by considering the measured reaction species that readily react with OH and their corresponding concentrations, as given in equation 5.3. Since OH is highly reactive and can react with various trace gases, only a few of those species were measured during the campaign. First, this section presents the loss rates that can be characterized using the measurements.

$$L_{(OH)}^{\text{characterized}} = k_{G4101}[OH] [CH_4] + k_{G4110}[OH] [CO] + k_{G2104}[OH] [O_3] + k_{G2112}[OH] [H_2O_2] + k_{G4107}[OH] [ROOH] + k_{G3202}[OH] [NO_2pss]$$
(5.3)
+ k_{G4108}[OH] [HCHO] + k_{G2109}[OH] [HO_2] + k_{G2114a}[OH]^2

Since NO_2 was also not measured during the BLUESKY campaign, it was calculated using the corresponding CAABA-MECCA box model output and HCHO data was taken from the EMAC dataset, as mentioned in section 5.2.

Figure 5.7 a and b shows the characterized OH production and loss rate during the BLUESKY campaign and is calculated using the available measurements as mentioned in section 5.4.1 and using Equations 5.1, 5.2 and 5.3. Figure 5.7 a shows the net OH budget for each point available from the campaign corresponds to the figure 5.4. Note that for Figure 5.7, only the measured species (except CH_4) were used. This indicates that HCHO and NO_2 in equation 5.3 were omitted. Figure 5.7 b shows the 1 km averaged OH budget above 7 km. On average, the total OH production rate above 7 km is between 4 to 7 $(\pm 1)10^5$ molec. $cm^{-3}s^{-1}$ of which 70 % - 75% are produced from the secondary production channel, which implies that most of the OH molecules in the atmosphere are recycled back. The combined secondary production channel contributes together on average $\approx 4 \ (\pm 1)10^5$ molec. $cm^{-3}s^{-1}$, in which the reaction of HO_2 with NO makes about $\approx 55\%$ or $4 \ (\pm 0.5)10^5$ molec. $cm^{-3}s^{-1}$ of produced OH followed by the reaction of HO_2 with O_3 at $\approx 20\%$ or 1.5

 $(\pm 0.5)10^5$ molec. $cm^{-3}s^{-1}$. The formation of OH from ozone photolysis weakens with the altitude as the water mixing ratio gets lower while other photolysis production channels become more important. During the BLUESKY campaign, the primary production channels contribute around $\approx 20\%$ - 25% of the total OH production in which the photolysis of ozone contributes about $\approx 11\%$ or 0.75 $(\pm 0.3)10^5$ molec. $cm^{-3}s^{-1}$., while the photolysis of hydrogen peroxides and organic peroxides contribute $\approx 13\%$ or $1 (\pm 0.4)10^5$ molec. $cm^{-3}s^{-1}$ and $\approx 3\%$ or $0.2 (\pm 0.1)10^5$ molec. $cm^{-3}s^{-1}$ respectively.

The average total characterized OH loss rate above 7 km is $4-6 (\pm 0.8)10^5$ molec. $cm^{-3}s^{-1}$. The reaction of OH with CO is the major contributor to this loss process accounting for $\approx 55 \%$ or $3.5 (\pm 0.5)10^5$ molec. $cm^{-3}s^{-1}$ while the reaction with O_3 contributes around 13% or $0.85 (\pm 0.3)10^5$ molec. $cm^{-3}s^{-1}$. However, these two reactions produce HO_2 , which later reacts with NO or O_3 to produce OH and thus helping to maintain the HOx cycle. Even though the reaction with CH_4 makes up only $\approx 8\%$ -10% of the total OH loss, on the other hand, this reaction acts as a major sink for CH_4 and influences the radiative forcing of the atmosphere. A more detailed study regarding CH_4 oxidation during the BLUESKY campaign will be discussed in the next chapter. OH is also lost via radical-radical recombination (OH+OH and OH + HO_2), reaction with methyl peroxy radical (CH_3O_2) which contribute together less than 8 per cent which is considered as 'rest' in Figure 5.7 and Figure 5.9

Since the lifetime of OH is very short (<1 second), it can be assumed that we measure the OH in a steady state, which implies that the total OH Loss rate (L_{OH}) should be equal to the total OH production rates based on the measured species $P_{OHtotal} = P_{OH} + S_{OH}$. The known reactivity of the OH due to its reaction with the species as mentioned in the equation 5.3 can be calculated by taking the ratio of total OH loss via equation 5.3 to the total OH concentration as given in equation 5.4

$$K_{(OH known)} = \frac{L(OH known)}{[OH]}.$$
(5.4)

This relation can be used to characterize the total known OH reactivity in units of s^{-1} . The missing reactivity (or unknown reactivity) that arises due to the limited representation of non-measured species can be represented by subtracting the known OH loss (L_{OH}) from the total OH production from measured species ($P_{OHtotal}$) and normalising by the measured OH concentration.

$$K_{(OH \text{ unknown})} = \frac{P_{(OH \text{ total})} - L_{(OH \text{ known})}}{[OH]}$$
(5.5)

Figure 5.8 shows the total known and unknown reactivity calculated using equation 5.5 and 5.4 for above 7 km altitude. The observations that are used in Equation 5.3 were able to explain about 85% - 94% of the total OH reactivity or the total OH budget. The remaining unknown factor is mainly due to the limited representation of trace gas species that were



(a)



Figure b shows the 1 km altitude average OH budget above 7 km during the BLUESKY campaign 2020. The budget is calculated from the available measurements from the campaign as mentioned in section 5.4.1.

* The "rest" mentioned in the LR OH panel represents reactions mainly involving CH_3O_2 and OH itself.



Figure 5.8: The known and unknown reactivity as a function of altitude calculated using equation 5.4, 5.5 and available measurements above 7 km and averaged into 1km altitude bins.

not measured during the campaign especially such as Non-Methane VOCs (NMVOCs) like HCHO. During deep convection events, air masses containing NMVOCs are transported from the ground to the upper troposphere and influence the oxidation process, especially for the OH loss (Lawrence & Lelieveld, 2010). The amount of NMVOC (mainly HCHO) that can contribute to OH loss is calculated using the steady-state CAABA MECCA Model with the same initialisation as mentioned in section 5.2. This contribution from NMVOC accredits an average OH loss of 5% or 0.35 (± 0.1)10⁵ molec. $cm^{-3}s^{-1}$ above 7 km and accounts for the missing reactivity and thus closing the OH budget as shown in figure 5.9.



Figure 5.9: Figure a shows 1 km averaged OH productions and loss rates above 7 km after including the contribution from the calculated NMVOC.

20%

13%

8%

Figure b shows the pie diagram corresponding to the contribution in percentage from each channel to the OH production and loss rates .

* The "rest" mentioned in the LR OH panel represents reactions mainly involving CH_3O_2 and OH itself.

5.4.2 *HO*₂ **budget calculation**

 HO_2 with a lifetime of 100 times that of OH, acts as a reservoir of OH in the atmosphere. Characterising the HO_2 budget is also necessary to comprehend how the HOx cycle behaves in terms of atmospheric oxidative capability. Many of the loss processes discussed in the OH budget eventually lead to the formation of HO_2 via direct or indirect steps. As described in table 2.1, the direct reaction of OH with CO, hydrogen peroxide, Ozone and formaldehyde leads to the formation of HO_2 . The known production of HO_2 can be described as

$$P_{(HO_2)} = k_{G4110}[OH][CO] + k_{G2112}[OH][H_2O_2] + k_{G2104}[OH][O_3] + k_m G4101.\phi_{HO_2}.[NO][RO2] + 2(j_{41001 b}[HCHO]) + j_{3202}[HNO_4] + k_{G4108}[OH][HCHO] (5.6)$$

Where ϕ_{HO_2} is the branching ratio of the RO_2 +NO reaction yielding HO_2 . Furthermore, HO_2 is also produced from the photolysis of HCHO (Cooke et al., 2010). The formaldehyde (HCHO) photolysis frequency is multiplied by two as the formed H atoms rapidly react with the atmosphere O_2 to form another HO_2 .

 RO_2 is mainly formed by the OH-initiated oxidation of VOC which creates a free radical that quickly reacts with atmospheric O_2 and this produced RO_2 can lead to the formation of HO_2 with intermediate steps. Even though, RO_2 was not measured during the BLUESKY campaign, it needs to be quantified to explain the total HO_2 budget. The first step is to estimate the steady-state concentration of RO_2 . For this, the total OH-initiated oxidation of methane, organic peroxide and previously calculated NMVOC is used. The losses for RO_2 are mainly from its reaction with NO, HO_2 and NO_2 which also needs to be considered while estimating the RO_2 concentration. An upper limit for RO_2 can be calculated using a steady state assumption as given in Equation 5.7. The reaction rates of CH_2O_2 as described in the CAABA MECCA box model(Appendix C) are considered as the reaction rates for RO_2 .

$$[\text{RO}_2] = \frac{(k_{\text{G4101}}[\text{OH}] [\text{CH}_4] + \text{L}(\text{OH})_{\text{NMVOC+OH}} + k_{\text{G4107}}[\text{OH}][\text{ROOH}])}{(k_{\text{G4104}}[\text{NO}] + k_{\text{G4103}} [\text{HO}_2] + k_{\text{G4114}} [\text{NO}_2])}$$
(5.7)

The formation of HO_2 from RO_2 mainly happens in intermediate steps and the major contribution is from the reaction of CH_3O_2 with NO giving CH_3O which in turn reacts with atmospheric O_2 to form HO_2 . These reactions are labelled as G4104a and G4118 as in (Appendix C).

The photolysis of HNO_4 is another way that HO_2 is produced. HNO_4 is formed when HO_2 and NO_2 combine, and have a typical lifetime of ≈ 2 days and can act as a buffer for HO_2 concentration. The HNO_4 concentration is calculated using a photochemical steady state approximation using the equation 5.8



Figure 5.10: Figure a shows the HO_2 production and loss rate in molecules $cm^{-3}s^{-1}$ for the data points shown in figure 5.4 during the BLUESKY 2020 campaign.

$$[HNO_4(PSS)] = \frac{k_{G3203} [NO_2] [HO_2]}{jHNO_4 + k_{G3207}}$$
(5.8)

The total loss rate of HO_2 can be calculated using the reaction rates in the HO_2 and measured species that react readily with HO_2 and their corresponding concentrations as described in equation 5.9.

$$L_{(HO_2)}^{\text{characterized}} = k_{G3201}[\text{NO}] [\text{HO}_2] + k_{G2107} [\text{O}_3] [\text{HO}_2] + k_{G3203} [\text{NO}_2] [\text{HO}_2] + k_{G2109}[\text{OH}] [\text{HO}_2] + k_{G2110} [\text{HO}_2]^2 + k_{G4103} [\text{RO}_2] [\text{HO}_2]$$
(5.9)

Figure 5.10 shows the HO_2 production and loss rate of the complete data available as mentioned in figure 5.4. Figure 5.11 shows the 1km averaged HO₂ budget above 7 km calculated using equation 5.6 and equation 5.9 during the BLUESKY campaign. As mentioned in the section 5.4.1, \approx 74% of the OH is produced from *HO*₂ while, figure 5.11 shows that about the same percentage of HO₂ is also formed from OH and this manifests the superiority of the HOx recycling channel in maintaining the OH and HO₂ concentration and thereby the oxidative capacity in the upper troposphere. On average, the total HO_2 production rate above 7 km is between 3 - 8 (± 1.5)10⁵ molec. $cm^{-3}s^{-1}$. The major source of HO_2 is coming from the reaction of OH with CO which accounts for 54% or 3 $(\pm 1)10^5$ molec. $cm^{-3}s^{-1}$ followed by the reaction of O₃ with OH and hydrogen peroxides with OH contributing 13% or 0.72 (± 0.27)10⁵ molec. $cm^{-3}s^{-1}$ and 2% or 0.12 (± 0.06)10⁵ molec. $cm^{-3}s^{-1}$ respectively and thus contributing \approx 70% from the recycling channel. The second most significant contribution for HO₂ production below 11 km is coming from the reaction of RO₂ with NO equating 18% or 1 (± 0.38)10⁵ molec. $cm^{-3}s^{-1}$ while above 11 km the contribution of OH with O₃ becomes more relavent. In general, HCHO photolysis contributes up to 5% or 0.26 $(\pm 0.15)10^5$ molec. $cm^{-3}s^{-1}$. Reactions such as, HNO_4 photolysis are about 2% while the reactions involving methoxyl radical (CH_3O), and the hydroxymethyl peroxy ($HOCH_2O_2$) together contribute up to 6% or 0.6 $(\pm 0.1)10^5$ molec. $cm^{-3}s^{-1}$ which is considered as 'rest' in figure 5.11.

On average, the total loss rate of HO_2 above 7 km is between 2.5 - 8 (±1)10⁵ molec. $cm^{-3}s^{-1}$ in which the majority(>70%) goes for OH production when HO_2 react with NO or O_3 . The reaction of NO+ HO_2 and $O_3 + HO_2$ makes up 54% or 3 (±0.7)10⁵ molec. $cm^{-3}s^{-1}$ and 20% or 1 (±0.5)10⁵ molec. $cm^{-3}s^{-1}$ respectively. The radial-radical ($HO_2 + HO_2$) recombination contributes up to 14% or 0.7 (±0.1)10⁵ molec. $cm^{-3}s^{-1}$ HO_2 loss while, the remaining HO_2 is lost by its reaction with RO_2 (3%) and NO_2 (3%).



Figure 5.11: Figure a shows 1 km averaged HO_2 productions and loss rates above 7 km after including the contribution from the calculated NMVOC.

Figure b shows the pie diagram corresponding to the contribution in percentage from each channel to the HO_2 production and loss rates.

* The "rest" mentioned in the PR HO_2 panel represents reactions mainly involving CH_3O and $HOCH_2O_2$ while in the LR HO_2 panel it mainly represents reaction with $HCHO + HO_2$.

Chapter 6

Impact of reduced emissions during COVID-19 lockdown on HOx chemistry in the upper troposphere

The COVID-19 pandemic had a significant impact on global societies, economies, and industries, with one of the most severely affected sectors being aviation. As the virus spread rapidly across borders, countries implemented widespread lockdowns and travel restrictions to curb the transmission of the virus. These unprecedented measures significantly disrupted the aviation sector, causing a cascade of challenges that reverberated throughout the entire industry. According to the 2022 European aviation environmental report (E. A. E. Report, 2022), total aircraft traffic, including all flight types, decreased by approximately 55-60% during the peak of the first COVID-19 lockdown in April-May 2020, as depicted in figure 6.1 a.

The composition of aircraft emission plumes mainly consists of CO_2 , NOx, H_2O , particular matter (PM) and sulfur compounds. While carbon dioxide (CO_2) emissions are frequently highlighted as the main contributor to aviation-induced climate change, they account for only about one-third of aviation's overall climate impact. The other two-thirds are attributed to reactive non- CO_2 emissions, primarily nitrogen oxides (NOx), water vapour (H_2O), and particulate matter (PM). The exact percentage depends on factors such as the engine design, fuel type, and operating conditions. These emissions interact with ambient air through chemical and microphysical processes, leading to the formation and depletion of radiatively active substances, which ultimately disrupt the atmospheric energy balance (Tait, Khan, Bullock, Lowenberg, & Shallcross, 2022). This chapter will discuss how the reduction in NOx emission due to the reduced aircraft emission affected the HOx chemistry and thereby the recycling capacity in the upper troposphere by comparing the findings from the BLUESKY campaign (which can be considered as a no-flight scenario) with another campaign HOOVER II (normal air traffic scenario) which was conducted in 2007 along a similar flight path over Europe.

6.1 Measurement campaigns

6.1.1 HOOVER II

HOOVER II campaign was designed to investigate the spatial variability of the oxidation capacity in the midsummer troposphere across Europe. The measurement campaign took place in the late spring/early summer of 2007 from July 18 to July 27, 2007, with the campaign base located in Hohn, Germany. Measurements were carried out in a Learjet - 34 aircraft. A total of 11 trace gas species including NO, CO, O_3 , OH, HO_2 , CH_4 , H_2O , photolysis frequency etc were measured between Mediterranean ($\approx 41^\circ$ N) and sub-polar northern Scandinavian region ($\approx 68^\circ$ N) during this time. More details about the HOOVER II campaign can be found in (Klippel et al., 2011; Bozem et al., 2017). OH and HO_2 were measured using earlier versions of the HORUS instrument which has similar working principles but with a different design as per Learjet - 34 configurations. A comprehensive analysis of OH and HO_2 and the instrument during the HOOVER II campaign can be found in Regelin et al. (2013).

Figure 6.1 b shows the complete flight path of BLUESKY (blue) and HOOVER II (red) measurement campaigns. The measured data from the two campaigns were filtered between 44 - 55 degree latitude and 7 - 14 degree longitude region (figure 6.1 b , black box) and is used for further investigation in this chapter.











Figure b shows the total flight paths of BLUESKY (blue) and HOOVER II (red). The box (black) represents the area used for further comparison for this chapter.

6.2 BLUESKY v/s HOOVER II: An insight into the impact of reduced aircraft emissions on HOx Chemistry in the upper troposphere

Figure 6.2 shows the comparison of measured vertical profiles of some selected trace gases during BLUESKY (green) and HOOVER II (red) campaigns averaging over 1 km altitude. In general, most of the trace gases mixing ratios decreased in the upper troposphere during BLUESKY compared to HOOVER II. Compared to 0.59 ± 0.3 (1 σ , statistical) pptv during HOOVER II, the mean OH mixing ratio in the upper troposphere (above 7km) during BLUESKY is 50 - 60 % lower at 0.28 ± 0.07 pptv while the mean HO_2 mixing ratio decreased by 30 - 35% from 13.2± 4.7 (1 σ , statistical) pptv during HOOVER II to 9.5 ± 4 pptv during BLUESKY. The total measurement uncertainty of OH and HO₂ during HOOVER II is 18% (Regelin et al., 2013). The NO vertical profile shows the typical C- shaped profile for both BLUESKY and HOOVER II campaigns with mixing ratio of 0.12 ± 0.11 (1 σ) ppbv and 0.45 ± 0.37 (1 σ) ppbv below 1000 m (0–1000 m) and 0.08 ± 0.04 ppbv and 0.21 ± 0.03 ppbv in the upper troposphere for BLUESKY and HOOVER II respectively (Nussbaumer et al., 2022). The reduction in the NO mixing ratio in the upper troposphere can be attributed mainly to the reduced anthropogenic emissions, especially the reduced emissions from aircraft during the COVID-19 lockdown. Similar findings related to declined NOx concentrations during the COVID-19 lockdown period in the ground level and upper troposphere using satellite and ground-based observations can be found in (Venter et al., 2020; Higham, Ramírez, Green, & Morse, 2021; He et al., 2021). This reduction in NO in the upper troposphere greatly impacts the HOx cycle, which will be described in the upcoming sections.

In figure 6.2, the NO mixing ratio at ground level is higher during the BLUESKY campaign compared to the HOOVER II campaign, which contrasts with most observations. This discrepancy is attributed to the fact that the HOOVER II campaign, based in Hohn Germany, collected most of the data below 5 km from rural areas, while the BLUESKY campaign measured most of its data below 2 km from airports or urban cities such as Berlin, Amsterdam, Barcelona, Madrid, and Frankfurt. However, only data measured above 7 km will be discussed in the upcoming sections.

Hydrogen peroxides and Organic peroxides also showed a considerable decline during BLUESKY compared to HOOVER II. On average, the Hydrogen peroxide and Organic peroxides mixing ratio decreases from 1.64 ± 0.83 ppbv and 1.1 ± 0.83 ppbv during the HOOVER II campaign compared to 0.32 ± 0.25 ppbv and 0.20 ± 0.1 ppbv during BLUESKY respectively. Clouds and precipitation scavenging strongly influenced this decline in peroxides and organic peroxides during the BLUESKY measurement period (Hamryszczak et al., 2022).

Ozone mixing ratios were lowest at the ground level (below 50 ppbv) and increased with altitude with a maximum above 10 km with a mixing ratio of an average of 120 -150



Figure 6.2: 1 km averaged vertical profiles of different atmospheric trace gases during BLUESKY (green) and HOOVER II (red). The shaded area represents the 1σ standard deviation of the measurements. The number of data points averaged per altitude bin can be found in the appendix table 1.

ppbv. Between the 2 campaigns, the O_3 mixing ratio showed only a small increase during BLUESKY above 10 km which can be mainly due to factors such as seasonal variation between the two campaigns, precursors level etc. Several studies about O_3 concentrations during the COVID-19 lockdown showed a reduction in the lower troposphere ("COVID-19 Crisis Reduces Free Tropospheric Ozone Across the Northern Hemisphere", 2021; Mertens et al., 2021) while other cases found higher O_3 concentrations during the similar lockdown period (Zhang et al., 2022). These variations in O_3 concentration can be attributed to various factors including precursor levels such as NOx, VOCs, local metrology and seasonal variation (Tavella & da Silva Júnior, 2021). A more detailed study about the O_3 production during the BLUESKY and HOOVER II campaign can be found in (Nussbaumer et al., 2022). The CO mixing ratios in the upper troposphere during BLUESKY were 78±15ppbv compared to 90±20 ppbv during HOOVER II, but overall, there was no discernible changes were visible. Detailed descriptions of other trace gas concentrations, VOCs, aerosol etc can be found in (Voigt et al., 2022).

6.3 Changes in OH primary production during COVID-19 lockdown

As mentioned in 5.4.1, the major contribution to OH primary production is from the photolysis of ozone and its subsequent collision with water. However, H_2O_2 which was considered a secondary source in section 5.4.1 has a typical lifetime of more than 3x that of HOx life-



Figure 6.3: Comparison data of 1 km averaged primary production of OH from ozone and peroxide photolysis above 7 km during BLUESKY 2020 and HOOVER II campaigns.

time, and due to this, the measurement of these species cannot be considered a product of in-situ measured one cycle of HOx. This fraction of peroxides that are produced within one HOx cycle needs to be distinguished from the total concentration since this fraction can photolyze to produce OH and act as a primary source. To separate peroxides with respect to their primary and secondary contributions, photochemical steady state (PSS) concentrations are calculated using the in-situ measured concentration of OH, HO_2 as shown in equation 6.1 where jH_2O_2 is the measured photolysis frequency.

$$[H_2O_2]_{PSS} = \frac{k_{G_{2110}} [HO_2]^2}{k_{G_{2112}}[OH] + jH_2O_2}$$
(6.1)

Figure 6.3 shows the comparison of OH primary production during the BLUESKY and HOOVER II campaigns. On average, the total OH primary production above 7 km during BLUESKY is $\approx 1.35 \ (\pm 0.7) 10^5$ molec. $cm^{-3}s^{-1}$ which is around 50% lower compared to $\approx 3 \ (\pm 0.8) 10^5$ molec. $cm^{-3}s^{-1}$ during the HOOVER II campaign.

The contribution of hydrogen peroxide photolysis to OH primary production during BLUESKY was around $4.4 (\pm 3)10^4$ molec. $cm^{-3}s^{-1}$ compared to $10 (\pm 3)10^4$ molec. $cm^{-3}s^{-1}$ during HOOVER II which is expected since the concentration of H_2O_2 and ROOH is relatively low during BLUESKY, as shown in figure 6.2. A sensitivity study conducted by Hamryszczak et al. (2022) using the EMAC model and measurements during both campaigns revealed that the decline in peroxide concentration during the BLUESKY campaign is mainly due to the enhanced presence of clouds and subsequent wet scavenging.



Figure 6.4: Comparison of measured (left) and EMAC calculated (right) humidity during BLUESKY (green) and HOOVER II (red). The datas are averaged for a 1 km altitude bin.

The contribution of ozone photolysis and its subsequent collision with water molecules to the OH primary production above 7 km during the BLUESKY was 8.1 $(\pm 0.5)10^4$ molec. $cm^{-3}s^{-1}$, which is more than 50% lower compared to 2.3 (±1)10⁵ molec. $cm^{-3}s^{-1}$ during HOOVER II. As previously noted in figure 6.2, the ozone concentration during the BLUESKY campaign was either somewhat equivalent or higher than that of HOOVER II; nevertheless, the OH production from ozone photolysis was lower during BLUESKY than it was during HOOVER II. This behaviour is mostly due to a particularly dry atmosphere during the BLUESKY measurement period since the produced O^1D from ozone photolysis needs to collide with water molecules to produce OH. Figure 6.4 shows the measured (left) and EMAC-modeled (right) water mixing ratios during BLUESKY (green) and HOOVER II (red) campaigns. In this study, the EMAC water mixing ratios are shown to confirm the scenario of a relatively dry atmosphere during BLUESKY. Both measured and EMACcalculated water mixing ratios show that the atmosphere was comparatively dry during the BLUESKY measurement period. The mean water mixing ratio between 7 and 11 km during the HOOVER II ranges between 1100 - 78 ppm compared to 800 - 40 ppm for the same altitude during the BLUESKY campaign.

In summary, compared to HOOVER II, the primary OH production throughout the BLUESKY campaign decreased by an average of 50-60%. Nonetheless, this decrease cannot be attributed directly to the COVID-19 lockdown's effects and is mostly the result of the different metrological conditions during the two campaign measurement periods.

6.4 Changes in total HOx production during the COVID-19 lockdown

Figure 6.5 shows the 1 km averaged total OH production and loss rates above 7 km during the BLUESKY (top panel) and HOOVER II (bottom panel) campaigns. In general, the OH production during the BLUESKY campaign showed a drastic decline compared to HOOVER II. The total OH production declined by approximately a factor of 2 from 13 $(\pm 1)10^5$ molec. $cm^{-3}s^{-1}$ to 7 $(\pm 1)10^5$ molec. $cm^{-3}s^{-1}$ at 7 km and by a factor of 6 from $32 (\pm 1.5)10^5$ molec. $cm^{-3}s^{-1}$ to 5 $(\pm 0.5)10^5$ molec. $cm^{-3}s^{-1}$ at 11 km. The decline in the OH and HO_2 production and loss channels (in percentage) during BLUESKY compared to HOOVER II can be seen in Figure 6.7. On average, the secondary production of OH from the reaction of NO and HO_2 decreased by more than 50% -70% or 10 $(\pm 2)10^5$ molec. $cm^{-3}s^{-1}$ during the BLUESKY while the contribution of HO_2 reacting with O_3 decreased by 20 % or 5 $(\pm 1)10^5$ molec. $cm^{-3}s^{-1}$. The total primary production is the photolysis of ozone and peroxides also decreased by 50% - 70% as mentioned in the previous section, 6.3. The principal cause of the decrease in secondary OH production is the decline in the NO concentration in the upper troposphere as a result of reduced aircraft emissions during the COVID-19 lockdown (Nussbaumer et al., 2022; Reifenberg et al., 2022).

While comparing the two campaigns, the overall OH loss rates exhibited a very similar pattern to the production rate and decreased by approximately the same amount as in the case of production rates. Each reaction of OH with CO, CH_4 , O_3 declined by 30% - 50% during the BLUESKY measurement period. The contribution of radical radical loss by OH - HO_2 reaction was also reduced by 50 % - 70%. These reductions in loss rates are mainly attributed to the lower production of OH during the BLUESKY campaign.

The total mean HO_2 production rates above 7 km during the BLUESKY campaign also decreased by 40 - 60% from 19 (±8)10⁵ molec. $cm^{-3}s^{-1}$ to 7 (±1)10⁵ molec. $cm^{-3}s^{-1}$ when compared to HOOVER II. The contributions from production channels like OH-initiated O_3 and CO oxidations and reactions of RO_2 + NO decreased on average by 30% - 80%. The reason for the decline in OH and NO is already discussed in the previous section. The total reduction in HO_2 production is reflected as it is in the total HO_2 loss rates by the same factors while the loss contribution from HO_2 reacting with NO, O_3 and radical-radical recombination decreased between 20 - 80% when compared to HOOVER II.



Figure 6.5: Figure shows 1 km averaged *OH* productions and loss rates above 7 km during BLUESKY (top panel) and HOOVER II (bottom panel) campaigns.

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Figure 6.6: Figure shows 1 km averaged HO_2 productions and loss rates above 7 km during BLUESKY (top panel) and HOOVER II (bottom panel) campaigns.



Figure 6.7: The mean difference (in %) between HOOVER II and BLUESKY campaigns for each production (left panels) and loss (right panels) channels for OH (top panels) and *HO*₂ (bottom panels).

6.5 Influence of Vertical Transport

Trace gases such as NOx, peroxides, HCHO, and VOCs etc from the boundary layer can be transported up to the upper troposphere by deep convection within hours (Bozem et al., 2017; Lelieveld & Crutzen, 1994; Scala et al., 1990; H. Fischer et al., 2003). These uplifted trace gases can undergo chemical or photochemical reactions and influence the production and loss rates of other species. Transport of these species to the UT in the convective clouds has a significant impact on its oxidising capacity since it affects both the primary production and secondary production of OH. For example, the NOx that is uplifted by the convection can react with HO_2 to enhance OH production or can increase/decrease the O_3 concentrations depending on the chemical regime.

6.5.1 FLEXPART

The effect of this precursor that is brought up by deep convection on OH production in the upper troposphere should be accounted for properly to differentiate and understand how much of the air sampled during both campaigns was influenced by the boundary layer. For this purpose, a Lagrangian transport and dispersion model, FLEXPART (FLEXible PARTicle dispersion model) has been used to calculate the backward trajectory of the air parcel and the air residence time inside the boundary layer. FLEXPART can simulate the transport, diffusion, dry and wet deposition, radioactive decay, and 1st-order chemical reactions (e.g.,



Figure 6.8: FLEXPART calculated boundary layer fraction (Boundary layer residence time/ Total air residence time) for a given location during HOOVER II (top panel) and BLUESKY (bottom panel). The residence time is calculated for a back trajectory for 0 - 168 hours. Plot created by Sergey Gromov.

OH oxidation) of tracers released from point, line, area or volume sources, or filling the whole atmosphere (Stohl, Forster, Frank, Seibert, & Wotawa, 2005; Pisso et al., 2019). A more detailed description of FLEXPART initialisation, working theory, technical aspects etc can be found at https://www.flexpart.eu/

For this study, the FLEXPART model was initialized using geospatial data obtained from the corresponding measurement campaigns and all the relevant meteorological variables such as wind speed, cloud fraction, humidity etc were taken from ERA 5 (ECMWF Re-Analysis) reanalysis data. The model was subjected to calculate the total and the boundary layer air residence time at a given point for back trajectories corresponding to 0 - 2 hours, 2 - 6 hours, 6 - 24 hours and 24 -168 hours lookback windows. Figure 6.8 shows the calculated boundary layer fraction, ie, the residence time of the sampled air mass in the boundary layer to the total age of the air mass for a back trajectory of 0 - 168 hours for BLUESKY (bottom panel) and HOOVER II(top panel). As mentioned earlier, Nitric Oxide (NO), acts as the major precursor for OH in the upper troposphere which contributes more than 50 % of its production. Typically, NO has a lifetime of a few hours to days in the atmosphere. Figure 6.9 show the FLEXPART calculated boundary layer fraction for 2 - 6 hours (top panel) and HOOVER

II (right panel). During BLUESKY, the amount of air mass influenced by the boundary layer (or vertical transport) is much less compared to that during HOOVER II for both lookback windows. Some parts of the HOOVER II campaign experienced influence from the boundary layer. This is mainly due to the difference in the measurement period since the BLUESKY campaign was conducted during late spring in May 2020 while HOOVER II was conducted during the summer of 2007, July when the frequency of vertical transport was usually higher. This also implies that vertical transport also played a minor role in higher OH production during HOOVER II compared to BLUESKY. A comprehensive view of the influence of the season (summer vs autumn) and its effect on OH concentration in the upper during the HOOVER II campaign can be found in (Regelin et al., 2013) and a detailed study of vertical transport influence on the chemical composition of the upper troposphere during HOOVER II can be found in (Bozem et al., 2017).

6.5.2 Understanding Reduced Nitric Oxide (NO) Levels During BLUESKY

As mentioned earlier, aircraft emissions, vertical transport from the boundary layer and lightning are the main sources of NO in the upper troposphere. The influence of vertical transport on the sampled air for the given area in this study is already discussed in section 6.5. An extensive study was conducted by Reifenberg et al. (2022) and Nussbaumer et al. (2022) to understand the effect of COVID-19 lockdown on different trace gases and particles using EMAC (see section 5.1.2) global chemistry model. In these studies, the model was constrained to simulate different scenarios during the BLUESKY measurement period. This includes a usual emissions scenario including aircraft emissions which is referred to as BLUESKY No Lockdown (BLUESKY NL) and a scenario without aircraft emissions which is referred to as BLUESKY No Lockdown No aircraft (BLUESKY NL no aircraft) as per Nussbaumer et al. (2022) nomenclatures. This study (Figure 6.10, Nussbaumer et al. (2022) showed that the in-situ measured NO mixing ratio during the BLUESKY agreed very well with the EMAC simulated BLUESKY No lockdown No aircraft scenario which implies that the reduction in the NO concentration in the upper troposphere was mainly due to the reduced aircraft emissions during COVID -19 lockdown.



Figure 6.9: Flexpart calculated boundary layer fraction (Residence time in boundary layer / Total age of the air mass) for 2 - 6 hours (top panel) and 6-24 hours (bottom panel) during the BLUESKY (left panel) and HOOVER II (right panel) measurement period.


Figure 6.10: NO vertical profiles for BLUESKY (red), for the BLUESKY no-lockdown scenario (yellow) and for the BLUESKY no-lockdown scenario without aircraft emissions (blue) (model data). Upper-tropospheric NO reductions observed for BLUESKY can be attributed to reduced air traffic during the COVID-19 lockdowns. Figure and caption are taken from Nussbaumer et al. (2022).

6.6 OH recycling Probability

The oxidative capacity or the atmosphere's self-cleaning capacity is defined as the ability of the atmosphere to oxidize and remove pollutant trace gases. The OH radical plays a major role in determining the atmospheric oxidation potential. In addition to primary production, radical recycling via secondary production acts as a key component for maintaining OH concentration in the atmosphere and ensures that the OH radical is not lost after reacting with other tracers. Thus, once produced radicals react with other trace gas species and remain in the system (Lelieveld et al., 2004). Thus, the OH recycling probability (r_{OH}) can be defined as the probability of a single OH molecule recycling back through the atmospheric chemical system. The recycling probability (r_{OH}) is mathematically described as the ratio of secondary OH production sources to the total OH production.

$$r_{\rm OH} = \frac{S_{\rm (OH)}}{P_{\rm (OH)} + S_{\rm (OH)}} \tag{6.2}$$

From the budget calculations (figure 5.9 and figure 6.5), it is clear that most of the OH in the upper troposphere is produced from the reaction of NO with HO_2 and thus NO plays the crucial part in maintaining the OH concentration in the upper troposphere and thereby the recycling efficiency. Although OH is likewise produced via the interaction of HO_2 with O_3 , the reaction rate coefficients of this channel differ dramatically. Above 8 km, the reaction rate coefficient of $HO_2 + O_3$ is 1.3e-15 s^{-1} , which is 4 orders of magnitude less compared to the 1e-11 s^{-1} for the reaction HO_2 +NO. Nevertheless, the contribution from $HO_2 + O_3$ channel can be larger in certain scenarios when the concentration of O_3 is much higher compared to NO, especially in the lower stratosphere region (> 13 km altitude).

Figure 6.11 shows the calculated OH recycling probability r_{OH} as a function of NO mixing ratios from different airborne, ship-based and ground-based measurement campaigns from different parts of the world (taken from Hens (2014)). The r_{OH} values are usually modest between 0.2 - 0.5 when NO levels are in the <100 pptv range. On the other hand, r_{OH} levels rise to a maximum plateau with values over 0.90 when NO levels approach the ppbV range. A very high NO concentration in the upper troposphere may lead to $r_{OH} > 1$ and push the system to an auto-catalytic scenario. Reactions like RO_2 + NO and OH + NO_2 can act as a limiting factor for r_{OH} exceeding 1 and stopping autocatalytic conditions. On the other hand, a very low NO concentration can also lead to inefficient HOx recycling which leads to the accumulation of pollutants to a catastrophic level (Lelieveld et al., 2004; Lelieveld, Peters, Dentener, & Krol, 2002).



Figure 6.11: OH recycling probability (r_{OH}) as a function of the NO mixing ratio from numerous measurement campaigns in various environments. OOMPH – marine boundary layer, ship stack plume; SOS99 – metropolitan, biogenic VOCs; HOPE12 and PARADE – biogenic and anthropogenic VOCs; TexAQS – metropolitan, anthropogenic VOCs; Gabriel – tropical rainforest; Trace-P – Airborne East Asia and western pacific; HUMPPA–COPEC–2010 – boreal forest. Figure and caption information is taken from Hens (2013) and (Marno, 2021).

In order to calculate the recycling probability using equation 6.2, as mentioned in the section 6.3, the fraction of peroxides that are produced within one lifetime of HOx also needs to be distinguished. Thus the equation 6.2 can be expanded as

$$P_{(OH)} + S_{(OH)} = \begin{pmatrix} \varphi_{OH} \cdot j_{O^{1}D} [O_{3}] + j_{H_{2}O_{2}} [H_{2}O_{2}] + j_{MHP} [ROOH] \\ + k_{G2107} [O_{3}] [HO_{2}] + k_{G3201} [NO] [HO_{2}] \end{pmatrix}$$
(6.3)

$$S_{(OH)} = \begin{pmatrix} j_{H_2O_2} [H_2O_2]_{pss} + j_{MHP} [ROOH]_{pss} \\ +k_{G2107} [O_3] [HO_2] + k_{G3201} [NO] [HO_2] \end{pmatrix}$$
(6.4)

$$r_{\rm OH} = \frac{\begin{pmatrix} j_{\rm H_2O_2} \, [{\rm H_2O_2}]_{pss} + j_{\rm MHP} [{\rm ROOH}]_{pss} \\ + k_{\rm G2107} \, [{\rm O}_3] \, [{\rm HO_2}] + k_{\rm G3201} [{\rm NO}] \, [{\rm HO_2}] \end{pmatrix}}{\begin{pmatrix} \varphi_{\rm OH} \cdot j_{\rm O^1D} \, [{\rm O}_3] + j_{\rm H_2O_2} \, [{\rm H_2O_2}]_{transp} + j_{\rm MHP} [{\rm ROOH}] \\ + k_{\rm G2107} \, [{\rm O}_3] \, [{\rm HO_2}] + k_{\rm G3201} [{\rm NO}] \, [{\rm HO_2}] \end{pmatrix}}$$
(6.5)

Figure 6.12 shows the calculated r_{OH} for the complete data set (including data below 7 km) for BLUESKY and HOOVER II campaigns. Compared to figure 6.11, the majority of the calculated r_{OH} during BLUEKSKY (shown in figure 6.12) shows value between 0.7 and 0.95. For the BLUESKY campaign, the dependency of NO mixing ratios on r_{OH} can be categorised into 3 different parts. One part of the data (indicated by the blue line) shows the S-shaped curve similar to Figure 6.11 which shows the decrease of r_{OH} as the NO mixing ratio decreases. In this part, the recycling probability decreased from 0.95 to 0.6 as the NO mixing ratio decreased from 0.1 ppbv to 0.07 ppbv. The second part (indicated by the red line) shows a flatter response as the NO mixing ratios decrease. Here, the recycling probability stayed above 0.9 as the NO mixing ratios decreased. This is mainly due to the relatively larger contribution of other OH production channels (both primary and secondary) especially the improved buffering from $HO_2 + O_3$ channel compared to that from NO reacting with HO_2 . The third section (shown in the box) where the recycling probability showed an average 30- 60% decrease and the values stayed between 0.4 and 0.65 despite having the same NO concentration. This is mainly due to comparatively low OH yield from other primary and secondary production channels as discussed in section 6.3 and section 6.4.

Figure 6.13 shows the comparison of calculated r_{OH} above 7 km during BLUESKY (green) and HOOVER II (red) campaigns as a function of NO mixing ratios (left). During the HOOVER II campaign, the OH recycling probability stayed between 0.98 and 0.7 as the NO mixing ratio decreased from 1 ppbv to 0.03 ppbv. For the same NO mixing ratios, the recycling probability during the BLUESKY campaign partly showed similar values while partly showing a reduction of 30-60% due to a reduction in OH production from other secondary channels as discussed before. Moreover, the BLUESKY campaign also experienced a further reduction in NO mixing ratios (< 0.01 ppbv) which also reduced the total OH recycling



Figure 6.12: Calculated OH recycling probability (r_{OH}) as a function of NO mixing ratios and altitude during the entire BLUESKY campaign.

probability by 30 - 60%. As previously shown, while meteorological variables undoubtedly contributed to the decrease in NO and OH concentration in the upper troposphere during the BLUESKY campaign, the primary cause of the reduction of NO concentration was the decrease in aircraft emissions brought on by the COVID-19 lockdown. This implies that the oxidative capacity and, thus, the atmospheric recycling efficiency can be negatively impacted by a low aircraft emission scenario.

6.6.1 Impact of Reduced Upper Tropospheric OH Concentration on Methane Loss Rates

Methane is a potent greenhouse gas contributing to global warming and climate change. Methane has accounted for roughly 25 - 30 per cent of global warming since pre-industrial times and is proliferating faster than at any other time since record-keeping began in the 1980s. Methane can trap heat 28 times more effectively than carbon dioxide over a 100-year timescale (https://www.iea.org/reports/methane-tracker-2021). Emissions from wetlands (eg: bogs, and swamps) and aquatic systems (eg: ponds, and lakes) are responsible for around 30% of methane emissions. Agriculture activities including rice farming, waste management, and livestock account for another 20% of methane production. Activities related to oil, gas, and coal extraction release an additional 30%, while the remainder of methane emissions come from minor sources such as wildfire, biomass burning, permafrost,



Figure 6.13: The recycling probability (r_{OH}) above 7 km as a function of NO mixing ratios during BLUESKY (green) and HOOVER II (red) campaigns.

termites, dams, and the ocean (Programme, Climate, & Coalition, 2021).

The hydroxyl radical acts as the major sink for methane in the atmosphere. Oxidation of methane by OH radicals contributes up to 90% methane removal in the troposphere (Y. Wang et al., 2022). OH reacts with methane and produces methyl radicals which rapidly react with atmospheric oxygen to form methyl peroxy radicals.

$$CH_4 + OH + O_2 \rightarrow CH_3O_2 + H_2O \tag{6.6}$$

$$CH_{4_{loss rate}} = k_{g4101} \cdot [CH_4] \cdot [OH]$$
(6.7)

Followed by the production of methyl peroxy radicals, a series of parallel chain reactions leads to the formation of more stable products such as formaldehyde which in turn can produce HO_2 via photolysis. Figure 6.14 shows the calculated first-order approximation loss rate of methane via OH oxidation. The methane loss rate during the BLUESKY campaign shows a considerable decrease compared to HOOVER II. During the BLUESKY campaign, the average methane loss rate at the 7–13 km altitude was between $3 \cdot 10^4$ and $4(\pm 0.9) \cdot 10^4$, which is 50–60% lower than the $7 \cdot 10^4$ and $11(\pm 0.9) \cdot 10^4$ during the HOOVER II campaign. This implies that the methane lifetime and thereby the concentration increased in the upper troposphere during the COVID-19 lockdown.

There were several studies have been conducted around the world investigating the methane concentration and its radiative effects during the COVID-19 lockdown. A study



Figure 6.14: Calculated first-order approximation of methane loss rate via OH oxidation during BLUESKY (green) and HOOVER II (red).

conducted by Peng et al. (2022) revealed that, compared to 2019, the global net methane removal from reactions with OH decreased by 7.5 \pm 0.8 Tg yr^{-1} due to the reduced OH and NO concentration brought by the COVID-19 lockdown. Similarly, another independent study conducted by Qu et al. (2022) using GOSAT (Greenhouse Gases Observing Satellite) satellite measurements disclosed that the mean methane mixing ratios in 2020 rose by 15 ppbv compared to 2019 due to the increased imbalance between the methane source and sink and the decline in OH concentration contributed up to 14 % for this methane increase. Another study by Stevenson et al. (2021) also showed that compared to 2019, the annual methane growth rose by 50% due to the reduction in NOx levels due to the COVID-19 lockdown. All these studies point towards a potential future scenario that might happen due to a lower NOx concentration in the upper troposphere as a part of climate action plans.

Chapter 7

Summary and outlook

Due to the COVID-19 outbreak and subsequent lockdowns in spring 2020, there was a significant decrease in emissions from industry and transportation. To analyze the impact of these reductions on atmospheric composition and cloud properties, the BLUESKY airborne measurement campaign was conducted in May 2020. This campaign utilized 14 different instruments on board HALO (High Altitude LOng range) aircraft to measure various trace gases, aerosols, and meteorological parameters. Among these, OH and HO_2 were measured using the LIF-FAGE-based HORUS instrument, which was calibrated with the APACHE system, incorporating certain enhancements from previous procedures. The sensitivity of the HORUS instrument was estimated at 4 - 5 [cts s⁻¹pptv⁻¹mW⁻¹] for OH and 50 - 65 [cts s⁻¹pptv⁻¹mW⁻¹] for HO_2 , with calibration uncertainties of 30% and 32 % respectively.

The collected OH and HO_2 data were analyzed using the steady-state box model CAABA - MECCA, demonstrating good agreement, with over 90% for OH and 80% for HO_2 . In the upper troposphere, the average OH mixing ratio was recorded at 0.042 ± 0.02 (1 σ) pptv, while the HO_2 mixing ratio stood at 21 ± 5 (1 σ) pptv. The characterized sources of OH in the upper troposphere showed that approximately 55% originated from NO reacting with HO_2 , followed by HO_2 reacting with O_3 (20%), photolysis of peroxide (13%), and ozone (11%). The main pathways for OH loss were its reaction with CO (55%), followed by reactions with ozone (13%), CH_4 (8%), and HO_2 (5%). Conversely, about 54% of the HO_2 was produced from OH reacting with O_3 (13%). The primary losses for HO_2 were from its reaction with NO (54%), O_3 (20%), and itself (14%).

To ascertain the impact of the COVID-19 lockdown on HOx chemistry, data from the BLUESKY campaign was compared to another airborne campaign, HOOVER II. This comparison revealed a 2-6 fold reduction in total OH production in the upper troposphere during the BLUESKY campaign. The decrease in OH production, ranging from 50-70%, was mainly attributed to the reduced NO levels due to diminished air traffic from the lockdown, with meteorological factors also influencing OH production. This reduction in OH production from NO reacting with HO_2 led to a 30-60% decrease in the probability of OH

recycling, as NO is crucial for this process in the upper troposphere.

OH, a major sink for Methane (CH_4) — a significant greenhouse gas influencing global warming — saw its methane loss rate during the BLUESKY campaign decline by 50-60% in the upper troposphere compared to the HOOVER II campaign. These findings point to a possible future scenario where lowering NOx concentrations in the upper troposphere as part of climate action plans. Utilizing NOx in the upper troposphere to reduce CH_4 concentrations might serve as a viable geoengineering strategy to mitigate climate change impacts, provided that comprehensive modelling and environmental assessments confirm its efficacy and safety.

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References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., ... Troe, J. (2007). Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III - Gas phase reactions of inorganic halogens. *Atmospheric Chemistry and Physics*, 7(4), 981–1191. doi: https://doi.org/10.5194/acp-7-981-2007

Bailey, A. E., Heard, D. E., Henderson, D. A., & Paul, P. H. (1999). Collisional quenching of OH (A ${}^{2}\Sigma^{+}$, v=0) by H₂O between 211 and 294 K and the development of a unified model for quenching. *Chemical Physics Letters*, 302, 132-138. doi: https://doi.org/10.1016/S0009-2614(99)00076-7

Blake, A. J. (1979). An Atmospheric Absorption Model for the Schumann-Runge Bands of Oxygen. *Journal Of Geophysical Research*, 84, 1-17.

Bohn, B., & Lohse, I. (2017, 9). Calibration and evaluation of CCD spectroradiometers for ground-based and airborne measurements of spectral actinic flux densities. *Atmospheric Measurement Techniques*, 10(9), 3151–3174. Retrieved from https://amt.copernicus.org/articles/10/3151/2017/ doi: https://doi.org/10.5194/amt-10-3151-2017

Bozem, H., Pozzer, A., Harder, H., Martinez, M., Williams, J., Lelieveld, J., & Fischer, H. (2017, 10). The influence of deep convection on HCHO and H2O2 in the upper troposphere over Europe. *Atmospheric Chemistry and Physics*, 17(19), 11835– 11848. Retrieved from https://acp.copernicus.org/articles/17/11835/2017/ doi: https://doi.org/10.5194/acp-17-11835-2017

Burkholder, J. B., Sander, S. P., Abbatt, J. P. D., Barker, J. R., Huie, R. E., Kolb, C. E., ... Wine, P. H. (2015). Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18. *JPL Publications* 15-10(19), 1–153. Retrieved from https:// jpldataeval.jpl.nasa.gov/pdf/JPL_Publication_15-10.pdf

Burkholder, J. B., Sander, S. P., Abbatt, J. P. D., Barker, J. R., Huie, R. E., Kolb, C. E., ... Wine, P. H. (2020). Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 19. *JPL Publications* 19-5(19), 1–153. Retrieved from http://jpldataeval .jpl.nasa.gov/ Chan, C. Y., Hard, T. M., Mehrabzadeh, A. A., George, L. A., & O'Brien, R. J. (1990). Third-generation FAGE instrument for tropospheric hydroxyl radical measurement. *Journal of Geophysical Research: Atmospheres*, 95(D11), 18569-18576. Retrieved from https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/JD095iD11p18569 doi: https://doi.org/https://doi.org/10.1029/JD095iD11p18569

Cooke, M. C., Utembe, S. R., Carbajo, P. G., Archibald, A. T., Orr-Ewing, A. J., Jenkin, M. E., ... Shallcross, D. E. (2010). Impacts of formaldehyde photolysis rates on tropospheric chemistry. *Atmospheric Science Letters*, *11*, 33-38. doi: https://doi.org/10.1002/asl.251

Covid-19 crisis reduces free tropospheric ozone across the northern hemisphere. (2021). *Geophysical Research Letters*, 48, 1-11. doi: https://doi.org/10.1029/2020GL091987

Creasey, D. J., Halford-Maw, P. A., Heard, D. E., Pilling, M. J., & Whitaker, B. J. (1997). Implementation and initial deployment of a field instrument for measurement of OH and HO2 in the troposphere by laser-induced fluorescence. *Journal of the Chemical Society - Faraday Transactions*, 93, 2907-2913. doi: https://doi.org/10.1039/a701469d

Creasey, D. J., Heard, D. E., & Lee, J. D. (2000, 6). Absorption cross-section measurements of water vapour and oxygen at 185 nm. Implications for the calibration of field instruments to measure OH, HO2 and RO2 radicals. *Geophysical Research Letters*, 27(11), 1651–1654. doi: https://doi.org/10.1029/1999GL011014

Creasey, D. J., Heard, D. E., Pilling, M. J., Whitaker, B. J., Berzins, M., & Fairlie, R. (1997). Visualisation of a supersonic free-jet expansion using laser-induced fluorescence spectroscopy: Application to the measurement of rate constants at ultralow temperatures. *Applied Physics B: Lasers and Optics*, 65, 375-391. doi: https://doi.org/10.1007/s003400050285

Dieke, G. H., & Crosswhite, H. M. (1962). The ultraviolet bands of OH Fundamental data. *Journal of Quantitative Spectroscopy and Radiative Transfer*, *2*, 97-199. doi: https://doi.org/10.1016/0022-4073(62)90061-4

Dong H. Zhang, S.-Y. L., Michael A. Collins. (2000). First-Principles Theory for the H+H2O, D2O Reactions. *Science*, 445-450. doi: https://doi.org/10.1126/science.290.5493.961.

Dorn, H. P., Neuroth, R., & Hofzumahaus, A. (1995). Investigation of OH absorption cross sections of rotational transitions in the band under atmospheric conditions. *Journal of Geophysical Research: Atmospheres*, 100, 7397-7409.

Edwards, G. D., Cantrell, C. A., Stephens, S., Hill, B., Goyea, O., Shetter, R. E., ... Eisele, F. L. (2003, 10). Chemical Ionization Mass Spectrometer Instrument for the Measurement of Tropospheric HO2 and RO2. *Analytical Chemistry*, 75(20), 5317–5327. doi: https://doi.org/10.1021/ac034402b

Eisele, F. L., Mount, G. H., Tanner, D., Jefferson, A., Shetter, R., Harder, J. W., & Williams, E. J. (1997). Understanding the production and interconversion of the hydroxyl radical during the Tropospheric OH Photochemistry Experiment. *Journal of Geophysical Research Atmospheres*, 102, 6457-6465. doi: https://doi.org/10.1029/96jd02207

Engel, V., Staemmler, V., Wal, R. L. V., Crim, F. F., Sension, R. J., Hudson, B., ... Schinke, R. (1992). Photodissociation of water in the first absorption band: A prototype for dissociation on a repulsive potential energy surface. *Journal of Physical Chemistry*, *96*, 3201-3213. doi: https://doi.org/10.1021/j100187a007

Faloona, I. C., Tan, D., Lesher, R. L., Hazen, N. L., Frame, C. L., Simpas, J. B., ... Brune, W. H. (2004). A Laser-induced Fluorescence Instrument for Detecting Tropospheric OH and HO2: Characteristics and Calibration. *Journal of Atmospheric Chemistry*, 47, 139–167.

Felton, C. C. J. C. M. J. (1988). Measurements of the diurnal OH cycle by a 14C-tracer method. *Nature*, 9-11. doi: https://doi.org/10.1038/335053a0

Fischer, E. V., Jacob, D. J., Yantosca, R. M., Sulprizio, M. P., Millet, D. B., Mao, J., ... Deolal, S. P. (2014, 3). Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution. *Atmospheric Chemistry and Physics*, 14, 2679-2698. Retrieved from https://acp .copernicus.org/articles/14/2679/2014/ doi: https://doi.org/10.5194/acp-14-2679-2014

Fischer, H., Reus, M. D., Traub, M., Williams, J., Lelieveld, J., Gouw, J. D., ... Siegmund, P. (2003). Deep convective injection of boundary layer air into the lowermost stratosphere at midlatitudes. *Atmospheric Chemistry and Physics*, *3*, 739-745. doi: https://doi.org/10.5194/acp-3-739-2003

Fuchs, H., Bohn, B., Hofzumahaus, A., Holland, F., Lu, K. D., Nehr, S., ... Wahner, A. (2011, 6). Detection of HO2 by laser-induced fluorescence: calibration and interferences from RO2. *Atmospheric Measurement Techniques*, 4(6), 1209–1225. Retrieved from https://amt.copernicus.org/articles/4/1209/2011/ doi: https://doi.org/10.5194/amt-4-1209-2011

Fuchs, H., Dorn, H.-P., Bachner, M., Bohn, B., Brauers, T., Gomm, S., ... Wahner, A. (2012, 7). Comparison of OH concentration measurements by DOAS and LIF during SAPHIR chamber experiments at high OH reactivity and low NO concentration. *Atmospheric Measurement* Techniques, 5, 1611-1626. Retrieved from https://amt.copernicus.org/articles/5/1611/ 2012/ doi: https://doi.org/10.5194/amt-5-1611-2012

Guevara, M., Jorba, O., Soret, A., Petetin, H., Bowdalo, D., Serradell, K., … Pérez Garciá-Pando, C. (2021, 1). Time-resolved emission reductions for atmospheric chemistry modelling in Europe during the COVID-19 lockdowns. *Atmospheric Chemistry and Physics*, 21(2), 773–797. doi: https://doi.org/10.5194/acp-21-773-2021

Hamryszczak, Z. T., Pozzer, A., Obersteiner, F., Bohn, B., Steil, B., Lelieveld, J., & Fischer, H. (2022, 7). Distribution of hydrogen peroxide over Europe during the BLUESKY aircraft campaign. *Atmospheric Chemistry and Physics*, 22(14), 9483–9497. doi: https://doi.org/10.5194/acp-22-9483-2022

Hard, T. M., O'Brien, R. J., Cook, T. B., & Tsongas, G. A. (1979). Interference suppression in HO fluorescence detection. *Applied Optics*, *18*, 3216. doi: https://doi.org/10.1364/ao.18.003216

He, C., Yang, L., Cai, B., Ruan, Q., Hong, S., & Wang, Z. (2021). Impacts of the COVID-19 event on the NOx emissions of key polluting enterprises in China. *Applied Energy*, 281, 116042. Retrieved from https://www.sciencedirect.com/science/article/pii/S0306261920314781 doi: https://doi.org/https://doi.org/10.1016/j.apenergy.2020.116042

Heard, D. E., & Henderson, D. A. (2000). Quenching of OH (${}^{2}\Sigma^{+}$, ' = 0) by several collision partners between 200 and 344 K. Cross-section measurements and model comparisons. *Physical Chemistry Chemical Physics*, 2, 67-72. doi: https://doi.org/10.1039/a908221b

Heard, D. E., & Pilling, M. J. (2003). Measurement of OH and HO2 in the Troposphere. *Chemical Reviews*, 103, 5163-5198. doi: https://doi.org/10.1021/cr020522s

Hens, K. (2014). *The oxidation capacity of the atmosphere-OH and HO 2 radical measurements in a boreal forest environment using laser induced fluorescence spectroscopy* (Doctoral dissertation, Mainz). doi: https://doi.org/http://doi.org/10.25358/openscience-4292

Herbin, H., Hurtmans, D., Clarisse, L., Turquety, S., Clerbaux, C., Rinsland, C. P., ... Coheur, P. F. (2009). Distributions and seasonal variations of tropospheric ethene (C 2H4) from Atmospheric Chemistry Experiment (ACE-FTS) solar occupation spectra. *Geophysical Research Letters*, *36*, 3-7. doi: https://doi.org/10.1029/2008GL036338

Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., Horányi, A., Muñoz-Sabater, J., ...

Thépaut, J. N. (2020). The ERA5 global reanalysis. *Quarterly Journal of the Royal Meteorological Society*, 146(730), 1999–2049. doi: https://doi.org/10.1002/qj.3803

Higham, J. E., Ramírez, C. A., Green, M. A., & Morse, A. P. (2021). UK COVID-19 lockdown: 100 days of air pollution reduction? *Air Quality, Atmosphere and Health,* 14, 325-332. doi: https://doi.org/10.1007/s11869-020-00937-0

Holland, F., Hessling, M., & Hofzumahaus, A. (1995, oct). In Situ Measurement of Tropospheric OH Radicals by Laser-Induced Fluorescence–A Description of the KFA Instrument. *Journal of the Atmospheric Sciences*, 52(19), 3393-3401. doi: https://doi.org/10.1175/1520-0469(1995)052j3393:ISMOTO¿2.0.CO;2

Incropera, F. P., DeWitt, D. P., Bergman, T. L., & Lavine, A. S. (2011). *Fundamentals of Heat and Mass Transfer* (6th ed.). John Wiley & Sons. Retrieved from https://hyominsite.wordpress.com/wp-content/uploads/2015/03/fundamentals-of -heat-and-mass-transfer-6th-edition.pdf

Jenkin, M. E., Young, J. C., & Rickard, A. R. (2015, 10). The MCM v3.3.1 degradation scheme for Isoprene. *Atmospheric Chemistry and Physics*, 15(20), 11433–11459. Retrieved from https://acp.copernicus.org/articles/15/11433/2015/ doi: https://doi.org/10.5194/acp-15-11433-2015

Jeuken, A. B., Siegmund, P. C., Heijboer, L. C., Feichter, J., & Bengtsson, L. (1996). On the potential of assimilating meteorological analyses in a global climate model for the purpose of model validation. *Journal of Geophysical Research Atmospheres*, 101(D12), 16939–16950. doi: https://doi.org/10.1029/96JD01218

Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., ... Kern, B. (2010, 12). Development cycle 2 of the Modular Earth Submodel System (MESSy2). *Geoscientific Model Development*, 3(2), 717–752. Retrieved from https://gmd.copernicus.org/articles/3/717/2010/ doi: https://doi.org/10.5194/gmd-3-717-2010

Klippel, T., Fischer, H., Bozem, H., Lawrence, M. G., Butler, T., Jöckel, P., ... Lelieveld, J. (2011, 5). Distribution of hydrogen peroxide and formaldehyde over Central Europe during the HOOVER project. *Atmospheric Chemistry and Physics*, 11(9), 4391–4410. Retrieved from https://acp.copernicus.org/articles/11/4391/2011/ doi: https://doi.org/10.5194/acp-11-4391-2011

Krautstrunk, M., & Giez, A. (2012). The transition from FALCON to HALO era airborne atmospheric research. In U. Schumann (Ed.), *Atmospheric physics: Background - methods - trends* (pp. 609–624). Springer-Verlag Berlin Heidelberg.

Kubistin, D. (2009). *OH-und HO 2-Radikale über dem tropischen Regenwald* (Doctoral dissertation, Johannes Gutenberg-Universität Mainz, Mainz). doi: https://doi.org/10.25358/openscience-2249

Kukui, A., Ancellet, G., & Bras, G. (2009, 10). Chemical ionisation mass spectrometer for measurements of OH and Peroxy radical concentrations in moderately polluted atmospheres. *Journal of Atmospheric Chemistry*, *61*, 133-154. doi: https://doi.org/10.1007/s10874-009-9130-9

Lawrence, M. G., & Lelieveld, J. (2010, 11). Atmospheric pollutant outflow from southern Asia: a review. *Atmospheric Chemistry and Physics*, 10, 11017-11096. Retrieved from https://acp.copernicus.org/articles/10/11017/2010/ doi: https://doi.org/10.5194/acp-10-11017-2010

Lelieveld, J., & Crutzen, P. J. (1994). Role of deep cloud convection in the ozone budget of the troposphere. *Science*, *264*, 1759-1761. doi: https://doi.org/10.1126/science.264.5166.1759

Lelieveld, J., Dentener, F. J., Peters, W., & Krol, M. C. (2004, 11). On the role of hydroxyl radicals in the self-cleansing capacity of the troposphere. *Atmospheric Chemistry and Physics*, 4(9/10), 2337–2344. Retrieved from https://acp.copernicus.org/articles/4/2337/2004/ doi: https://doi.org/10.5194/acp-4-2337-2004

Lelieveld, J., Gromov, S., Pozzer, A., & Taraborrelli, D. (2016, 10). Global tropospheric hydroxyl distribution, budget and reactivity. *Atmospheric Chemistry and Physics*, *16*(19), 12477–12493. Retrieved from https://acp.copernicus.org/articles/16/12477/2016/ doi: https://doi.org/10.5194/acp-16-12477-2016

Lelieveld, J., Peters, W., Dentener, F. J., & Krol, M. C. (2002). Stability of tropospheric hydroxyl chemistry. *Journal of Geophysical Research: Atmospheres*, 107(D23). doi: https://doi.org/10.1029/2002JD002272

Levy, H. (1971). Normal atmosphere: Large radical and formaldehyde concentrations predicted. *Science*, *173*(3992), 141–143. doi: https://doi.org/10.1126/science.173.3992.141

Liu, Y., Ivanov, A. V., & Molina, M. J. (2009, 2). Temperature dependence of OH diffusion in air and He. *Geophysical Research Letters*, *36*(3). doi: https://doi.org/10.1029/2008GL036170

Löffler, M., Brinkop, S., & Jöckel, P. (2016, 5). Impact of major volcanic eruptions on stratospheric water vapour. *Atmospheric Chemistry and Physics*, 16(10), 6547– 6562. Retrieved from https://acp.copernicus.org/articles/16/6547/2016/ doi: https://doi.org/10.5194/acp-16-6547-2016 Logan, J. A., Prather, M. J., Wofsy, S. C., & Mcelroy, M. B. (1981). Tropospheric chemistry: A global perspective. *Journal of Geophysical Research*, *86*, 7210-7254. doi: https://doi.org/10.1029/JC086iC08p07210

Mallik, C., Tomsche, L., Bourtsoukidis, E., Crowley, J. N., Derstroff, B., Fischer, H., ... Harder, H. (2018, 7). Oxidation processes in the eastern Mediterranean atmosphere: evidence from the modelling of HOx measurements over Cyprus. *Atmospheric Chemistry and Physics*, 18(14), 10825–10847. Retrieved from https://acp.copernicus.org/articles/18/ 10825/2018/ doi: https://doi.org/10.5194/acp-18-10825-2018

Mao, J., Ren, X., Zhang, L., Duin, D. M. V., Cohen, R. C., Park, J.-H., ... Brune, W. H. (2012, 9). Insights into hydroxyl measurements and atmospheric oxidation in a california forest. *Atmospheric Chemistry and Physics*, 12, 8009-8020. Retrieved from https://acp.copernicus.org/articles/12/8009/2012/ doi: https://doi.org/10.5194/acp-12-8009-2012

Marno, D. (2021). The Oxidation Capacity of the Summertime Asian Monsoon Anticyclone-Airborne measurements of OH and HO 2 radicals in the Upper Troposphere using Laser Induced Fluorescence Spectroscopy (Doctoral dissertation, Johannes Gutenberg-Universität Mainz,). doi: https://doi.org/http://doi.org/10.25358/openscience-6037

Marno, D., Ernest, C., Hens, K., Javed, U., Klimach, T., Martinez, M., ... Harder, H. (2020, 5). Calibration of an airborne HOx instrument using the All Pressure Altitude-based Calibrator for HOx Experimentation (APACHE). *Atmospheric Measurement Techniques*, *13*(5), 2711–2731. doi: https://doi.org/10.5194/amt-13-2711-2020

Marshall, J., & Plumb, R. (2008). *Atmosphere, Ocean and Climate Dynamics, Volume 93: An Introductory Text.* Bulington, MA USA. Pg.

Martinez, M., Harder, H., Kubistin, D., Rudolf, M., Bozem, H., Eerdekens, G., ... Lelieveld, J. (2010). Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: airborne measurements. *Atmos. Chem. Phys*, *10*, 3759–3773. Retrieved from www.atmos-chem-phys .net/10/3759/2010/

Mertens, M., Jockel, P., Matthes, S., Nutzel, M., Grewe, V., & Sausen, R. (2021, 6). COVID-19 induced lower-tropospheric ozone changes. *Environmental Research Letters*, *16*(6). doi: https://doi.org/10.1088/1748-9326/abf191

Novelli, A. (2015). *The formation of OH radicals from Criegee intermediates: a LIF-FAGE study from laboratory to ambient* (Doctoral dissertation, Johannes Gutenberg-Universität). doi: https://doi.org/http://doi.org/10.25358/openscience-1835

Nussbaumer, C. M., Pozzer, A., Tadic, I., Roder, L., Obersteiner, F., Harder, H., ... Fischer, H. (2022, 5). Tropospheric ozone production and chemical regime analysis during the COVID-19 lockdown over Europe. *Atmospheric Chemistry and Physics*, 22(9), 6151–6165. doi: https://doi.org/10.5194/acp-22-6151-2022

Peng, S., Lin, X., Thompson, R. L., Xi, Y., Liu, G., Hauglustaine, D., ... Ciais, P. (2022). Wetland emission and atmospheric sink changes explain methane growth in 2020. *Nature*, 612, 477-482. doi: https://doi.org/10.1038/s41586-022-05447-w

Petäjä, T., R. L. Mauldin, I., Kosciuch, E., McGrath, J., Nieminen, T., Paasonen, P., ... Kulmala, M. (2009, 10). Sulfuric acid and OH concentrations in a boreal forest site. *Atmospheric Chemistry and Physics*, 9, 7435-7448. Retrieved from https://acp.copernicus.org/ articles/9/7435/2009/ doi: https://doi.org/10.5194/acp-9-7435-2009

Pisso, I., Sollum, E., Grythe, H., Kristiansen, N. I., Cassiani, M., Eckhardt, S., ... Stohl, A. (2019, 12). The Lagrangian particle dispersion model FLEXPART version 10.4. *Geoscientific Model Development*, 12(12), 4955–4997. Retrieved from https://gmd.copernicus.org/articles/12/4955/2019/ doi: https://doi.org/10.5194/gmd-12-4955-2019

Price, W. C., & Collinss, G. (1935). The Far Ultraviolet Absorption Spectrum of Oxygen. *American Physical Society*, 187. Retrieved from https://link.aps.org/doi/10.1103/ PhysRev.48.714 doi: https://doi.org/10.1103/PhysRev.48.714

Programme, U. N. E., Climate, & Coalition, C. A. (2021). *Benefits and Costs of Mitigating Methane Emissions*. Retrieved from https://www.unep.org/resources/report/global -methane-assessment-benefits-and-costs-mitigating-methane-emissions

Qu, Z., Jacob, D. J., Zhang, Y., Shen, L., Varon, D. J., Lu, X., ... Parker, R. J. (2022). Attribution of the 2020 surge in atmospheric methane by inverse analysis of GOSAT observations. *Environmental Research Letters*, *17*(9). doi: https://doi.org/10.1088/1748-9326/ac8754

Regelin, E., Harder, H., Martinez, M., Kubistin, D., Tatum Ernest, C., Bozem, H., ... Lelieveld, J. (2013, 11). HOx measurements in the summertime upper troposphere over Europe: a comparison of observations to a box model and a 3-D model. *Atmospheric Chemistry and Physics*, *13*(21), 10703–10720. Retrieved from https://acp.copernicus.org/articles/ 13/10703/2013/ doi: https://doi.org/10.5194/acp-13-10703-2013

Reifenberg, S. F., Martin, A., Kohl, M., Bacer, S., Hamryszczak, Z., Tadic, I., ... Pozzer, A. (2022, 8). Numerical simulation of the impact of COVID-19 lockdown on tropospheric composition and aerosol radiative forcing in Europe. *Atmospheric Chemistry and Physics*,

22(16), 10901-10917. Retrieved from https://acp.copernicus.org/articles/22/10901/ 2022/ doi: https://doi.org/10.5194/acp-22-10901-2022

Report, E. A. E. (2022). European Aviation Environmental Report 2022. European Union Aviation Safety Agency.

Report, E. C. (2021). Special report on the impact of the COVID-19 pandemic on the U.S and European ANS systems. *European Commission Report*.

Roeckner, E., Brokopf, R., Esch, M., Giorgetta, M. A., Hagemann, S., Kornblueh, L., ... Schulzweida, U. (2006). Sensitivity of simulated climate to horizontal and vertical resolution in the ECHAM5 atmosphere model. *Journal of Climate*, *19*(16), 3771–3791. doi: https://doi.org/10.1175/JCLI3824.1

Rohloff, R. (2022). *Konvektiver Einfluss auf das OH-Oxidationspotential der oberen tropischen Troposphäre* (Doctoral dissertation, Johannes Gutenberg-Universitat). doi: https://doi.org/http://doi.org/10.25358/openscience-6844

Saha, L., Kumar, A., Kumar, S., Korstad, J., Srivastava, S., & Bauddh, K. (2022). The impact of the COVID-19 lockdown on global air quality: A review. *Environmental Sustainability*, *5*, 5-23. Retrieved from https://doi.org/10.1007/s42398-021-00213-6 doi: https://doi.org/10.1007/s42398-021-00213-6

Sander, R. (2015, 4). Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics*, *15*(8), 4399–4981. doi: https://doi.org/10.5194/acp-15-4399-2015

Sander, R., Baumgaertner, A., Gromov, S., Harder, H., Jöckel, P., Kerkweg, A., ... Xie, Z.-Q. (2011, 5). The atmospheric chemistry box model CAABA/MECCA-3.0. *Geoscientific Model Development*, 4(2), 373–380. Retrieved from https://gmd.copernicus.org/articles/ 4/373/2011/ doi: https://doi.org/10.5194/gmd-4-373-2011

Sander, R., Kerkweg, A., Jöckel, P., & Lelieveld, J. (2005, 2). Technical note: The new comprehensive atmospheric chemistry module MECCA. *Atmospheric Chemistry and Physics*, 5(2), 445–450. Retrieved from https://acp.copernicus.org/articles/5/445/2005/ doi: https://doi.org/10.5194/acp-5-445-2005

Sander, S. P., Abbatt, J., Friedl, R. R., Barker, J. R., Burkholder, J. B., Golden, D. M., ... Wine, P. H. (2011). Chemical kinetics and photochemical data for use in atmospheric studies evaluation Nb. 17. *JPL Publication 10-6, Jet Propulsion Laboratory, Pasadeba*(17). Retrieved from http://jpldataeval.jpl.nasa.gov Scala, J. R., Garstang, M., Tao, W. K., Pickering, K. E., Thompson, A. M., Simpson, J., ... Khalil, M. A. (1990). Cloud draft structure and trace gas transport. *Journal of Geophysical Research*, 95, 15-17. doi: https://doi.org/10.1029/jd095id10p17015

Schiller, C. L., Bozem, H., Gurk, C., Parchatka, U., Königstedt, R., Harris, G. W., ... Fischer, H. (2008). Applications of quantum cascade lasers for sensitive trace gas measurements of CO, CH4, N2O and HCHO. *Applied Physics B: Lasers and Optics*, *92*(3 SPECIAL ISSUE), 419–430. doi: https://doi.org/10.1007/s00340-008-3125-0

Stevens, P. S., Mather, J. H., & Brune, W. H. (1994). Measurement of tropospheric OH and HO2 by laser-induced fluorescence at low pressure. *Journal of Geophysical Research*, 99, 3543-3557. doi: https://doi.org/10.1029/93JD03342

Stevenson, D., Derwent, R., Wild, O., & Collins, W. (2021). COVID-19 lockdown NOx emission reductions can explain most of the coincident increase in global atmospheric methane. *Atmospheric Chemistry and Physics Discussions*, 2021, 1-8. Retrieved from https://acp.copernicus.org/preprints/acp-2021-604/

Stockwell, W. R., Kirchner, F., Kuhn, M., & Seefeld, S. (1997). A new mechanism for regional atmospheric chemistry modelling. *Journal of Geophysical Research Atmospheres*, 102(22). doi: https://doi.org/10.1029/97jd00849

Stohl, A., Forster, C., Frank, A., Seibert, P., & Wotawa, G. (2005). Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2. *Atmospheric Chemistry and Physics*, *5*, 2461-2474. doi: https://doi.org/10.5194/acp-5-2461-2005

Tadic, I., Nussbaumer, C. M., Bohn, B., Harder, H., Marno, D., Martinez, M., ... Fischer, H. (2021, 5). Central role of nitric oxide in ozone production in the upper tropical troposphere over the Atlantic Ocean and western Africa. *Atmospheric Chemistry and Physics*, 21(10), 8195–8211. Retrieved from https://acp.copernicus.org/articles/21/8195/2021/doi: https://doi.org/10.5194/acp-21-8195-2021

Tait, K. N., Khan, M. A. H., Bullock, S., Lowenberg, M. H., & Shallcross, D. E. (2022). Aircraft Emissions, Their Plume-Scale Effects, and the Spatio-Temporal Sensitivity of the Atmospheric Response: A Review. *Aerospace*, *9*. doi: https://doi.org/10.3390/aerospace9070355

Taraborrelli, D., Lawrence, M. G., Butler, T. M., Sander, R., & Lelieveld, J. (2009,
4). Mainz Isoprene Mechanism 2 (MIM2): an isoprene oxidation mechanism for regional and global atmospheric modelling. *Atmospheric Chemistry and Physics*, 9(8), 2751–2777. Retrieved from https://acp.copernicus.org/articles/9/2751/2009/ doi: https://doi.org/10.5194/acp-9-2751-2009

Tavella, R. A., & da Silva Júnior, F. M. R. (2021). Watch out for trends: did ozone increased or decreased during the COVID-19 pandemic? *Environmental Science and Pollution Research*, *28*, 67880-67885. Retrieved from https://doi.org/10.1007/s11356-021-17142-w doi: https://doi.org/10.1007/s11356-021-17142-w

T.M.Hard, R.J.O'Brien, Chan, C., & Mehrabzadeh, A. (1984). Tropospheric free radical determination by fluorescence assay with gas expansion. *Environmental Science and Technology*, *18*(10), 768-777. doi: https://doi.org/10.1021/es00128a009

Venter, Z. S., Aunan, K., Chowdhury, S., & Lelieveld, J. (2020, 8). COVID-19 lockdowns cause global air pollution declines. *Proceedings of the National Academy of Sciences*, 117(32), 18984–18990. Retrieved from https://pnas.org/doi/full/10.1073/pnas.2006853117 doi: https://doi.org/10.1073/pnas.2006853117

Voigt, C., Lelieveld, J., Schlager, H., Schneider, J., Curtius, J., Meerkötter, R., ... Rapp, M. (2022, 8). Cleaner Skies during the COVID-19 Lockdown. *Bulletin of the American Meteorological Society*, 103(8), E1796-E1827. Retrieved from https://journals.ametsoc.org/view/journals/bams/103/8/BAMS-D-21-0012.1.xml doi: https://doi.org/10.1175/BAMS-D-21-0012.1

Wang, C. C., & Davis, L. I. (1974, Feb). Measurement of Hydroxyl Concentrations in Air Using a Tunable UV Laser Beam. *Phys. Rev. Lett.*, 32, 349– 352. Retrieved from https://link.aps.org/doi/10.1103/PhysRevLett.32.349 doi: https://doi.org/10.1103/PhysRevLett.32.349

Wang, Y., Ming, T., Li, W., Yuan, Q., de Richter, R., Davies, P., & Caillol, S. (2022). Atmospheric removal of methane by enhancing the natural hydroxyl radical sink. *Greenhouse Gases: Science and Technology*, *12*, 784-795. doi: https://doi.org/10.1002/ghg.2191

Watanabe, T., Yoshida, M., Fujiwara, S., Abe, K., Onoe, A., Hirota, M., & Igarashi, S. (1982). Spin Trapping of Hydroxyl Radical in the Troposphere for Determination by Electron Spin Resonance and Gas Chromatography/Mass Spectrometry. *Analytical Chemistry*, *54*, 2470-2474. doi: https://doi.org/10.1021/ac00251a015

White, J. U. (1942). Long Optical Paths of Large Aperture. *Journal of the Optical Society of America*, 32, 285-288. Retrieved from https://api.semanticscholar.org/CorpusID: 120553855

Winterstein, F., & Jöckel, P. (2021, 2). Methane chemistry in a nutshell – the new submodels CH4 (v1.0) and TRSYNC (v1.0) in MESSy (v2.54.0). *Geoscientific Model Development*, 14,661-674. Retrieved from https://gmd.copernicus.org/articles/14/661/2021/ doi: https://doi.org/10.5194/gmd-14-661-2021

Yoshino, K., Esmond, J. R., Cheung, A. S., Freeman, D. E., & Parkinson, W. H. (1992). High resolution absorption cross sections in the transmission window region of the Schumann-Runge bands and Herzberg continuum of O2. *Planetary and Space Science*, 40, 185-192. doi: https://doi.org/10.1016/0032-0633(92)90056-T

Yoshino, K., Freeman, D. E., & Parkinson, W. H. (1984). Atlas of the Schumann–Runge Absorption Bands of O2 in the Wavelength Region 175–205 nm. *Journal of Physical and Chemical Reference Data*, *13*, 207-227. doi: https://doi.org/10.1063/1.555702

Zahn, A., Weppner, J., Widmann, H., Schlote-Holubek, K., Burger, B., Kühner, T., & Franke, H. (2012, 2). A fast and precise chemiluminescence ozone detector for eddy flux and airborne application. *Atmospheric Measurement Techniques*, 5(2), 363–375. Retrieved from https://amt.copernicus.org/articles/5/363/2012/ doi: https://doi.org/10.5194/amt-5-363-2012

Zauner-Wieczorek, M., Heinritzi, M., Granzin, M., Keber, T., Kürten, A., Kaiser, K., ... Curtius, J. (2022, 9). Mass spectrometric measurements of ambient ions and estimation of gaseous sulfuric acid in the free troposphere and lowermost stratosphere during the CAFE-EU/BLUESKY campaign. *Atmospheric Chemistry and Physics*, 22(17), 11781– 11794. Retrieved from https://acp.copernicus.org/articles/22/11781/2022/ doi: https://doi.org/10.5194/acp-22-11781-2022

Zhang, K., Liu, Z., Zhang, X., Li, Q., Jensen, A., Tan, W., ... Li, L. (2022, 4). Insights into the significant increase in ozone during COVID-19 in a typical urban city of China. *Atmospheric Chemistry and Physics*, 22, 4853-4866. Retrieved from https://acp.copernicus.org/articles/22/4853/2022/ doi: https://doi.org/10.5194/acp-22-4853-2022

Zimmermann, P. H., Brenninkmeijer, C. A. M., Pozzer, A., Jöckel, P., Winterstein, F., Zahn, A., ... Lelieveld, J. (2020, 5). Model simulations of atmospheric methane (1997–2016) and their evaluation using noaa and agage surface and iagos-caribic aircraft observations. *Atmospheric Chemistry and Physics*, 20, 5787-5809. Retrieved from https://acp.copernicus.org/articles/20/5787/2020/ doi: https://doi.org/10.5194/acp-20-5787-2020

Appendix

Appendix A



Figure A.1: Specifications of the UV ring lamp utilized in APACHE, designed by uv-technik Speziallampen GmbH.


Figure A.2: Technical data sheet of the 193 x15 nm bandpass filter used for the experiment described in section 4.3.1.



Page : 1-1

CALIBRATION CERTIFICATE

We herewith certify that the instrument mentioned below has been calibrated in accordance with the stated values and conditions. The calibration standards used are traceable to national standards of the Dutch Metrology Institute VSL.

= Identifications	3					-
	Calibrated Instrument		Calibratio Standard			A B
Type : Serial number : Model number : Certificate no. :	Flow controller M16203666A F-106AI-PAD-0 BHTG04/20555	(D) 3-V 585	Turbine m 80037 FTM T-25 Nmi/G145	neter 60-TD 53518	N.C	a la
= Conditions :	Customer				Calibration	
Eliza	AID	7 17		- Ban	AiD	
Pressure : Temperature : Flow (*) : Output range :	AIR 2 20 2000 0 - 100	bar (a) °C In/min %	Fluid Pressu Tempe Room Atm. p	re rature temperature ressure	AIR 0.0 22.5 22.5 1010	bar (g) °C °C hPa
Nominal Flow Setting	Calibrated Output Sign	d nal	Customer Flow (*)		Deviation	
0.0 % 25.0 % 50.0 % 75.0 % 100.0 %	0.0000 24.99 50.04 75.02 100.0	% % %	0.0000 502.4 1004 1502 2003	In/min In/min In/min In/min	0.0 %F5 -0.1 %F5 -0.2 %F5 -0.1 %F5 -0.1 %F5	
 Notes Reference con * The calibrated 	ditions of flow unit flow is converted t	s: 0.00 °(to custon	C, 1013.25 hPa her flow using E	ı (a). 3ronkhorst High	n-Tech FLUIDAT®	software.
Calibrator : B.S.				Date : 29	Apr 2016	\sim
Signed :	2 million	5		QC :		
CalSys V6.05		FLI	JIDAT® V5.73 (datab	ase: 17-03-2003)		V2.13

Figure A.3: The datasheet for the Bronkhorst F-106AI-PAD-03-V mass flow controller which is used to regulate the high flows through APACHE.



Cylinder Number: 2336

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

a montat fui chemie
c Chemistry, Hahn-Meitner-Weg 1, z, Germany

CALIBRATION DATE: 27 September 2017

AMOUNT FRACTION:

	Component	Amount fraction / (µmol/mol)]
	Nitrogen monoxide Nitrogen	5.004 ± 0.025 Balance	
The reported expandation $k = 2$, providing has been been been been been been been bee	nded uncertainty is based on ng a coverage probability of s been carried out in accorda	a standard uncertainty r approximately 95 %. T nce with UKAS requin	nultiplied by a coverage he uncertainty evaluatio ements.
METHODS:	Preparation: gravimetry; Analysis: non-dispersive ultraviolet		
TRACEABILITY:	The values on this certific	ate are traceable to N	PL Primary Standards
EXPIRY:	Certificate valid for 1 year from the date of issue		
PRESSURE:	Fill pressure: 100 bar; Minimum utilisation pressure: 5 bar		
STORAGE:	No special precautions are required		
HANDLING:	Refer to ISO 16664		
OUTLET:	BS341 No. 14 valve		
INTENDED USE:	Calibration standard		

Reference:	2017060311	Date of issue: 28 September 2017
Signed:	Subar .	(Authorised Signatory)
Name:	Dr P J Brewer	(on behalf of NPLML)
Checked by:	an	Page 1 of 1
CIPM MRA	This certificate is consist the CIPM. Under the M measurement certificate (for details see http://www	stent with the capabilities that are included in Appendix C of the MRA drawn up by MRA, all participating institutes recognise the validity of each other's calibration and es for the quantities, ranges and measurement uncertainties specified in Appendix C ww.bipm.org).

Figure A.4: The National Physical Laboratory standard NO bottle that used for experiments to calculate the sampling area inside the APACHE chamber and the photon flux of the UV ring lamp.

Products / Baratron® Capacitance Manometers / General Performance Pressure Transducers and Switches / General Performance Absolute Pressure Transducers / 722C 1-25,000 Torr, General Purpose Absolute Baratron® Capacitance Manometer / 722C131GA2FA

Vacuum Pressure Transducer, Absolute, 1000 Torr, 0-10 VDC, NW16 ISO-KF, DB9



Overview

The 722C13TGA2FA General Purpose Absolute Baratron® Capacitance Manometer features 1000 Torr Full Scale pressure measurement with ±0.5% of reading accuracy and a size NW16 ISO-KF fitting. Electrical connections for the +13 to +32 VDC power requirements and 0-10 VDC proportional analog output are made with a 9-pin Type "D" electrical connector. It features a flexible design making it an ideal solution for retrofit applications as well as new equipment designs. Robust sensor construction provides high overpressure tolerances, reducing errors caused by occasional line pressure spikes. All sensor wetted surfaces are made from Inconel® to ensure maximum compatibility with many process gases. Sophisticated technology and strict process controls ensure clean, smooth finishes (<10 Ra) on all wetted surfaces. Signal conditioning circuitry is assembled using the latest techniques in surface mount technology. All transducers are backed with a full two-year warranty.

Technical Specs			
Туре	Vacuum/pressure Transducer	Zero Temperature Coefficient	0.008% of F.S./°C (10 Torr through 25,000 Torr),
Measurement Type	Absolute		0.020% of F.S. (1 and 2 Torr)
Full Scale Range	1000 Torr	Span Temperature Coefficient	0.04% of Rdg./°C
Fitting Type	NW16 ISO-KF	Operating Temperature Range	0-50°C
Analog Output	0-10 VDC	Overpressure Limit	45 psia or 2 x F.S.,
Electrical Connector	9-pin D-sub		whichever is greater
Accuracy	0.5% of Reading	Burst Pressure	10 x F.S. or 100 psi, whichever is greater
Response Time	<20 msec	Exposed Materials	Inconel®
		Power Requirements	13-32 VDC

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Figure A.5: The datasheet for the 722C13TGA2FA Pressure sensor is used for pressure monitoring in APACHE.



DESCRIPTION:

Epoxy Coated interchangeable chip thermistors with bare tinned 180 alloy lead-wires.

FEATURES:

- Precision, solid state temperature sensor
- Interchangeability down to ± 0.1 °C
- Suitable for use over range of -80°C to +150°C
- High sensitivity greater than -4%/°C at 25°C
- Suitable for temperature measurement, control and compensation
- High reliability and stability over interchangeable range
- Most popular R-vs-T curves are available
- Resin coated for good mechanical strength
- and resistance to solvents • .008" (.2 mm) dia. bare tinned 180 alloy
- lead-wires



DIMENSIONS:



Select appropriate part number below for resistance and temperature tolerance desired

R _{25°C}	MATERIAL SYSTEM	± .2°C -20°C to +50°C	± .1°C 0°C to 70°C	± .2℃ 0℃ to 70℃	
100	Q	EC95Q101U			
300	Q	EC95Q301U			
1000	R	EC95R102U		EC95R102W	RS 151-215 = EC95F302W
1000	S	EC95S102U		EC95S102W	RS 151-221 = EC95F502W
2252	F	EC95F232U	EC95F232V	EC95F232W	RS 151-237 = EC95F103W
3000	F	EC95F302U	EC95F302V	EC95F302W	
5000	F	EC95F502U	EC95F502V	EC95F502W	
10000	F	EC95F103U	EC95F103V	EC95F103W	
10000	Y	EC95Y103U	EC95Y103V	EC95Y103W	
30000	н	EC95H303U	EC95H303V	EC95H303W	
50000	G	EC95G503U	EC95G503V	EC95G503W	
100000	G		EC95G104V	EC95G104W	

OPTIONS:

- Consult factory for availability of options: • Other resistance values in the range of
- Other resistance values in 100Ω - 100kΩ
- Other tolerances or ranges
- Alternative lead-wires or lengths
- Non standard R-vs-T curves
- · Controlled dimensions

DATA:

THERMAL AND ELECTRICAL PROPERTIES:

Dissipation constant:	(still air)	1 mW/°C
	(stirred oil)	8 mW/°C
Thermal time constant:	(still air)	10 sec.
	(stirred oil)	1 sec.
Maximum power at 25°C		75mW
(derated from 100% at 25%	C to 0% at 1	(0°C)

(derated from 100% at 25°C to 0% at 100°C)

Figure A.6: The datasheet for the NTC-EC95302V thermistor is used for temperature monitoring in APACHE.

Air Liquide

DISTICKSTOFFMONOXID N50 / N20



Figure A.7: The data sheet of the N_2O bottle used for photon flux calculation as described in section 4.3.4.



Technical Data Sheet Chem-Ad[®] VPP, VPP-E, VPP-S Peristaltic Pumps WT.490.250.500.EE.DS.0414

	Chem-Ad VPP	Chem-Ad VPP-E	Chem-Ad VPP-S
Motor	Direct curr	ent motor	Step motor
Electrical supply	AC 230 V (+/-10%) 50/60Hz or 24 V AC/DC	AC 230 V (+/-10%) 50/60Hz	AC 100-240 V (+/-10%) 50/60Hz
Enclosure		IP 65	
Power consumption	max.	15 W	max. 18 W
Power supply fusing	200 m	AMT	2.0 A MT
Capacity depending on capacity kit	up to 4000 ml/h	up to 4000 ml/h	up to 10000 ml/h
Adjusting the conscitu	with Poter	ntiomator	with monu
Microprocessor control	with Pote	X	X
Suction height		nav. 2 m water column (20 °C	
Viecosity	-	< 850 mPas	<i>,</i>)
Duty cycle		100 % ED	
Storage and operation		5 – 45 °C	
Hose connections	ID 4 v 1 mm		
Equipment versions		10 4 % 1 11111	
ON/OFF key		×	×
Rapid-action suction key		X	x
Operation mode	ON/OFF by mains	Potential-free input or 4-20 mA Signal input	Extern, 0-20 mA, 4-20 m 20-0 mA, 20-4 mA, x-y mA, Pulse, charge, flocculation with 2 sets of parameters
Suction lance / empty alarm to connect	-	х	X
Output relay contact (potential-free)		х	x
Operation LED	-	Х	X
Display	-	-	2-line
Alarm LED	-	X	X
Dimensions W x H x D		95 x 175 x 130 mm	
Weight	approx.	1.2 kg	approx. 1.8 kg
color coding)	Capacity VPP/VPP-E VPP-S Range Standard (S)	Capacity VPP-S Range High (H)	max. back pressure VPP/VPP-E/VPP-S bar

,	VPP-S Range Standard (S) ml/h	VPP-S Range High (H) ml/h	bar
150 PH (blue)	8 – 150	8 - 375	3.0
600 PH (black)	15 - 600	15 - 1500	2.5
2000 PH (green)	45 - 2000	45 - 5000	1.5
4000 PH (red)	150 - 4000	150 - 10000	1.5
Evoqua	© Evoqua Water Technologies GmbH 2014	Chem-Ad and Wallace & Tiernan are trader	narks of Evoqua its subsidiaries

	Water Technologies GmbH	WT.490.250.500.EE.DS.0414 Subject to change without prior notice.	and affiliates.
	Germany +49 8221 9040 wtger@evoqua.com		The information provided in this literature contains merely general descriptions or characteristics of performance which in actual case of use do not always apply as described or which may change as a result of further development of the products. An obligation to provide the respective characteristics shall only exist if expressly agreed in the terms of the contract.
	United Kingdom		
	+44 1732 771777		
	info.uk@evoqua.com		
-			

www.evoqua.com

Figure A.8: Technical data sheet of the peristaltic pump used for APACHE ground calibration. The one used for the experiment was model Chem-Ad-VPP-E.



Mitutoyo

Produktdetails

Digital ABS AOS Messschieber, AD/ID-Hartmetallmessflächen

Spezifikationen		
Tiefenmessstab:		flach
Datenausgabe:		Ja
Grenzwert der Messabweichung E MPE:		±0,02 mm
Grenzwert der Messabweichung S MPE:		±0,04 mm
Ziffernschrittwert:		0,01 mm
Max. Reaktions- geschwindigkeit:		Unbegrenzt
ORIGIN (ABS Nullpunkt):		Ja
ON/OFF:		Ja
ABS/INC (INC ZERO):		Ja
Alarm niedrige Spannung:		Ja
Batterielebensdauer:		Ca. 5 Jahre bei normalem Gebrauch
Gewicht:		168 g
Abmessungen		
	L: 233 mm A: 16.5 mm B: 21 mm C: 14,5 mm D: 40 mm H: 16 mm	

Figure A.9: Data sheet of the digital ABS AOS calliper used for measuring physical parameters described in chapter 4.

Appendix B



Figure B.1: Absorption cross section of O_2 at 184.9 \pm 0.045 nm for various O_2 column densities from (Yoshino et al., 1992). The red box highlights the O_2 cross section for typical column densities during APACHE ground calibration.



Figure B.2: The NO monitor calibration using the NPL standard NO reference material as given in Appendix A.4.



Figure B.3: The divergence of the UV ring lamp from a single 4 mm pin hole (of the flux reducer) in the APACHE chamber, as a function of distance from the wall.



Figure B.4: The calculated mean OH productions in ppt under the UV lamp for different O_2 mixing ratios for different APACHE pressures as described in section. 4.3.4. The error bar indicates the 1σ measurement variability.



Figure B.5: The calculated alpha transition as described in section 4.4



Figure B.6: A schematic showing the time between laser pulses (dark grey areas) when photon detection occurs in a LIF-FAGE technique. The first and second gating times are described as t1 and t2 respectively. The large background signal caused by events such as Mie and Raleigh scattering and wall reflections are removed by the turning on the detectors sufficiently after the initial laser pulse. The light grey area is the integrated fluorescence signal that is directly proportional to the concentration of the initially excited OH molecules in the sampled air. (A modified version of the schematic in (Faloona et al., 2004). Taken from (Marno, 2021))



Figure B.7: Measured time series data during flight number 1



Figure B.8: Measured time series data during flight number 2



Figure B.9: Measured time series data during flight number 3



Figure B.10: Measured time series data during flight number 4



Figure B.11: Measured time series data during flight number 5



Figure B.12: Measured time series data during flight number 7



Figure B.13: EMAC *CH*₄ calculations (red) and CARIBIC-2 observations (blue) from 2007 to 2014 – all flight samples. Taken from Figure 16 (Zimmermann et al., 2020)

Altitude [km]	BLUESKY	HOOVER II
0-2	11	50
2-3	20	30
3-4	16	30
4-5	20	31
5-6	21	37
6-7	37	55
7-8	37	70
8-9	69	130
9-10	153	170
10-11	141	200
11-12	251	41

Table 1: Number of data points averaged per altitude bin for the BLUESKY and HOOVER II experimental values

Appendix C

The Chemical Mechanism of MECCA

KPP version: 2.2.3_rs3 MECCA version: 4.0 Date: October 17, 2022 Batch file: CAFE_EU.bat Integrator: rosenbrock_posdef Gas equation file: gas.eqn Replacement file: Selected reactions: "St && Tr && G && !S && !Cl && !Br && !I && !Hg" Number of aerosol phases: 0 Number of species in selected mechanism: Gas phase: 145Aqueous phase: 0 All species: 145Number of reactions in selected mechanism: Gas phase (Gnnn): 82 Aqueous phase (Annn): 0 0 Henry (Hnnn): Photolysis (Jnnn): 21Aqueous phase photolysis (PHnnn): 0 Heterogeneous (HETnnn): 0 Equilibria (EQnn): 0 Isotope exchange (IEXnnn): 0 Tagging equations (TAGnnn): 0 Dummy (Dnn): 0 All equations: 103

Table 1: Gas phase reactions

#	labels	reaction	rate coefficient	reference
G1000	UpStTrG	$O_2 + O(^1D) \rightarrow O(^3P) + O_2$	3.3E-11*EXP(55./temp)	Burkholder et al. (2015)
G1001	UpStTrG	$O_2 + O(^{3}P) \rightarrow O_3$	6.0E-34*((temp/300.)**(-2.4))	Burkholder et al. (2015)
			*cair	
G2100	UpStTrG	$H + O_2 \rightarrow HO_2$	k_3rd(temp,cair,4.4E-32,1.3,	Burkholder et al. (2015)
			7.5E-11,-0.2,0.6)	
G2104	UpStTrG	$OH + O_3 \rightarrow HO_2 + O_2$	1.7E-12*EXP(-940./temp)	Burkholder et al. (2015)
G2105	UpStTrG	$OH + H_2 \rightarrow H_2O + H$	2.8E-12*EXP(-1800./temp)	Burkholder et al. (2015)
G2107	UpStTrG	$\mathrm{HO}_2 + \mathrm{O}_3 \rightarrow \mathrm{OH} + 2 \mathrm{O}_2$	1.E-14*EXP(-490./temp)	Burkholder et al. (2015)
G2109	UpStTrG	$\rm HO_2 + OH \rightarrow H_2O + O_2$	4.8E-11*EXP(250./temp)	Burkholder et al. (2015)
G2110	UpStTrG	$\mathrm{HO}_2 + \mathrm{HO}_2 \rightarrow \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2$	k_H02_H02	Burkholder et al. $(2015)^*$
G2111	UpStTrG	$H_2O + O(^1D) \rightarrow 2 OH$	1.63E-10*EXP(60./temp)	Burkholder et al. (2015)
G2112	UpStTrG	$\rm H_2O_2 + OH \rightarrow \rm H_2O + \rm HO_2$	1.8E-12	Burkholder et al. (2015)
G2117	UpStTrG	$H_2O + H_2O \rightarrow (H_2O)_2$	6.521E-26*temp*EXP(1851.09/temp)	Scribano et al. $(2006)^*$
			*EXP(-5.10485E-3*temp)	
G2118	UpStTrG	$(H_2O)_2 \rightarrow H_2O + H_2O$	1.E0	see note [*]
G3101	UpStTrGN	$N_2 + O(^1D) \rightarrow O(^3P) + N_2$	2.15E-11*EXP(110./temp)	Burkholder et al. (2015)
G3103	UpStTrGN	$NO + O_3 \rightarrow NO_2 + O_2$	3.0E-12*EXP(-1500./temp)	Burkholder et al. (2015)
G3106	StTrGN	$NO_2 + O_3 \rightarrow NO_3 + O_2$	1.2E-13*EXP(-2450./temp)	Burkholder et al. (2015)
G3108	StTrGN	$NO_3 + NO \rightarrow 2 NO_2$	1.5E-11*EXP(170./temp)	Burkholder et al. (2015)
G3109	UpStTrGN	$NO_3 + NO_2 \rightarrow N_2O_5$	k_N03_N02	Burkholder et al. $(2015)^*$
G3110	StTrGN	$N_2O_5 \rightarrow NO_2 + NO_3$	k_NO3_NO2/(5.8E-27*EXP(10840./	Burkholder et al. $(2015)^*$
			temp))	
G3201	UpStTrGN	$\rm NO + HO_2 \rightarrow NO_2 + OH$	3.3E-12*EXP(270./temp)	Burkholder et al. (2015)
G3202	UpStTrGN	$NO_2 + OH \rightarrow HNO_3$	k_3rd(temp,cair,1.8E-30,3.0,	Burkholder et al. (2015)
			2.8E-11,0.,0.6)	
G3203	StTrGN	$NO_2 + HO_2 \rightarrow HNO_4$	k_N02_H02	Burkholder et al. $(2015)^*$
G3206	StTrGN	$HNO_3 + OH \rightarrow H_2O + NO_3$	k_HNO3_OH	Dulitz et al. $(2018)^*$
G3207	StTrGN	$HNO_4 \rightarrow NO_2 + HO_2$	k_NO2_HO2/(2.1E-27*EXP(10900./	Burkholder et al. $(2015)^*$
			temp))	
G3208	StTrGN	$HNO_4 + OH \rightarrow NO_2 + H_2O$	1.3E-12*EXP(380./temp)	Burkholder et al. (2015)
G4101	StTrG	$CH_4 + OH \rightarrow CH_3 + H_2O$	1.85E-20*EXP(2.82*LOG(temp)	Atkinson (2003)
			-987./temp)	
G4103a	StTrG	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	3.8E-13*EXP(780./temp)/(1.+1./	Atkinson et al. (2006)
			498.*EXP(1160./temp))	

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4103b	StTrG	$\rm CH_3O_2 + HO_2 \rightarrow \rm HCHO + \rm H_2O + \rm O_2$	3.8E-13*EXP(780./temp)/(1.+ 498.*EXP(-1160./temp))	Atkinson et al. (2006)
G4104a	StTrGN	$\rm CH_3O_2 + \rm NO \rightarrow \rm CH_3O + \rm NO_2$	2.3E-12*EXP(360./temp)*(1beta_ CH3N03)	Atkinson et al. (2006), Butkovskaya et al. (2012), Flocke et al. (1998)
G4104b	StTrGN	$CH_3O_2 + NO \rightarrow CH_3ONO_2$	2.3E-12*EXP(360./temp)*beta_ CH3NO3	Atkinson et al. (2006) , Butkovskaya et al. (2012) , Flocke et al. $(1998)^*$
G4106a	StTrG	$CH_3O_2 \rightarrow CH_3O + .5 O_2$	7.4E-13*EXP(-520./temp)*R02*2.	Atkinson et al. (2006)
G4106b	StTrG	$\mathrm{CH}_3\mathrm{O}_2 \rightarrow .5 \ \mathrm{HCHO} + .5 \ \mathrm{CH}_3\mathrm{OH} + .5 \ \mathrm{O}_2$	(k_CH302-7.4E-13*EXP(-520./temp)) *R02*2.	Atkinson et al. (2006)
G4107	StTrG	$CH_3OOH + OH \rightarrow .6 CH_3O_2 + .4 HCHO + .4 OH + H_2O$	k_CH300H_OH	Wallington et al. (2018)
G4108	StTrG	$\rm HCHO + OH \rightarrow \rm CO + H_2O + HO_2$	9.52E-18*EXP(2.03*LOG(temp) +636./temp)	Sivakumaran et al. (2003)
G4110	UpStTrG	$\rm CO + OH \rightarrow H + CO_2$	(1.57E-13+cair*3.54E-33)	McCabe et al. (2001)
G4114	StTrGN	$CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2$	k_N02_CH302	Burkholder et al. (2015)
G4115	StTrGN	$\rm CH_3O_2NO_2 \rightarrow \rm CH_3O_2 + \rm NO_2$	k_NO2_CH3O2/(9.5E-29*EXP(11234./ temp))	Burkholder et al. $(2015)^*$
G4116	StTrGN	$CH_3O_2NO_2 + OH \rightarrow HCHO + NO_3 + H_2O$	3.00E-14	see note [*]
G4117	StTrGN	$CH_3ONO_2 + OH \rightarrow H_2O + HCHO + NO_2$	4.0E-13*EXP(-845./temp)	Atkinson et al. (2006)
G4118	StTrG	$CH_3O \rightarrow HO_2 + HCHO$	1.3E-14*exp(-663./temp)*c(ind_02)	Chai et al. (2014)
G4119a	StTrGN	$CH_3O + NO_2 \rightarrow CH_3ONO_2$	k_3rd_iupac(temp,cair,8.1E-29, 4.5,2.1E-11,0.,0.44)	Atkinson et al. (2006)
G4119b	StTrGN	$CH_3O + NO_2 \rightarrow HCHO + HONO$	9.6E-12*EXP(-1150./temp)	Atkinson et al. (2006)
G4120a	StTrGN	$CH_3O + NO \rightarrow CH_3ONO$	<pre>k_3rd_iupac(temp,cair,2.6E-29, 2.8,3.3E-11,0.6,REAL(EXP(-temp/ 900.),SP))</pre>	Atkinson et al. (2006)
G4120b	StTrGN	$CH_3O + NO \rightarrow HCHO + HNO$	2.3E-12*(temp/300.)**0.7	Atkinson et al. (2006)
G4121	StTrG	$CH_3O_2 + O_3 \rightarrow CH_3O + 2 O_2$	2.9E-16*exp(-1000./temp)	Burkholder et al. (2015)
G4122	StTrGN	$CH_3ONO + OH \rightarrow H_2O + HCHO + NO$	1.E-10*exp(-1764./temp)	Nielsen et al. (1991)
G4123	StTrG	$\rm HCHO + HO_2 \rightarrow \rm HOCH_2O_2$	9.7E-15*EXP(625./temp)	Atkinson et al. (2006)
G4124	StTrG	$\mathrm{HOCH}_2\mathrm{O}_2 \to \mathrm{HCHO} + \mathrm{HO}_2$	2.4E12*EXP(-7000./temp)	Atkinson et al. (2006)
G4125	StTrG	$\begin{array}{l} \mathrm{HOCH_2O_2+HO_2\rightarrow.5HOCH_2OOH+.5HCOOH+.2}\\ \mathrm{OH+.2HO_2+.3H_2O+.8O_2} \end{array}$	5.6E-15*EXP(2300./temp)	Atkinson et al. (2006)
G4126	StTrGN	$\mathrm{HOCH}_2\mathrm{O}_2 + \mathrm{NO} \rightarrow \mathrm{NO}_2 + \mathrm{HO}_2 + \mathrm{HCOOH}$	0.7275*2.3E-12*EXP(360./temp)	Atkinson et al. $(2006)^*$

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4127	StTrGN	$HOCH_2O_2 + NO_3 \rightarrow NO_2 + HO_2 + HCOOH$	1.2E-12	see note [*]
G4129a	StTrG	$\mathrm{HOCH}_2\mathrm{O}_2 \to \mathrm{HCOOH} + \mathrm{HO}_2$	(k_CH302*5.5E-12)**0.5*R02*2.	Atkinson et al. (2006)
G4129b	StTrG	$\text{HOCH}_2\text{O}_2 \rightarrow .5 \text{ HCOOH} + .5 \text{ HOCH}_2\text{OH} + .5 \text{ O}_2$	(k_CH302*5.7E-14*EXP(750./temp)) **0.5*R02*2.	Atkinson et al. (2006)
G4130a	StTrG	$HOCH_2OOH + OH \rightarrow HOCH_2O_2 + H_2O$	k_roohro	Taraborrelli (2010)*
G4130b	StTrG	$HOCH_2OOH + OH \rightarrow HCOOH + H_2O + OH$	k_rohro + k_s*f_sooh*f_soh	Taraborrelli (2010)*
G4132	StTrG	$HOCH_2OH + OH \rightarrow HO_2 + HCOOH + H_2O$	2.*k_rohro + k_s*f_soh*f_soh	Taraborrelli (2010)*
G4133	StTrG	$CH_3O_2 + OH \rightarrow CH_3O + HO_2$	1.4E-10	Bossolasco et al. $(2014)^*$
G4134	StTrG	$\rm CH_2OO \rightarrow \rm CO + \rm HO_2 + \rm OH$	1.124E+14*EXP(-10000/temp)	see note [*]
G4135	StTrG	$\rm CH_2OO + H_2O \rightarrow \rm HOCH_2OOH$	k_CH200_N02*3.6E-6	Ouyang et al. $(2013)^*$
G4136	StTrG	$\rm CH_2OO + (H_2O)_2 \rightarrow \rm HOCH_2OOH + H_2O$	5.2E-12	Chao et al. (2015), Lewis et al. (2015)*
G4137	StTrGN	$CH_2OO + NO \rightarrow HCHO + NO_2$	6.E-14	Welz et al. $(2012)^*$
G4138	StTrGN	$\rm CH_2OO + NO_2 \rightarrow \rm HCHO + NO_3$	k_CH200_N02	Welz et al. (2012), Stone et al. (2014)*
G4140	StTrG	$CH_2OO + CO \rightarrow HCHO + CO_2$	3.6E-14	Vereecken et al. (2012)
G4141	StTrG	$CH_2OO + HCOOH \rightarrow 2 HCOOH$	1.E-10	Welz et al. $(2014)^*$
G4142	StTrG	$CH_2OO + HCHO \rightarrow 2 LCARBON$	1.7E-12	Stone et al. $(2014)^*$
G4143	StTrG	$CH_2OO + CH_3OH \rightarrow 2 LCARBON$	5.E-12	Vereecken et al. $(2012)^*$
G4144	StTrG	$CH_2OO + CH_3O_2 \rightarrow 2 LCARBON$	5.E-12	Vereecken et al. $(2012)^*$
G4145	StTrG	$CH_2OO + HO_2 \rightarrow LCARBON$	5.E-12	Vereecken et al. (2012)
G4146	StTrG	$CH_2OO + O_3 \rightarrow HCHO + 2 O_2$	1.E-12	Vereecken et al. (2014)
G4147	StTrG	$CH_2OO + CH_2OO \rightarrow 2 HCHO + O_2$	6.E-11	Buras et al. (2014)
G4148	StTrGN	$\mathrm{HOCH}_2\mathrm{O}_2 + \mathrm{NO}_2 \rightarrow \mathrm{HOCH}_2\mathrm{O}_2\mathrm{NO}_2$	k_N02_CH302	see note [*]
G4149	StTrGN	$\mathrm{HOCH_2O_2NO_2} \rightarrow \mathrm{HOCH_2O_2} + \mathrm{NO_2}$	k_NO2_CH3O2/(9.5E-29*EXP(11234./ temp))	Barnes et al. $(1985)^*$
G4150	StTrGN	$HOCH_2O_2NO_2 + OH \rightarrow HCOOH + NO_3 + H_2O$	9.50E-13*EXP(-650./temp)*f_soh	see note [*]
G4151	StTrG	$\rm CH_3 + O_2 \rightarrow \rm CH_3O_2$	<pre>k_3rd_iupac(temp,cair,7.0E-31, 3.,1.8E-12,-1.1,0.33)</pre>	Atkinson et al. (2006)
G4152	StTrG	$\rm CH_3 + O_3 \rightarrow .956 \ \rm HCHO + .956 \ \rm H + .044 \ \rm CH_3O + O_2$	5.1E-12*exp(-210./temp)	Albaladejo et al. (2002), Ogryzlo et al. (1981)
G4153	StTrG	$\rm CH_3 + O(^3P) \rightarrow .83~HCHO + .83~H + .17~CO + .17~H_2 + .17~H$	1.3E-10	Atkinson et al. (2006)
G4154	StTrG	$\rm CH_3O + O_3 \rightarrow \rm CH_3O_2 + O_2$	2.53E-14	Albaladejo et al. $(2002)^*$

Table 1: Gas phase reactions $(\dots \text{ continued})$

#	labels	reaction	rate coefficient	reference
G4155	StTrG	CH ₃ O + O(³ P) → .75 CH ₃ + .75 O ₂ + .25 HCHO + .25 OH	2.5E-11	Baulch et al. (2005)
G4156	StTrG	$CH_3O_2 + O(^{3}P) \rightarrow CH_3O + O_2$	4.3E-11	Zellner et al. (1988)
G4157	StTrG	$\begin{array}{l} \mathrm{HCHO}+\mathrm{O}(^{3}\mathrm{P})\rightarrow.7\mathrm{OH}+.7\mathrm{CO}+.3\mathrm{H}+.3\mathrm{CO}_{2}+\\ \mathrm{HO}_{2} \end{array}$	3.4E-11*EXP(-1600./temp)	Burkholder et al. (2015)
G42080	StTrGCN	$\mathrm{C_2H_5O_2} + \mathrm{NO_2} \rightarrow \mathrm{C_2H_5O_2NO_2}$	k_3rd_iupac(temp,cair,1.3E-29, 6.2,8.8E-12,0.0,0.31)	Atkinson et al. (2006)
G42081	StTrGCN	$\mathrm{C_2H_5O_2NO_2} \rightarrow \mathrm{C_2H_5O_2} + \mathrm{NO_2}$	<pre>k_3rd_iupac(temp,cair, REAL(4.8E-4*EXP(-9285./temp) ,SP),0.0,REAL(8.8E15*EXP(-10440./ temp),SP),0.0,0.31)</pre>	Atkinson et al. (2006)
G42082	StTrGCN	$\mathrm{C_2H_5O_2NO_2} + \mathrm{OH} \rightarrow \mathrm{CH_3CHO} + \mathrm{NO_3} + \mathrm{H_2O}$	9.50E-13*EXP(-650./temp)	Sander et al. $(2018)^*$

General notes

Three-body reactions

Rate coefficients for three-body reactions are defined via the function k_3rd(T, M, k_0^{300} , n, $k_{\rm inf}^{300}$, m, f_c). In the code, the temperature T is called temp and the concentration of "air molecules" M is called cair. Using the auxiliary variables $k_0(T)$, $k_{\rm inf}(T)$, and $k_{\rm ratio}$, k_3rd is defined as:

$$k_{0}(T) = k_{0}^{300} \times \left(\frac{300\text{K}}{T}\right)^{n}$$
(1)

$$k_{\text{inf}}(T) = k_{\text{inf}}^{300} \times \left(\frac{300\text{K}}{T}\right)^{m}$$
(2)

$$k_{\text{ratio}} = \frac{k_{0}(T)M}{k_{\text{inf}}(T)}$$
(3)

$$k_{-}\text{3rd} = \frac{k_{0}(T)M}{1+k_{\text{ratio}}} \times f_{c}^{\left(\frac{1}{1+(\log_{10}(k_{\text{ratio}}))^{2}\right)}$$
(4)

A similar function, called k_3rd_iupac here, is used by Wallington et al. (2018) for three-body reactions. It has the same function parameters as k_3rd and it is defined as:

$$k_{0}(T) = k_{0}^{300} \times \left(\frac{300\text{K}}{T}\right)^{n}$$
(5)

$$k_{\text{inf}}(T) = k_{\text{inf}}^{300} \times \left(\frac{300\text{K}}{T}\right)^{m}$$
(6)

$$k_{\text{ratio}} = \frac{k_{0}(T)M}{k_{\text{inf}}(T)}$$
(7)

$$N = 0.75 - 1.27 \times \log_{10}(f_{\text{c}})$$
(8)

k_3rd_iupac =
$$\frac{k_0(T)M}{1+k_{\text{ratio}}} \times f_c^{\left(\frac{1}{1+(\log_1(0/k_{\text{ratio}})/N)^2}\right)}(9)$$

Structure-Activity Relationships (SAR)

Some unmeasured rate coefficients are estimated with structure-activity relationships, using the following parameters and substituent factors:

k for	H-abstraction by OH in $\mathrm{cm}^{-3}\mathrm{s}^{-1}$
k_p	$4.49\times 10^{-18}\times (T/{\rm K})^2 \exp(-320{\rm K}/T)$
k_s	$4.50\times 10^{-18}\times (T/{\rm K})^2 \exp(253{\rm K}/T)$
k_t	$2.12\times 10^{-18}\times (T/{\rm K})^2 \exp(696{\rm K}/T)$
k_rohro	$2.1\times 10^{-18}\times (T/{\rm K})^2 \exp(-85{\rm K}/T)$
k_co2h	$0.7 \times k_{\rm CH_3CO_2H+OH}$
k_roohro	$0.6 \times k_{\rm CH_3OOH+OH}$
f_alk	1.23
f_soh	3.44
f_toh	2.68
f_sooh	8.
f_tooh	8.
f_ono2	0.04
f_ch2ono2	0.20
f_cpan	0.25
f_allyl	3.6
f_cho	0.55
f_co2h	1.67
f_co	0.73
f_o	8.15
f_pch2oh	1.29
f_tch2oh	0.53

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k for OH-add	lition to double bonds in $\mathrm{cm}^{-3}\mathrm{s}^{-1}$
k_adp	$4.5\times 10^{-12}\times (T/300{\rm K})^{-0.85}$
k_ads	$1/4 \times (1.1 \times 10^{-11} \times \exp(485{\rm K}/T) +$
	$1.0 \times 10^{-11} \times \exp(553{\rm K}/T))$
k_adt	$1.922 \times 10^{-11} \times \exp(450{\rm K}/T) - k_{\rm ads}$
k_adsecprim	3.0×10^{-11}
k_adtertprim	5.7×10^{-11}
a_pan	0.56
a_cho	0.31
a_coch3	0.76
a_ch2oh	1.7
a_ch2ooh	1.7
a_coh	2.2
a_cooh	2.2
a_co2h	0.25
a_ch2ono2	0.64

RO_2 self and cross reactions

The self and cross reactions of organic peroxy radicals are treated according to the permutation reaction formalism as implemented in the MCM (Rickard and Pascoe, 2009), as decribed by Jenkin et al. (1997). Every organic peroxy radical reacts in a pseudo-first-order reaction with a rate constant that is expressed as $k^{\rm 1st} = 2 \times \sqrt{k_{\rm self} \times {\rm k.CH302} \times [{\rm RO}_2]}$ where $k_{\rm self} =$ second-order rate coefficient of the self reaction of the organic peroxy radical, k_CH302 = second-order rate coefficient of CH₃O₂, and [RO₂] = sum of the concentrations of all organic peroxy radicals.

Specific notes

G2110: The rate coefficient is: $k_H02_H02 =$ (3.0E-13*EXP(460./temp)+2.1E-33*EXP(920./temp) *cair)*(1.+1.4E-21*EXP(2200./temp)*C(ind_H20)).

G2117: Converted to Kc [molec-1 cm3] = Kp*R*T/NA, where R is 82.05736 [cm3atmK1mol1].

G2118: Assuming fast equilibrium

G3109: The rate coefficient is: $k_NO3_NO2 = k_$ 3rd(temp,cair,2.4E-30,3.0,1.6E-12,-0.1,0.6).

G3110: The rate coefficient is defined as backward reaction divided by equilibrium constant.

G3203: The rate coefficient is: $k_NO2_HO2 = k_G4132$: SAR for H-abstraction by OH. 3rd(temp,cair,1.9E-31,3.4,4.0E-12,0.3,0.6).

G3206: The rate coefficient is: $k_{\tt HNO3_OH}$ = 1.32E-14 * EXP(527/temp) + 1 / (1 / (7.39E-32 * EXP(453/temp)*cair) + 1 / (9.73E-17 * EXP(1910/temp)))

G3207: The rate coefficient is defined as backward reaction divided by equilibrium constant.

 $\tt G4104b:$ Methyl nitrate yield according to Banic et al. (2003) but reduced by a factor of 10 according to the upper limit derived from measurements by Munger et al. (1999)

G4115: The rate coefficient is defined as backward reaction divided by equilibrium constant.

G4116: Same value as for PAN + OH.

G4126: Same as for G4104 but scaled to match the recommeded value at 298K.

G4127: Same as for CH3O2 + NO3 in G4105.

G4130a: SAR for H-abstraction by OH.

G4130b: SAR for H-abstraction by OH.

G4133: Lower limit of the rate constant. Products uncertain but CH₃OH can be excluded because of a likely high energy barrier (L. Vereecken, pers. comm.). CH₂OO production cannot be excluded.

 ${\tt G4134}:$ Estimate based on the decomposition lifetime of 3 s (Olzmann et al., 1997) and a 20 kcal/mol energy barrier (Vereecken and Francisco, 2012).

G4135: Rate constant for $CH_2OO + NO_2$ (G4138) multiplied by the factor from Ouyang et al. (2013). G4136: Average of two measurements.

G4137: Upper limit.

G4138: Average of 7.E-12 and 1.5E-12.

G4141: HOOCH₂OCHO forms and then decomposes to formic anhydride (Gruzdev et al., 1993) which hydrolyses in the humid atmosphere (Conn et al., 1942).

G4142: High-pressure limit.

G4143: Generic estimate for reaction with alcohols.

G4144: Generic estimate for reaction with RO_2 .

G4148: Same value as for $NO_2 + CH_3O_2$.

G4149: Barnes et al. (1985) estimated a decomposition rate equal to that of $CH_3O_2NO_2$.

G4150: Value for $CH_3O_2NO_2 + OH$, H-abstraction enhanced by the HO-group by f_soh.

G4154: Products assumed to be $\rm CH_3O_2+O_2$ (could also be $HCHO + O_2 + OH$).

G42082: Same rate constant as for PAN + OH.

Table 2: Photolysis reactions

#	labels	reaction	rate coefficient	reference
J (gas)				
J1000a	UpStTrGJ	$O_2 + h\nu \to O(^{3}P) + O(^{3}P)$	jx(ip_O2)	Sander et al. (2014)
J1001a	UpStTrGJ	$O_3 + h\nu \rightarrow O(^1D) + O_2$	jx(ip_O1D)	Sander et al. (2014)
J1001b	UpStTrGJ	$O_3 + h\nu \to O(^3P) + O_2$	jx(ip_O3P)	Sander et al. (2014)
J2101	UpStTrGJ	$H_2O_2 + h\nu \rightarrow 2 \text{ OH}$	jx(ip_H2O2)	Sander et al. (2014)
J3101	UpStTrGJN	$NO_2 + h\nu \rightarrow NO + O(^{3}P)$	jx(ip_NO2)	Sander et al. (2014)
J3103a	UpStTrGJN	$NO_3 + h\nu \rightarrow NO_2 + O(^{3}P)$	jx(ip_NO2O)	Sander et al. (2014)
J3103b	UpStTrGJN	$NO_3 + h\nu \rightarrow NO + O_2$	jx(ip_NOO2)	Sander et al. (2014)
J3104	StTrGJN	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$	jx(ip_N2O5)	Sander et al. (2014)
J3201	StTrGJN	$HNO_3 + h\nu \rightarrow NO_2 + OH$	jx(ip_HNO3)	Sander et al. (2014)
J3202	StTrGJN	$HNO_4 + h\nu \rightarrow .667 \text{ NO}_2 + .667 \text{ HO}_2 + .333 \text{ NO}_3 + .333 \text{ OH}$	jx(ip_HNO4)	Sander et al. (2014)
J41000	StTrGJ	$CH_3OOH + h\nu \rightarrow CH_3O + OH$	jx(ip_CH3OOH)	Sander et al. (2014)
J41001a	StTrGJ	$\rm HCHO + h\nu \rightarrow H_2 + CO$	jx(ip_COH2)	Sander et al. (2014)
J41001b	StTrGJ	$\rm HCHO + h\nu \rightarrow \rm H + \rm CO + \rm HO_2$	jx(ip_CHOH)	Sander et al. (2014)
J41004	StTrGJN	$CH_3ONO + h\nu \rightarrow CH_3O + NO$	jx(ip_CH3ONO)	Sander et al. (2014)
J41005	StTrGJN	$CH_3ONO_2 + h\nu \rightarrow CH_3O + NO_2$	jx(ip_CH3NO3)	Sander et al. (2014)
J41006	StTrGJN	$\label{eq:ch3} \begin{array}{l} {\rm CH_3O_2NO_2+h\nu\to.667\;NO_2+.667\;CH_3O_2+.333\;NO_3+.333}\\ {\rm CH_3O} \end{array}$	jx(ip_CH302N02)	Sander et al. $(2014)^*$
J41007	StTrGJ	$HOCH_2OOH + h\nu \rightarrow HCOOH + OH + HO_2$	jx(ip_CH3OOH)	Sander et al. (2014)
J41008	StTrGJ	$CH_3O_2 + h\nu \rightarrow HCHO + OH$	jx(ip_CH3O2)	Sander et al. (2014)
J41009	StTrGJ	$\rm HCOOH + h\nu \rightarrow \rm CO + \rm HO_2 + \rm OH$	jx(ip_HCOOH)	Sander et al. (2014)
J41010	StTrGJN	$HOCH_2O_2NO_2 + h\nu \rightarrow .667 \text{ NO}_2 + .667 \text{ HOCH}_2O_2 + .333 \text{ NO}_3$	jx(ip_CH302N02)	Sander et al. (2014)
740004	OUT OLON	$+ .333 \text{ HCOOH} + .333 \text{ HO}_2$. (
J42021	SUITGJCN	$C_2H_5O_2NO_2 + n\nu \rightarrow .007 NO_2 + .007 C_2H_5O_2 + .333 NO_3 + .222 CU CUO_1222 HO$	JX(1p_CH3U2NU2)	Sander et al. $(2018)^*$
DIL		$.555 \cup 113 \cup 110 + .555 \dots 102$		
гп (aqueous)				

General notes

j-values are calculated with an external module (e.g., JVAL) and then supplied to the MECCA chemistry. Values that originate from the Master Chemical Mech-

anism (MCM) by Rickard and Pascoe (2009) are translated according in the following way:

 $\begin{array}{l} j(11) \rightarrow jx(\texttt{ip_COH2}) \\ j(12) \rightarrow jx(\texttt{ip_CHOH}) \\ j(15) \rightarrow jx(\texttt{ip_HOCH2CHO}) \\ j(18) \rightarrow jx(\texttt{ip_MACR}) \\ j(22) \rightarrow jx(\texttt{ip_ACETOL}) \\ j(23)+j(24) \rightarrow jx(\texttt{ip_MVK}) \\ j(31)+j(32)+j(33) \rightarrow jx(\texttt{ip_GLYOX}) \end{array}$

 $\begin{array}{l} {\rm j(34)} \rightarrow {\rm jx(ip_MGLYOX)} \\ {\rm j(41)} \rightarrow {\rm jx(ip_CH300H)} \\ {\rm j(53)} \rightarrow {\rm j(isopropyl nitrate)} \\ {\rm j(54)} \rightarrow {\rm j(isopropyl nitrate)} \\ {\rm j(55)} \rightarrow {\rm j(isopropyl nitrate)} \\ {\rm j(56)} + {\rm j(57)} \rightarrow {\rm jx(ip_NOA)} \end{array}$

Specific notes

 $\mathsf{J41006:}\xspace$ product distribution as for HNO4

J42021: In analogy to what is assumed for $\rm CH_3O_2NO_2$ photolysis as in (Sander et al., 2014).

Table 3: Reversible (Henry's law) equilibria and irreversible ("heterogenous") uptake

# labels reaction	rate coefficient	reference	

General notes

The forward (k_exf) and backward (k_exb) rate coefficients are calculated in subroutine mecca_aero_calc_k_ex in the file messy_mecca_aero.f90 using accommodation coefficients and Henry's law constants from chemprop (see $\verb|chemprop.pdf|).$

subsequent reaction with H_2O , Cl^- , and Br^- in H3201, the branching between hydrolysis and the halide reaction H_2O and H_2O and H_2O and H_2O and H_2O and HH6300, H6301, H6302, H7300, H7301, H7302, H7601, and H7602, we define:

$$k_{\mathrm{exf}}(\mathbf{X}){=}\frac{k_{\mathrm{mt}}(\mathbf{X})\times \mathrm{LWC}}{[\mathrm{H}_{2}\mathrm{O}]+5\times 10^{2}[\mathrm{Cl}^{-}]+3\times 10^{5}[\mathrm{Br}^{-}]}$$

Here, $k_{\rm mt}$ = mass transfer coefficient, and LWC = liquid water content of the aerosol. The total uptake rate For uptake of X (X = N_2O_5 , ClNO₃, or BrNO₃) and of X is only determined by k_{mt} . The factors only affect

tions. The factor 5×10^2 was chosen such that the chloride reaction dominates over hydrolysis at about [Cl⁻] > 0.1 M (see Fig. 3 in Behnke et al. (1997)), i.e. when the ratio $[H_2O]/[Cl^-]$ is less than 5×10^2 . The ratio $5{\times}10^2/3{\times}10^5$ was chosen such that the reactions with chloride and bromide are roughly equal for sea water composition (Behnke et al., 1994). These ratios were measured for uptake of N_2O_5 . Here, they are also used for $ClNO_3$ and $BrNO_3$.

Table 4: Heterogeneous reactions

	# labels reaction	rate coefficient	reference	
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General notes

Heterogeneous reaction rates are calculated with an external module (e.g., MECCA_KHET) and then supplied to the MECCA chemistry (see www.messy-interface.org for details)

Table 5: Acid-base and other equilibria

	# labels reaction	$K_0[M^{m-n}]$	$-\Delta H/R[K]$	reference	
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Specific notes

Table 6: Aqueous phase reactions

	#	labels reaction	$k_0 \left[M^{1-n} s^{-1} \right]$	$-E_a/R[K]$	reference	
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Specific notes

References

- Albaladejo, J., Jiménez, E., Notario, A., Cabañas, B., and Martínez, E.: CH₃O yield in the CH₃ + O₃ reaction using the LP/LIF technique at room temperature, J. Phys. Chem. A, 106, 2512–2519, doi: 10.1021/jp0122490, 2002.
- Atkinson, R.: Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes, Atmos. Chem. Phys., 3, 2233–2307, doi:10.5194/ACP-3-2233-2003, 2003.
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and IUPAC Subcommittee: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625–4055, doi:10.5194/ACP-6-3625-2006, 2006.
- Banic, C. M., Beauchamp, S. T., Tordon, R. J., Schroeder, W. H., Steffen, A., Anlauf, K. A., and Wong, H. K. T.: Vertical distribution of gaseous elemental mercury in Canada, J. Geophys. Res., 108D, 4264, doi:10.1029/2002JD002116, 2003.
- Barnes, I., Becker, K. H., Fink, E. H., Reimer, A., Zabel, F., and Niki, H.: FTIR spectroscopic study of the gas-phase reaction of HO₂ with H₂CO, Chem. Phys. Lett., 115, 1–8, doi:10.1016/0009-2614(85) 80091-9, 1985.
- Baulch, D. L., Bowman, C. T., Cobos, C. J., Cox, R. A., Just, T., Kerr, J. A., Pilling, M. J., Stocker, D., Troe, J., Tsang, W., Walker, R. W., and Warnatz, J.: Evaluated kinetic data for combustion modeling: Supplement II, J. Phys. Chem. Ref. Data, 34, 757–1397, doi:10.1063/1.1748524, 2005.

- Behnke, W., Scheer, V., and Zetzsch, C.: Production of BrNO₂, Br₂ and ClNO₂ from the reaction between sea spray aerosol and N₂O₅, J. Aerosol Sci., 25, S277– S278, doi:10.1016/0021-8502(94)90369-7, 1994.
- Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO₂ from the reaction of gaseous N₂O₅ with NaCl solution: Bulk and aerosol experiments, J. Geophys. Res., 102D, 3795–3804, doi: 10.1029/96JD03057, 1997.
- Bossolasco, A., Faragó, E. P., Schoemaecker, C., and Fittschen, C.: Rate constant of the reaction between CH₃O₂ and OH radicals, Chem. Phys. Lett., 593, 7– 13, doi:10.1016/j.cplett.2013.12.052, 2014.
- Buras, Z. J., Elsamra, R. M. I., and Green, W. H.: Direct determination of the simplest Criegee intermediate (CH₂OO) self reaction rate, J. Phys. Chem. Lett., 5, 2224–2228, doi:10.1021/jz5008406, 2014.
- Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 18, JPL Publication 15-10, Jet Propulsion Laboratory, Pasadena, http://jpldataeval.jpl.nasa.gov, 2015.
- Butkovskaya, N., Kukui, A., and Le Bras, G.: Pressure and temperature dependence of methyl nitrate formation in the $CH_3O_2 + NO$ reaction, J. Phys. Chem. A, 116, 5972–5980, doi:10.1021/jp210710d, 2012.
- Chai, J., Hu, H., Dibble, T. S., Tyndall, G. S., and Orlando, J. J.: Rate constants and kinetic isotope effects for methoxy radical reacting with NO₂ and O_2 , J. Phys. Chem. A, 118, 3552–3563, doi:10.1021/jp501205d, 2014.

- Chao, W., Hsieh, J.-T., Chang, C.-H., and Lin, J. J.-M.: Direct kinetic measurement of the reaction of the simplest Criegee intermediate with water vapor, Science, 347, 751–754, doi:10.1126/science.1261549, 2015.
- Conn, J. B., Kistiakowsky, G. B., Roberts, R. M., and Smith, E. A.: Heats of organic reactions. XIII. Heats of hydrolysis of some acid anhydrides, Journal of the American Chemical Society, 64, 1747–1752, doi: 10.1021/ja01260a001, 1942.
- Dulitz, K., Amedro, D., Dillon, T. J., Pozzer, A., and Crowley, J. N.: Temperature (208–318 K) and pressure (18–696 Torr) dependent rate coefficients for the reaction between OH and HNO₃, Atmos. Chem. Phys., 18, 2381–2394, doi:10.5194/acp-18-2381-2018, 2018.
- Flocke, F., Atlas, E., Madronich, S., Schauffler, S. M., Aikin, K., Margitan, J. J., and Bui, T. P.: Observations of methyl nitrate in the lower stratosphere during STRAT: implications for its gas phase production mechanisms, Geophys. Res. Lett., 25, 1891–1894, doi: 10.1029/98GL01417, 1998.
- Gruzdev, A. N., Elokhov, A. S., Makarov, O. V., and Mokhov, I. I.: Some recent results of Russian measurements of surface ozone in Antarctica. A meteorological interpretation, Tellus, 45B, 99–105, doi: 10.3402/TELLUSB.V45I2.15584, 1993.
- Jenkin, M., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: A protocol for mechanism development, Atmos. Environ., 31, 81–104, doi:10.1016/ S1352-2310(96)00105-7, 1997.
- Lewis, T. R., Blitz, M. A., Heard, D. E., and Seakins, P. W.: Direct evidence for a substantive reaction

between the Criegee intermediate, CH_2OO , and the water vapour dimer, Phys. Chem. Chem. Phys., 17, 4859–4863, doi:10.1039/C4CP04750H, 2015.

- McCabe, D. C., Gierczak, T., Talukdar, R. K., and Ravishankara, A. R.: Kinetics of the reaction OH + CO under atmospheric conditions, Geophys. Res. Lett., 28, 3135–3138, doi:10.1029/2000GL012719, 2001.
- Munger, J. W., Jacob, D. J., Fan, S.-M., Colman, A. S., and Dibb, J. E.: Concentrations and snowatmosphere fluxes of reactive nitrogen at Summit, Greenland, J. Geophys. Res., 104D, 13721–13734, doi:10.1029/1999JD900192, 1999.
- Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Rate constants for the gas-phase reactions of OH radicals and Cl atoms with *n*-alkyl nitrites at atmospheric pressure and 298 K, Int. J. Chem. Kinetics, 23, 1095–1109, doi:10.1002/kin.550231204, 1991.
- Ogryzlo, E. A., Paltenghi, R., and Bayes, K. D.: The rate of reaction of methyl radicals with ozone, Int. J. Chem. Kinetics, 13, 667–675, doi:10.1002/kin. 550130707, 1981.
- Olzmann, M., Kraka, E., Cremer, D., Gutbrod, R., and Andersson, S.: Energetics, kinetics, and product distributions of the reactions of ozone with ethene and 2,3-dimethyl-2-butene, J. Phys. Chem. A, 101, 9421– 9429, doi:10.1021/JP971663E, 1997.
- Ouyang, B., McLeod, M. W., Jones, R. L., and Bloss, W. J.: NO₃ radical production from the reaction between the Criegee intermediate CH₂OO and NO₂, Phys. Chem. Chem. Phys., 15, 17070–17075, doi: 10.1039/c3cp53024h, 2013.
- Rickard, A. and Pascoe, S.: The Master Chemical Mechanism (MCM), http://mcm.leeds.ac.uk, 2009.

- Sander, R., Jöckel, P., Kirner, O., Kunert, A. T., Landgraf, J., and Pozzer, A.: The photolysis module JVAL-14, compatible with the MESSy standard, and the JVal PreProcessor (JVPP), Geosci. Model Dev., 7, 2653–2662, doi:10.5194/GMD-7-2653-2014, 2014.
- Sander, R., Baumgaertner, A., Cabrera-Perez, D., Frank, F., Grooß, J.-U., Gromov, S., Harder, H., Huijnen, V., Jöckel, P., Karydis, V. A., Niemeyer, K., Pozzer, A., Riede, H., Schultz, M., Taraborrelli, D., and Tauer, S.: The atmospheric chemistry box model CAABA/MECCA-4.0gmdd, Geosci. Model Dev. Discuss., doi:10.5194/gmd-2018-201, 2018.
- Scribano, Y., Goldman, N., Saykally, R. J., and Leforestier, C.: Water dimers in the atmosphere III: Equilibrium constant from a flexible potential, J. Phys. Chem. A, 110, 5411–5419, doi:10.1021/jp056759k, 2006.
- Sivakumaran, V., Hölscher, D., Dillon, T. J., and Crowley, J. N.: Reaction between OH and HCHO: temperature dependent rate coefficients (202-399 K) and product pathways (298 K), Phys. Chem. Chem. Phys., 5, 4821–4827, doi:10.1039/B306859E, 2003.
- Stone, D., Blitz, M., Daubney, L., Howes, N. U. M., and Seakins, P.: Kinetics of CH₂OO reactions with SO₂, NO₂, NO, H₂O and CH₃CHO as a function of pressure, Phys. Chem. Chem. Phys., 16, 1139–1149, doi:10.1039/c3cp54391a, 2014.
- Taraborrelli, D.: Isoprene oxidation and its impacts on the atmospheric composition, Ph.D. thesis, Johannes Gutenberg-Universität, Mainz, Germany, http:// d-nb.info/1003538770/34, 2010.
- Vereecken, L. and Francisco, J. S.: Theoretical studies of atmospheric reaction mechanisms in the troposphere, Chem. Soc. Rev., 41, 6259–6293, doi:10.1039/ c2cs35070j, 2012.

- Vereecken, L., Harder, H., and Novelli, A.: The reaction of Criegee intermediates with NO, RO₂, and SO₂, and their fate in the atmosphere, Phys. Chem. Chem. Phys., 14, 14682–14695, doi:10.1039/c2cp42300f, 2012.
- Vereecken, L., Harder, H., and Novelli, A.: The reactions of Criegee intermediates with alkenes, ozone, and carbonyl oxides, Phys. Chem. Chem. Phys., 16, 4039–4049, doi:10.1039/c3cp54514h, 2014.
- Wallington, T. J., Ammann, M., Cox, R. A., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeill, V., Mellouki, A., Rossi, M. J., and Troe, J.: IUPAC Task group on atmospheric chemical kinetic data evaluation: Evaluated kinetic data, http://iupac. pole-ether.fr, 2018.
- Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Direct kinetic measurements of Criegee intermediate (CH₂OO) formed by reaction of CH₂I with O₂, Science, 335, 204–207, doi:10.1126/science.1213229, 2012.
- Welz, O., Eskola, A. J., Sheps, L., Rotavera, B., Savee, J. D., Scheer, A. M., Osborn, D. L., Lowe, D., Booth, A. M., Xiao, P., Khan, M. A. H., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Rate coefficients of C1 and C2 Criegee intermediate reactions with formic and acetic acid near the collision limit: Direct kinetics measurements and atmospheric implications, Angew. Chem., 126, 4635–4638, doi:10.1002/ange.201400964, 2014.
- Zellner, R., Hartmann, D., Karthäuser, J., Rhäsa, D., and Weibring, G.: A laser photolysis/LIF study of the reactions of O(³P) atoms with CH₃ and CH₃O₂ radicals, J. Chem. Soc. Faraday Trans. 2, 84, 549– 568, doi:10.1039/f29888400549, 1988.

Acronyms

- APACHE All Pressure Altitude-based Calibrator for HOx Experimentation
- **CAABA-MECCA** Chemistry As A Box Model Application Module Efficiently Calculating the Chemistry of the Atmosphere
- CAFE Chemistry of Atmosphere Field Experiment
- **ECWMF** European Centre for Medium-Range Weather Forecasts
- ERA 5 Fifth-generation ECMWF Re-analysis
- FWHM Full Width at Half Maximum
- FLEXPART FLEXible PARTicle dispersion model
- HALO High Altitude LOng Range
- HORUS HydrOxyl Radical Measurement Unit based on fluorescence Spectroscopy

IPI Inlet Pre-Injector

LIF-FAGE Light Induced Fluorescence-Fluorescence Assay by Gas Expansion

MFC Mass Flow Controller

- **molec** cm^{-3} molecules per cubic centimetre
- NMVOC Non-Methane Volatile Organic Compound

ppt parts per trillion

ppb parts per billion

ppm parts per million

PSS Photo Stationary State

PTFE Polytetrafluoroethylene

SLPM Standard Liters Per Minute

- UTC Universal Time Coordinates
- UTLS Upper Troposphere Lower Stratosphere
- **VOC** Volatile Organic Compound
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Mata - Pita, Guru- Daivam - From Mother to Father, From Teacher to Divinity.

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Erklärung:

Ich erkläre, dass ich diese Arbeit selbstständig verfasst und nur die angegebenen Quellen und Hilfsmittel benutzt habe. AI-Tools wie ChatGPT und Grammarly wurden für die Umformulierung, Rechtschreib- und Grammatikprüfung verwendet.

Heidelberg, den (30.07.2024)

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