On the understanding of tropospheric fast photochemistry: airborne observations of peroxy radicals during the EMeRGe-Europe campaign

Midhun George1, Maria Dolores Andrés Hernández1, Vladyslav Nenakhov1*, Yangzhuoran Liu1, John Philip Burrows2; Birger Bohn3; Eric Förster3, Florian Obersteiner3, Andreas Zahn3; Theresa Harlaß4, Helmut Ziereis4, Hans Schlager4; Benjamin Schreiner5, Flora Kluge5, Katja Bigge5, and Klaus Pfeilsticker5

1 Institute of Environmental Physics, University of Bremen, Germany
2 Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany
3 Institute of Meteorology and Climate Research, Karlsruhe Institute of Technology, Karlsruhe, Germany
4 Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Physik der Atmosphäre, Oberpfaffenhofen, Germany
5 Institute of Environmental Physics, University of Heidelberg, Heidelberg, Germany

Correspondence to M. George (midhun@iup.physik.uni-bremen.de) and M. D. Andrés Hernández (lola@iup.physik.uni-bremen.de).

Abstract. In this study, airborne measurements of the sum of hydroperoxyl (HO2) and organic peroxy (RO2) radicals that react with NO to produce NO2, i.e. RO2•, coupled with actinometry and other key trace gases measurements, have been used to test the current understanding of the fast photochemistry in the outflow of major population centres (MPCs). All measurements were made during the airborne campaign of the EMeRGe (Effect of Megacities on the transport and transformation of pollutants on the Regional to Global scales) project in Europe on-board the High Altitude Long range research aircraft (HALO). The on-board measurements of RO2• were made using the in-situ instrument Peroxy Radical Chemical Enhancement and Absorption Spectrometer (PeRCEAS). RO2• mixing ratios up to 120 pptv were observed in air masses of different origins and composition under different local actinometrical conditions during seven HALO research flights in July 2017 over Europe.

The range and variability of the RO2• measurements agree reasonably well with radical production rates estimated using photolysis frequencies and RO2• precursor concentrations measured on-board. RO2• is primarily produced following the photolysis of ozone (O3), formaldehyde (HCHO), glyoxal (CHOCHO), and nitrous acid (HONO) in the airmasses investigated. The suitability of photostationary steady-state (PSS) assumptions to estimate the mixing ratios and the variability of RO2• during the airborne observations is investigated. The PSS assumption is robust enough to calculate RO2• mixing ratios for most conditions encountered in air masses measured. The similarities and discrepancies between measured and calculated RO2• mixing ratios are analysed stepwise. The parameters, which predominantly control the RO2• mixing ratios under different chemical and physical regimes, are identified during the analysis. The dominant removal processes of RO2• in the airmasses measured up to 2000 m are the loss of OH and RO through the reaction with NO2 during the radical interconversion. Above 2000 m, HO2 – HO2 and HO2 – RO2 reactions dominate RO2• loss reactions. RO2• calculations underestimated (< 20 %) the measurements by the analytical expression inside the pollution plumes probed. The underestimation is attributed to the limitations of the PSS analysis to take into account the production of RO2• through oxidation and photolysis of the OVOCs not measured during EMeRGe.

1. Introduction

Hydroperoxyl (HO2) and organic peroxy (RO2, where R stands for any organic group) radicals are reactive species that play a key role in the chemistry of the troposphere. In combination with the hydroxyl (OH) radical, HO2 and RO2 take part in rapid
chemical processes that control the lifetime of many key trace constituents in the troposphere. Examples of key tropospheric processes involving HO\textsubscript{2} and RO\textsubscript{2} are as follows:

- the catalytic cycles, which produce and destroy ozone (O\textsubscript{3})
- the generation of key inorganic acids, which are precursors of aerosol (e.g. sulphuric acid, H\textsubscript{2}SO\textsubscript{4}) and important chemical constituents (e.g. nitric acid, HNO\textsubscript{3}) in both summer and winter smog
- the generation of organic acids; the production of hygroscopic hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and organic peroxides (ROO\textsubscript{2}), which enter aerosol and cloud droplets
- the generation of organic peroxy nitrates (RO\textsubscript{2}NO\textsubscript{2}), peroxyacetyl nitrate (CH\textsubscript{3}COOONO\textsubscript{2}, PAN) and other summer smog constituents.

The abundance of HO\textsubscript{2} and RO\textsubscript{2} in the free troposphere has a non-linear and complex dependency on photochemistry, initiated by solar actinic radiation, and on the concentration of the precursors, such as carbon monoxide (CO), volatile organic compounds (VOCs), and peroxides. It also strongly depends on the amounts of nitrogen monoxide (NO) and nitrogen dioxide (NO\textsubscript{2}) due to the gas-phase reactions of NO and NO\textsubscript{2} with the OH and organic oxy (RO) radicals formed during the radical interconversion.

The main production and loss processes of HO\textsubscript{2} and RO\textsubscript{2} in the troposphere are summarised as follows:

a) Production processes of HO\textsubscript{2} and RO\textsubscript{2} through photolysis and oxidation by OH formed through photolysis

\begin{align*}
\text{O}_3 + \text{hv} (\lambda < 320 \text{ nm}) & \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \quad \text{(R1)} \\
\text{O}(^1\text{D}) + \text{H}_2\text{O} & \rightarrow 2\text{OH} \quad \text{(R2a)} \\
\text{O}(^1\text{D}) + \text{N}_2 & \rightarrow \text{O}(^3\text{P}) + \text{N}_2 \quad \text{(R2b)} \\
\text{O}(^1\text{D}) + \text{O}_2 & \rightarrow \text{O}(^3\text{P}) + \text{O}_2 \quad \text{(R2c)} \\
\text{HONO} + \text{hv} (\lambda \leq 400 \text{ nm}) & \rightarrow \text{OH} + \text{NO} \quad \text{(R3)} \\
\text{H}_2\text{O}_2 + \text{hv} & \rightarrow 2\text{OH} \quad \text{(R4)} \\
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{(R5)} \\
\text{OH} + \text{CO} + \text{O}_2 & \rightarrow \text{HO}_2 + \text{CO}_2 \quad \text{(R6)} \\
\text{(}\ast\text{)OH} + \text{CH}_4 + \text{O}_2 & \rightarrow \text{CH}_2\text{O}_2 + \text{H}_2\text{O} \quad \text{(R7)} \\
\text{(**)HCHO} + \text{hv} (\lambda < 340 \text{ nm}) + 2\text{O}_2 & \rightarrow 2\text{HO}_2 + \text{CO} \quad \text{(R8)} \\
\text{(*)(**)CH}_3\text{CHO} + \text{hv} (\lambda < 340 \text{ nm}) + 2\text{O}_2 & \rightarrow \text{CH}_3\text{O}_2 + \text{HO}_2 + \text{CO} \quad \text{(R9)} \\
\text{(**) CH}_3\text{C(O)CH}_3 + \text{hv} (\lambda < 340 \text{ nm}) + 2\text{O}_2 & \rightarrow 2\text{CH}_3\text{O}_2 + \text{CO} \quad \text{(R10)} \\
\text{(**)CHOCHO} + \text{hv} + 2\text{O}_2 & \rightarrow \text{M} \text{HO}_2 + 2\text{CO} \quad \text{(R11)}
\end{align*}

(*) The CH\textsubscript{3} produced from the oxidation of CH\textsubscript{4} or the photolysis of VOCs further reacts with O\textsubscript{2} to form CH\textsubscript{2}O\textsubscript{2}. The net reaction is written since the formation of CH\textsubscript{2}O\textsubscript{2} is much faster than the CH\textsubscript{3} formation due to the high amount of O\textsubscript{2} present in the atmosphere.

(**) H and CHO formed through the VOC photolysis further react with O\textsubscript{2} to form HO\textsubscript{2}. The net reaction is written since the formation of HO\textsubscript{2} is much faster than the H and CHO formation due to the high amount of O\textsubscript{2} present in the atmosphere.
VOCs + OH → OH + HO₂ + RO₂ and other oxidation products \( (R12) \)

alkenes + O₃ → OH + RO₂ + other oxidation products \( (R13) \)

b) Loss processes of HO₂ and RO₂

\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \] \( (R14) \)

\[ \text{HO}_2 + \text{RO}_2 \rightarrow \text{ROOH} + \text{O}_2 \] \( (R15) \)

\[ \text{RO}_2 + \text{RO}_2 \rightarrow \text{ROOH} + \text{R}_1\text{CHO} + \text{O}_2 \] \( (R16a) \)

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \] \( (R17) \)

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \] \( (R18) \)

\[ \text{OH} + \text{NO} \rightarrow \text{HONO} \] \( (R19) \)

\[ \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \] \( (R20) \)

\[ \text{OH} + \text{HONO} \rightarrow \text{H}_2\text{O} + \text{NO}_2 \] \( (R21) \)

\[ \text{RO} + \text{NO} \rightarrow \text{RONO} \] \( (R22) \)

In addition, HO₂ and RO₂ undergo radical interconversion processes through the following reactions:

\[ \text{RO}_2 + \text{RO}_2 \rightarrow \text{RO} + \text{RO} + \text{O}_2 \] \( (R16b) \)

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \] \( (R23) \)

\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \] \( (R24) \)

\[ \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \] \( (R25) \)

\[ \text{RO} + \text{O}_2 \rightarrow \text{R}_{\text{H}_1}\text{O} + \text{HO}_2 \] \( (R26) \)

R23 is one of the most important reactions in the troposphere as it leads to O₃ formation through R27 and R28.

Provided that there is sufficient insolation to ensure rapid photochemical processing and all species involved are known, the sum of HO₂ and RO₂ that react with NO to produce NO₂ can be estimated from a photochemical steady-state (PSS) assumption in which production and loss mechanisms are equally important. The HO₂ + RO₂ concentrations and mixing ratios can be estimated using the PSS assumption for NO₂ by considering the following reactions:

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \] \( (R23) \)

\[ \text{RO}_2 + \text{NO} + \text{O}_2 \rightarrow \text{R}_1\text{O} + \text{NO}_2 + \text{HO}_2 \] \( (R25 + R26) \)

\[ \text{NO}_2 + h\nu (\lambda < 400 \text{ nm}) \rightarrow \text{NO} + \text{O} \] \( (R27) \)
O + O₂ → O₃  \quad (R28)

NO + O₃ → NO₂ + O₂ \quad (R29)

Assuming a PSS for NO₂, this leads to Eq. 1

$$\left[\text{HO}_2 + \text{RO}_2\right]_{\text{PSS}} = \frac{k_{\text{NO} + \text{O}_3}}{k_{\text{NO} + (\text{HO}_2 + \text{RO}_2)}} \left(\frac{k_{\text{NO}_2 + \text{NO}}}{k_{\text{NO}_2 + \text{O}_2}} - [\text{O}_3]\right)$$

(Eq. 1)

where \(k_{\text{NO}_2}\) is the photolysis frequency of NO₂; \(k_{\text{NO} + \text{O}_3}\) (\(1.9 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}\)) is the rate coefficient of the reaction of NO with O₃ and \(k_{\text{NO} + (\text{HO}_2 + \text{RO}_2)}\) is the weighted average rate coefficient assumed for the reactions of peroxy radicals with NO.

The comparison of \(\left[\text{HO}_2 + \text{RO}_2\right]_{\text{PSS}}\) calculated using Eq. 1 with ground-based (e.g. Ridley et al., 1992; Cantrell et al., 1997; Carpenter et al., 1998; Volz-Thomas et al., 2003), and airborne measurements, has shown in the past different degree of agreement. The underestimations and overestimations found in air masses with different chemical compositions are not well understood. In the case of airborne measurements, the PSS calculation generally overestimates that measured peroxy radicals (Cantrell et al., 2003a, 2003b). The differences observed could not be attributed to systematic changes in NO, altitude, water vapour and temperature, although these variables are often correlated.

Ground-based (Mihelcic et al., 2003; Kanaya et al., 2007, 2012; Elshorbany et al., 2012; Lu et al., 2012, 2013; Tan et al., 2017, 2018; Whalley et al., 2018, 2021; Lew et al., 2020) and airborne (Crawford et al., 1999; Tan et al., 2001; Cantrell et al., 2003b) measurements have also been compared with model simulations of HO₂ and RO₂. The discrepancies encountered depend upon the chemical composition of the air mass and the chemical mechanisms and constraints used in the model simulations. Tan et al., 2019 and Whalley et al., 2021 reported experimental radical budget calculations based on the published reaction rate coefficients of fundamental reactions (R1 to R26) controlling OH, HO₂ and RO₂ in the lower troposphere and ground-based measurements of all relevant reactants and photolysis frequencies. In this study, a similar approach has been used to calculate the amount of peroxy radicals in the air masses measured on-board the High Altitude Long range (HALO) research aircraft over Europe during the first campaign of the EMerGe (Effect of Megacities on the transport and transformation of pollutants on the Regional to Global scales) project. The available on-board measurements of RO₂⁺ are defined as the total sum of OH, RO and peroxy radicals reacting with NO to produce NO₂ (i.e., RO₂⁺ = OH + ΣRO + HO₂ + ΣRO₂, where RO₂ are the organic peroxy radicals reacting with NO to produce NO₂). Since the amount of OH and RO is much smaller, RO₂⁺ to a good approximation is the sum of HO₂ and those RO₂ radicals that react with NO to produce NO₂. For the calculation, RO₂⁺ is assumed to be in PSS, and an analytical expression is developed with a manageable degree of complexity to estimate the concentration and mixing ratios of RO₂⁺. The simultaneous on-board measurements of trace gases and photolysis frequencies are used to constrain the estimate of the RO₂⁺ concentration.

In contrast to other experimental deployments, the concentrations and/or mixing ratios of the majority of the key species involved in reactions R1 to R26 were continuously measured on-board HALO during the EMerGe campaign. This minimises the number of assumptions required for the calculations of RO₂⁺. Consequently, this data set provides an excellent opportunity to gain a deeper insight into the source and sink reactions of RO₂⁺ and the applicability of the PSS assumption for the different pollution regimes and related weather conditions in the free troposphere.
2. EMeRGe field campaign in Europe

The overarching objective of the EMeRGe project is to test and improve the current understanding of the photochemical and heterogeneous processing of pollution outflows from major population centres (MPCs) and their impact on the atmosphere. Two intensive observational periods (IOP) were carried out to investigate selected European and Asian MPC outflows. The European IOP took place from 10 to 28 July 2017 (http://www.iup.uni-bremen.de/emerge/home/home.html). An extensive set of in-situ and remote-sensing airborne measurements of trace gases and aerosol particles were made on-board the HALO aircraft (see www.halo-spp.de) along flight tracks in the lower layers of the troposphere from northwest Europe to the Mediterranean region.

HALO carried out a total of 53 flight hours distributed over seven flights to investigate the chemical composition of the outflows from the target MPCs: London, Paris, Benelux/ Ruhr metropolitan area, Po Valley, and urban agglomerations such as Rome, Madrid, and Barcelona. The flight tracks are shown in Fig. 1. All HALO flights started from the HALO base at the DLR in Oberpfaffenhofen, southwest of Munich, Germany. To achieve the scientific goals, 60% of the flights were carried out below 3000 m. Vertical profiles of trace constituents were typically made in three stable flight levels upwind and downwind of the target MPCs. The flights are named E-EU-FN, where E stands for EMeRGe, EU for Europe, and FN is the two-digit flight number. More details about the EMeRGe IOP in Europe and the set of instruments deployed on-board the HALO aircraft are described elsewhere (Andrés Hernández et al., 2021).

Figure 1: The research flight tracks made by HALO during the EMeRGe-Europe campaign on 11, 13, 17, 20, 24, 26 and 28 July 2017 (E-EU-03 to E-EU-09, respectively, colour coded). MPC target areas are colour coded by shading, and the targeted locations/regions are marked with red stars, M: Madrid, B: Barcelona, P: Paris, L: London; BNL: BeNeLux; Ru: Ruhr area; PV: Po Valley; R: Rome. The location of the HALO base at the DLR in Oberpfaffenhofen, Germany (OP) is indicated by a yellow star.

3. PeRCEAS and other instruments on-board

The RO₂⁺ measurements on-board the HALO research aircraft during EMeRGe were made using the Peroxy Radical Chemical Enhancement and Absorption Spectrometer (PeRCEAS). PeRCEAS combines the Peroxy Radical Chemical Amplification
(PeRCA) and Cavity Ring-Down Spectroscopy (CRDS) techniques in a dual-channel instrument. Each channel has a separate chemical reactor and detector, which operate alternatively in both background and amplification modes, i.e. without and with the addition of CO₂ to account for the rapid background variations during airborne measurements. In the amplification mode, the sum of the NO₂ produced from ambient RO₂• through the chain reaction, the ambient NO₂, the NO₂ produced from the ambient O₃ – NO reagent gas reaction and the NO₂ produced in the inlet from any other sources (e.g. thermal decomposition of PAN) is measured. In the background mode, the sum of the ambient NO₂, the NO₂ produced from the ambient O₃ – NO reagent gas reaction and NO₂ produced in the inlet from any other sources is measured. The RO₂• is retrieved by dividing the difference in NO₂ concentration (ΔNO₂) between amplification and background mode by the conversion efficiency of RO₂• to NO₂, which is referred to as eCL (effective chain length). The PeRCEAS instrument and its specifications have been described in detail elsewhere (Horstjann et al., 2014, George et al., 2020).

The two chemical reactors for sampling the ambient air are part of the DUal channel Airborne peroxy radical Chemical Amplifier (DUALER) inlet installed inside a pylon located on the outside of the HALO fuselage. During the EMeRGe campaign in Europe, a reagent gas mixing ratio of 30 ppmv NO ([NO] = 1.46 ×10¹⁴ molecules cm⁻³ at 296 K) and of 9% CO ([CO] = 4.4 ×10¹⁷ molecules cm⁻³ at 296 K) were added to the sample flow for the chemical conversion of RO₂• to NO₂. The DUALER inlet was operated at an internal pressure of 200 mbar to achieve stable chemical conversion. The average eCL under these operational conditions was determined to be 50 ± 8 from laboratory calibrations, where the error is the standard deviation estimated from the reproducibility of the experimental determinations. The HO₂ and RO₂ detection sensitivity depends on the reagent gas NO concentration due to the rate coefficient of reaction R22 being larger than that for R19. For the measurement conditions used during the IOP in Europe, the ratio α = eCL₂H₂O₂/eCL₂HO₂ is 65% (George et al., 2020).

Although the DUALER pressure is kept constant below the ambient pressure, variations in dynamical pressure > 10 mbar during the flight can change the residence time and induce turbulences inside the inlet (Kartal et al., 2010; George et al., 2020). These may lead to different physical losses of radicals before amplification and affect the eCL. In the measurements presented in this study, variations in dynamical pressure of this magnitude were only encountered during flight level changes of the aircraft. When used during the analysis, these data sets are either excluded or flagged (P_flag). The effect of the ambient air humidity on eCL (Mihale and Hastie, 1998; Mihale et al., 1999; Reichert et al., 2003) has been accounted for by a calibration procedure reported in George et al. (2020).

In addition to the measurement of RO₂• from PeRCEAS, other in-situ and remote-sensing measurements and basic aircraft data from HALO are used in this study. Details of the corresponding instruments are summarised in Table 1. Concerning the data obtained by the remote sensing instruments, the miniDOAS retrieves the Slant Column Density (SCD) of the target gas and a scaling gas (O₂) towards the horizon at the flight altitude. From this, mixing ratios of the targeted gas within the line of sight is estimated using RT modelling (Stutz et al., 2017; Hüneke et al., 2017; Kluge et al., 2020; Rotermund et al., 2021). The HAIĐI instrument retrieves SCDs below the aircraft. The SCDs from HAIĐI are then converted to mixing ratios using the corresponding geometric Air Mass Factor (AMF) under a well-mixed NO₂ layer assumption. As a result of this assumption, the calculated mixing ratios for HAIĐI target gases are lower limits and close to the actual values while flying within and close to a well-mixed boundary layer. Despite the differences in sampling volume and temporal and spatial resolution in the in-situ and remote sensing measurement techniques, the concentration of common and related species obtained are in reasonable agreement (Schumann, 2020).
Table 1: List of the airborne measurements and instrumentation used in this study. PeRCA: Peroxy Radical Chemical Amplification; CRDS: Cavity Ring-Down Spectroscopy; PTR-MS: Proton-Transfer-Reaction Mass Spectrometer; AT-BS: Adsorption Tube and Bag air Sampler; TD-GC-MS: Thermal Desorption Gas Chromatography and Mass Spectrometry; DOAS: Differential Optical Absorption Spectrometry; Univ: University; KIT: Karlsruher Institut für Technologie; DLR: Deutsches Zentrum für Luft- und Raumfahrt; IPA: Institut für Physik der Atmosphäre; FZ: Forschungszentrum; FX: Flugperimente.

| Trace gas-in situ measurements | Species/parameters | Acronym | Institution | Technique/Instrument | Reference |
|-------------------------------|--------------------|---------|-------------|----------------------|-----------|
| RO₂ = HO₂ + ∑RO₂              | PeRCEAS            | Univ. Bremen | PeRCA + CRDS | George et al., 2020  |
| OVOC                          | HKMS               | KIT Karlsruhe | PTR-MS       | Brito and Zahn, 2011 |
| O₃                            | FAIRO              | KIT Karlsruhe | UV-Photometry/Chemioluminescence | Zahn et al., 2012 |
| O₅, CO                        | AMTEX              | DLR-IPA | UV-Photometry/VUV-Fluorimetry | Gerbig et al., 1996 |
| NO, NO₂                       | AENEAS             | DLR-IPA | Chemiluminescence/Gold converter | Ziereis et al., 2004 |
| CO₂, CH₄                      | CATS               | DLR-IPA | CRDS        | Chen et al., 2010   |

| Trace gas- remote sensing measurements | Species/parameters | Acronym | Institution | Technique/Instrument | Reference |
|----------------------------------------|--------------------|---------|-------------|----------------------|-----------|
| NO₂, HONO, CH₂O, C₂H₂O₂, C₂H₄O₂      | miniDOAS           | Univ. Heidelberg | DOAS / UV-nIR; 2D optical spectrometer | Hüneneke et al., 2017 |
| NO₂                                    | HAIDI              | Univ. Heidelberg | DOAS / 3x2D-imaging spectrometers | General et al., 2014 |

| Other parameters                      | Species/parameters | Acronym | Institution | Technique/Instrument | Reference |
|---------------------------------------|--------------------|---------|-------------|----------------------|-----------|
| Spectral actinic flux density (up/down) Photolysis frequencies | HALO-SR       | FZ Jülich | CCD spectro- radiometry | Bohn and Lohse, 2017 |
| Basic aircraft data                   | BAHAMAS            | DLR-FX | various      | Mallaun et al., 2015 |

4. Results and discussion

4.1. Airborne RO₂* measurements during EMeRG e in Europe

RO₂* mixing ratios up to 120 pptv were measured during the campaign, as shown in Fig. 2. Typically, the highest RO₂* mixing ratios were observed below 3000 m over Southern Europe. This is attributed to the higher insolation and temperatures favouring the rapid production of RO₂* from the photochemical oxidations of CO and VOCs.
The origin and thus the composition of the air sampled during the seven flights over Europe were different and heterogeneous. Typically, the air masses measured were influenced by emissions from MPCs and their surroundings, and sometimes by biomass burning transported over short or long distances. The concentration and mixing ratio of RO$_2^*$ depends on the insolation and the chemical composition of the air masses probed, particularly on the abundance of RO$_2^*$ precursors. Provided that insolation conditions and a sufficient number of key participating precursors are comparable, the air mass origin is irrelevant for calculating RO$_2^*$ concentrations and mixing ratios. This is because the RO$_2^*$ concentration is controlled by fast chemical and photochemical processes. Thus, the RO$_2^*$ variability and production rates provide insight into the photochemical activity of the air masses probed. Changes in RO$_2^*$ as a function of latitude and altitude, as shown in Fig. 2, confirm the heterogeneity of the photochemical activity in the air masses probed. Figure 3 shows the RO$_2^*$ vertical profiles averaged for the EMeRGe flights over Europe in 500 m altitude bins. The error bars are standard errors (i.e. ± 1σ standard deviation of each bin). The vertical profiles may be biased as the higher altitudes have fewer measurements than those below 3000 m, as mentioned in section 2. The vertical profiles are a composite from averaging different flights and are shown to summarise the variability in the composition of the air masses measured during the campaign.
Figure 3: Composite average vertical profiles of a) RO2*, b) jO(1D) and c) [H2O] observations. The measurements are binned over 220 500 m altitude. The error bars are the standard errors (i.e. ± 1σ standard deviation of each bin). Median values (red triangles) and the number of individual measurements, n, for each bin (in green) are additionally plotted.

Differences between mean and median values indicate less RO₂* variability in the air masses probed above 3000 m. Most of the EMeRGe measurements below 2000 m were carried out in the outflow of MPCs, which are expected to contain significant amounts of RO₂* precursors. HALO flew at the lowest altitudes over the English Channel, the Mediterranean and the North Sea. The H₂O concentration in the air masses decreases steadily with altitude as expected. The higher relative variability in H₂O observed at 3000 m and the increase at 5000 m is associated with measurements under stormy conditions, often over the Alps.

4.2. RO₂* production rates

The total production rate of OH and RO₂* (P_{OH+H₂O₂+RO₂}) can be estimated from the reactions R1 to R13 as follows:

\[ P_{OH+H₂O₂+RO₂} = 2j[O_3]^2 \left[ \frac{k_{OH+H₂O}[H₂O]}{k_{OH+H₂O}[H₂O]+k_{OH+O₂}[O₂]+k_{OH+N₂}[N₂]} + j_{HONO}[HONO] + 2jH₂O₂[H₂O₂] + 2 \sum j_i[OVOC_i] + \sum j_{OH+VOC_j}[OH][VOC_j] + \sum k_{O₃+alkenes}[O₃][alkenes] \right] \]

(Eq. 2)

In this work, Eq. 2 has been applied to the measurements taken within the EMeRGe campaign in Europe. There were no H₂O₂ measurements available for EMeRGe IOP. However, from the results reported by Tan et al. (2001), the OH production from the H₂O₂ photolysis become significant at low NOₓ conditions. Since the [NOₓ] > 8 × 10¹² molecules cm⁻³ for 60 % of the measurements during the IOP, as a first approximation, the production of OH from H₂O₂ photolysis is assumed to be negligible for the dataset considered in this study. Similarly, the VOC photolysis was assumed to dominate the RO₂* production over the oxidation by OH and ozonolysis of alkenes. The most abundant and reactive oxygenated volatile organic compounds (OVOCs)
measured have been taken as a surrogate for the sum of VOCs. These assumptions lead to Eq. 3, which estimates the RO$_2^*$ production rate ($P_{RO_2^*}$) as:

$$P_{RO_2^*} = 2I_{O_3}[O_3]\frac{k_{OH+H_2O}[H_2O]}{P_{O_3}+k_{OH+H_2O}[H_2O]} + 2I_{CH_3CH_2O}[HONO] + 2I_{CH_3CHO}[HCHO] +$$

$$2I_{CH_3C(O)CH_2}[CH_3C(O)CH_2] + 2I_{CHOCHO}[CHOCHO]$$  \hspace{1cm} \text{(Eq. 3)}$$

Eq. 3 yields the rate of production of RO$_2^*$ molecules. The production rate can be expressed in units of mixing ratio of RO$_2^*$ by dividing with the air concentration at each altitude, estimated from the pressure and temperature measurements. Figure 4 shows the composite averaged vertical profile of all measured RO$_2^*$ mixing ratios colour-coded with the estimated $P_{RO_2^*}$. Small circles show the 1-minute measurements binned for $P_{RO_2^*}$ up to 0.8 pptv s$^{-1}$ in 0.1 pptv s$^{-1}$ intervals. The production rates above 0.8 pptv s$^{-1}$ are binned to the 0.8 pptv s$^{-1}$ bin. Larger circles in the figure result from further binning the small circles over 500 m altitude steps. The error bars are the standard errors for each altitude bin. For the sake of representativeness and comparability, the number of measurements in each altitude bin is shown in Fig. 4b. Higher RO$_2^*$ mixing ratios observed below 4000 m are typically associated with $P_{RO_2^*} > 0.4$ pptv s$^{-1}$. Above 4000 m both $P_{RO_2^*}$ and RO$_2^*$ start to decrease with altitude, as expected. This is related to the decrease in H$_2$O and other radical precursor concentrations with altitude, as detailed in Fig. 5 and Fig. 6. In previous airborne campaigns at various parts of the world, RO$_2^*$ vertical distributions showed a local maximum between 1500 and 4000 m, as reported by Tan et al. (2001), Cantrell et al. (2003a, 2003b), and Andrés-Hernández et al. (2009). In the present work, this local maximum is more evident for measurements with $P_{RO_2^*} \geq 0.5$ pptv s$^{-1}$.

![Composite averaged vertical distribution of measured RO$_2^*$](image)

Figure 4: a) Composite averaged vertical distribution of measured RO$_2^*$ colour-coded according to the value of $P_{RO_2^*}$, b) the number of measurements in each altitude bin. Small circles are 1-minute individual measurements binned with $P_{RO_2^*}$ values in 0.1 pptv s$^{-1}$ intervals. Larger circles result from a further binning over 500 m altitude steps. All the production rates below 0.1 pptv s$^{-1}$ and above 0.8 pptv s$^{-1}$ are binned to 0.1 pptv s$^{-1}$ and 0.8 pptv s$^{-1}$, respectively.
Figure 5 shows the fractional contribution of the production rate from each radical precursor reaction included in Eq. 3 as a function of altitude. The data are classified into three groups according to the rate of change of production of the RO₂* mixing ratio P_{RO₂} < 0.07 pptv s⁻¹ (5a), 0.07 < P_{RO₂} < 0.8 pptv s⁻¹ (5b), and P_{RO₂} > 0.8 pptv s⁻¹ (5c) to show the lowest, most common, and highest ranges, respectively, encountered during the IOP. For 89% of the measurements, 0.07 < P_{RO₂} < 0.8 pptv s⁻¹ applies, while the rest of the data are equally distributed in the other two P_{RO₂} ranges. The data in each group are always binned over 500 m when available.

Typically, the high amount of H₂O in the air masses probed results in the O₃ photolysis and subsequent reaction of O¹D with H₂O (R1-R2a) and is the highest RO₂* radical production rate (≥ 50%) below 4000 m. As the amount of H₂O reduces with altitude, the relative contribution from O₃ photolysis decreases. Above 4000 m, HCHO, HONO, and CHOCHO photolysis contributions range between 20% to 40%, 2.5% to 30%, and 5% to 25%, respectively. The HCHO contribution increases up to 80% during measurements above 6000 m. The contributions of CH₃CHO and CH₂C(O)CH₃ photolysis are, in contrast, practically negligible (< 5%).

The vertical changes of the precursor mixing ratios and photolysis frequencies used to calculate P_{RO₂} in Fig. 5 are shown in Fig. 6a to 6f. P_{RO₂} < 0.07 pptv s⁻¹ is associated with measurements under cloudy conditions, towards sunset where the photolysis frequencies are low, or at altitudes above 5000 m in air masses with a low amount of RO₂* precursors. P_{RO₂} > 0.8 pptv s⁻¹ are found for air masses, measured below 2000 m in the outflow of MPCs over the sea, for conditions having sufficient insolation (j_0(¹D) > 3 × 10⁻³ S⁻¹) and a high content of RO₂* precursors (HCHO > 1000 pptv and HONO > 100 pptv). The increase in the photolysis frequencies as a function of altitude is concurrent with decreases in precursor concentrations. As a result, the P_{RO₂} do not significantly vary with altitude in the air masses investigated.

In previous airborne campaigns, Tan et al. (2001) and Cantrell et al. (2003b) reported a reduction of the fractional contribution of the reaction of O(¹D) with H₂O as the P_{RO₂} value decreases. At very low P_{RO₂} values (< 0.03 pptv s⁻¹), the sum of all other production terms exceeded the fraction from the O(¹D) + H₂O term. For these conditions, H₂O₂ and VOCs photolysis dominated the P_{RO₂}. In the case of the EMeRGe data set in Europe, only 6% of P_{RO₂} are below 0.06 pptv s⁻¹.
Figure 5: Total $\text{PRO}_2^*$ and fractional precursor contributions estimated using Eq. 5 as a function of altitude, for: a) $\text{PRO}_2^* < 0.07$ pptv s$^{-1}$, b) $0.07$ pptv s$^{-1} < \text{PRO}_2^* < 0.8$ pptv s$^{-1}$, and c) $\text{PRO}_2^* > 0.8$ pptv s$^{-1}$. Note the different scales in the number of measurements.
Figure 6: Vertical distribution and variation of a) to c) precursor mixing ratios; d) to f) photolysis frequencies for the \( P_{\text{RO}^2} \) bins as in Fig. 5. Note the different scales in the \( \text{H}_2\text{O} \) concentration.
4.3. PSS estimation of RO2∗ mixing ratios

Under most ambient conditions in the troposphere, the RO2∗, which to a first approximation is the sum of HO2 and RO2, are short-lived, and the chemical lifetime of RO2∗ is much shorter than the chemical transport time into and out of an air mass being probed. Consequently, pseudo-steady-state conditions prevail, and the radical production and loss rates are balanced:

\[ P_{\text{RO2+RO2}} = L_{\text{HO2+RO2}} \]  (Eq. 4)

If the interconversion reactions between OH, RO, HO2 and RO2 (R5 to R7, R12, R16b, and R23 to R26) occur without losses, then the radical number concentrations are calculated by solving Eq. 4. If the RO2∗ – RO2∗ reactions are assumed to be the dominant radical loss processes, Eq. 4 leads to Eq. 5.

\[
\frac{2j_{\text{O(1D)}}[O_3]}{k_{\text{O}_3+H_2O}[H_2O]} + \frac{k_{\text{O}_3+H_2O}[H_2O]}{k_{\text{O}_3+H_2O}[H_2O]} + \frac{k_{\text{O}_3+H_2O}[H_2O]}{k_{\text{O}_3+H_2O}[H_2O]} + \frac{k_{\text{O}_3+H_2O}[H_2O]}{k_{\text{O}_3+H_2O}[H_2O]} + \frac{j_{\text{HONO}}(\text{HONO})}{2j_{\text{HCHO}}[\text{HCHO}]} + 2j_{\text{HCHO}}[\text{HCHO}] + 2j_{\text{HCHO}}[\text{HCHO}]
\]

\[ k_{\text{RO}_2+\text{RO}_2} = k_{\text{RO}_2+\text{RO}_2} \]  (Eq. 5)

where \( k_{\text{RO}_2+\text{RO}_2} \) is the effective RO2∗ self-reaction rate coefficient, which is defined as the weighted average rate coefficient between HO2 – HO2, HO2 – RO2 and RO2 – RO2 reactions.

Consequently, the RO2∗ concentrations are expected to correlate with the square root of the \( P_{\text{RO2}} \).

Figure 7 shows the relationship between the measured [RO2∗] and the estimated \( \sqrt{P_{\text{RO2}}} \). Generally, both [RO2∗] and \( \sqrt{P_{\text{RO2}}} \) increase with the photolysis frequency of \( \text{O}_3 \) (\( j_{\text{O}_3(\text{1D})} \)). The [RO2∗] < 0.5 × 10^12 molecules cm^-3 and \( \sqrt{P_{\text{RO2}}} < 1000 \) with \( j_{\text{O}_3(\text{1D})} > 5 \times 10^4 \) belong to the measurements made above 6000 m, where the amount of RO2∗ precursors is low. The relatively weak correlation observed between [RO2∗] and \( \sqrt{P_{\text{RO2}}} \) indicates the presence of other radical loss processes and/or missing production terms in the \( P_{\text{RO2}} \) calculation. Apart from this, the spread in the diagram confirms that the effective RO2∗ self-reaction rate \( k_{\text{RO2+RO2}}[\text{RO2}]^2 \) varies widely in the air masses probed due to the effect of changes in HO2 and \( P_{\text{RO2}} \) concentrations in the individual loss reaction rate coefficients. As mentioned in section 4.1, photochemical processing was expected to be enhanced over Southern Europe due to the prevailing high insolation and temperatures during the measurements. This is also reflected in the higher \( P_{\text{RO2}} \) and [RO2∗] observed in Southern Europe as compared to those in Northern Europe (Fig. 7b).
The correlation between \([\text{RO}_2^*]\) and \(\sqrt{\text{PRo}_2^*}\) improves when the measurements south and north of 47°N are separately analysed (Fig. 8). For a given \([\text{RO}_2^*]\), the \(\text{PRo}_2^*\) calculated is higher for the measurements north of 47°N than south of 47°N. The lowest \([\text{RO}_2^*]\) to \(\sqrt{\text{PRo}_2^*}\) ratios are associated with higher NO\(_x\) (NO + NO\(_2\)), especially north of 47°N, indicating the urban character and higher content in \(\text{RO}_2^*\) precursors of the air probed (Fig. 8d). Note that these results are only valid for the data set acquired over Europe during EMeRGe and do not yield a relationship between \([\text{RO}_2^*]\) and \(\sqrt{\text{PRo}_2^*}\), which is generally applicable for these two latitude windows.
Figure 8: Plots of the measured $[\text{RO}_2^\ast]$ vs $\sqrt[2]{P_{\text{RO}_2^\ast}}$ for the following latitudes: a) and c) south of 47°N; b) and d) north of 47°N.

Note that a) and b) are colour-coded with $I_0(1^D)$; c) and d) are colour-coded by NO$_x$ mixing ratio. The dashed lines indicate the linear fit for visual support.

The relationship between $\text{RO}_2^\ast$ and $P_{\text{RO}_2^\ast}$ is further investigated to identify the dominant $\text{RO}_2^\ast$ loss process in the air masses considered in this study. As stated in section 3, HO$_2$ and RO$_2$ are not speciated but retrieved as $\text{RO}_2^\ast$ by the PeRCEAS instrument. So, the effect of changes in the HO$_2$ to the total $\text{RO}_2^\ast$ ratios, represented by $\delta$, i.e., $[\text{HO}_2] = \delta[\text{RO}_2^\ast]$ and $[\text{CH}_3\text{O}_2] = (1-\delta)[\text{RO}_2^\ast]$, is investigated. As a first approach, CH$_3$O$_2$ reactions are taken as a surrogate for all RO$_2$ reactions to reduce the complexity of the calculations. Consequently, Eq. 5 is accordingly modified:

$$2[O_3]\beta + 2[j_a\text{HONO}] + 2[j_b\text{HCHO}] + 2[j_s\text{CH}_3\text{CHO}] + 2(j_{10a} + j_{10b})[\text{CH}_3\text{C}(O)\text{CH}_3] + 2j_{11}[\text{CHOCHO}] = 2k_{15}\delta(1-\delta)[\text{RO}_2^\ast]^2 + 2k_{16a}(1-\delta)[\text{RO}_2^\ast]^2 + 2k_{14}[\delta[\text{RO}_2^\ast]]^2$$

(Eq. 6)

where $\beta$ is the effective yield of OH production in the reaction of O($^1D$) with H$_2$O given by:

$$\beta = \left(\frac{k_{2a}[\text{H}_2\text{O}]}{k_{2a}[\text{H}_2\text{O}]+k_{2b}[\text{O}_2]+k_{2c}[\text{N}_2]}\right)$$

From Eq. 6, $[\text{RO}_2^\ast]$ can be calculated as
\[ [RO_2^*] = \frac{P_{RO_2^*}}{2k_{RO_2^*}} \]  
(Eq. 7)

where

\[ k_{RO_2^*} = k_{15}\delta(1-\delta) + k_{16a}(1-\delta)^2 + k_{14}\delta^2 \]

\[ P_{RO_2^*} = 2l_1[O_2] + j_4[HONO] + 2l_6[HCHO] + 2l_8[CH_3CHO] + 2(j_{16a} + j_{10b})[CH_2C(O)CH_3] + 2l_{11}[CHOCHO] \]

The second solution gives negative values for \([RO_2^*]\), therefore has no physical meaning. A more detailed derivation of Eq. 6 and Eq. 7 are given in the supplementary information.

Figure 9 shows the measured \(RO_2^*\) (\(RO_2^{*m}\)) mixing ratio versus the calculated \(RO_2^*\) (\(RO_2^{*c}\)) mixing ratio using Eq. 7, colour-coded with respect to the NO mixing ratios. \(RO_2^{*m}\) and \(RO_2^{*c}\) are the measured and calculated \(RO_2^*\) respectively for \(\delta = 1\), i.e. \(RO_2^* = HO_2\) and \(\delta = 0.5\), i.e. \(HO_2 = RO_2\). The eCL corresponding to \(\delta = 1\) and \(\delta = 0.5\) used for the \(RO_2^{*m}\) retrievals were determined in laboratory experiments, as reported by George et al. (2020). The small circles represent 1-minute \(RO_2^{*m}\) whereas the large circles are the mean of the \(RO_2^{*m}\) binned over 10 pptv \(RO_2^{*c}\) intervals. Despite the limited number of production and loss processes considered, \(RO_2^{*c}\) reasonably agrees with \(RO_2^{*m}\) as indicated by the fit parameters (Table 2). \(RO_2^{*c}\) often overestimates \(RO_2^{*m}\) for NO mixing ratios above 250 pptv. The overestimation is also evident for \(RO_2^{*m}\) below 40 pptv. This may be due to the HO and RO losses during the radical interconversion by reacting with NO, producing HONO, HNO\(_3\), and organic nitrate.

Figure 9: \(RO_2^*\) measured (\(RO_2^{*m}\)) versus PSS \(RO_2^{*c}\) calculated (\(RO_2^{*c}\)) using Eq. 7 for a) \(\delta = 1\), b) \(\delta = 0.5\) by assuming only \(RO_2^*\) – \(RO_2^*\) loss reactions. The 1-minute (small circles), the mean of the binned \(RO_2^{*m}\) over 10 pptv \(RO_2^{*c}\) intervals (large circles), and the median of each bin (grey triangles) are shown. The error bars indicate the standard error of each bin. The linear regression for the binned values (solid line) and the 1:1 relation (dashed line) are also plotted for reference. The fit parameters are given in Table 2.

The PSS data presented in Fig. 9 are calculated assuming interconversion reactions between OH, RO and \(RO_2^*\) occur without losses and the limiting case of \([OH] \ll [HO_2+ RO_2]\) in the case of a low amount of NO and NO\(_2\). Furthermore, VOC oxidation processes are not considered as a source of radicals. To identify other major loss processes, Eq. 6 is extended with radical conversion reactions between oxy and peroxy radicals and OH and RO losses through HONO, HNO\(_3\), and organic nitrate.
In the resulting Eq. 8, CH₄, HCHO, CH₂CHO, CHOCHO, CH₃OH, and CH₂C(O)CH₃ measured on-board HALO are taken as surrogates for the dominant VOC acting as RO₂⁺ precursors through oxidation:

\[ (2j_{[O_3]} + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH₂CHO] + 2(j_{10a} + j_{10b})[CH₂C(O)CH₃] + 2j_{11}[CHOCHO] = \]

\[ \delta[RO₂⁺] \left[ k_{21}[NO] + k_{22}[O_3] \right] \rho + \left( 2k_{16a} \left( 1 - \delta \right) [RO₂⁺]² + k_{25} (1 - \delta) [RO₂⁺][NO] \right) \left( \frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_3])} \right) + 2k_{14} \delta (1 - \delta) [RO₂⁺]² \]

(Eq. 8)

where \( \beta \) is the OH production efficiency of the O₃ photolysis and \( \delta \) is the HO₂ to RO₂⁺ ratio as in Eq. 6, \( \rho \) is the OH loss during the OH – RO₂⁺ interconversion. As in Eq. 6, CH₂O₂ is taken as a surrogate for all RO₂ The detailed derivation of Eq. 8 is given in the supplementary information.

During the IOP in Europe, HCHO and CH₂CHO are the dominant radical precursors from OVOC oxidations. Their impact on the radical budget is similar because their respective concentrations compensate the difference in the rate coefficients of their reactions with OH (\( k_{OH+HCHO} = 8.5 \times 10^{-12} \) cm³ molecule⁻¹ s⁻¹ and \( k_{OH+CH₂CHO} = 1.5 \times 10^{-11} \) cm³ molecule⁻¹ s⁻¹). Despite the high mixing ratios measured, CH₂C(O)CH₃ is a less important source of RO₂⁺. This is because the rate coefficient \( k(T)_{OH+CH₂C(O)CH₃} \) is significantly slower than \( k_{OH+HCHO} \) and \( k_{OH+CH₂CHO} \) (see Table S1 in the supplement). Similarly, the RO₂⁺ production rate of CHOCHO and CH₃OH through oxidation is an order of magnitude lower than that of HCHO and CH₂CHO. Since \( k_{HO₂+O₃} \) is almost four orders of magnitude smaller than \( k_{HO₂+NO} \) and the NO concentrations remained about three orders of magnitude smaller than the O₃ measured, the HO₂ reaction with O₃ had a negligible effect in Eq. 8.

The impact of the methlyglyoxal (CH₂C(O)C(O)H) photolysis was also investigated by using the CH₂C(O)C(O)H⁺ measurements provided by the miniDOAS instrument. The CH₂C(O)C(O)H⁺ measured is the sum of CH₂C(O)C(O)H, and a fraction of other substituted dicarbonyls (mainly 2,3-butanedione, CH₃O₂), with similar visible absorption spectra. For the calculation, CH₂C(O)C(O)H was assumed to be half of CH₂C(O)C(O)H⁺ as recommended by Zarzana et al. (2017) and Kluge et al. (2020). The RO₂⁺ calculated by including CH₂C(O)C(O)H photolysis systematically overestimated the measurements. Since the adequacy of the recommended factor of 0.5 varies with the actual air mass composition, CH₂C(O)C(O)H was not included in the calculations.

The revised PSS [RO₂⁺] is then calculated from Eq. 8, as:

\[ [RO₂⁺] = \frac{(-4k_{10a})² - (k_{10a} [NO] + k_{26}[O_3])² k_{10a} [NO] k_{26}[O_3]}{2(-2k_{10a})²} \]  

(Eq. 9)

where

\[ k_{RO₂⁺} = \left( k_{16a} \left( \frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_3])} \right) + k_{16a} \right) (1 - \delta)² + k_{14} \delta (1 - \delta) + k_{14} \delta² \]

\[ L_{RO₂⁺} = \delta (k_{22}[NO] + k_{26}[O_3]) \rho + \left( \frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_3])} \right) k_{25} (1 - \delta) [NO] \]

\[ P_{RO₂⁺} = (2j_{[O_3]} + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH₂CHO] + 2(j_{10a} + j_{10b})[CH₂C(O)CH₃] + 2j_{11}[CHOCHO] \]

Applying Eq. 9 to the measured dataset reduces the overestimation of RO₂⁺m by RO₂⁺ at NO mixing ratios higher than 250 pptv (Fig. 10), especially for RO₂⁺m < 40 pptv but does not introduce significant changes in the overall correlations (Table 2). As in
Fig. 9, plots of the 1-minute $\text{RO}_2^*$ and the average of $\text{RO}_2^*$ binned over 10 pptv $\text{RO}_2^*$ intervals versus $\text{RO}_2^*$ are depicted for $\delta = 1$ and $\delta = 0.5$ in Fig. 10. The $\text{RO}_2^*$ data are colour-coded with the on-board NO measurements. The linear regression slopes are around 0.7 ($R^2 = 0.96$), indicating an overall $25 - 30\%$ underestimation of the $\text{RO}_2^*$, However, the $\text{RO}_2^*$ are mostly overestimated 4000 m under low insolation and underestimated in polluted plumes measured below 2000 m with NO mixing ratios approximately above 50 pptv (see Fig. 11 for $\delta = 0.5$). The $y$-axis intercept is below the instrumental detection limit for most measurement conditions.

Table 2: Linear regression parameters from $\text{RO}_2^*$ versus $\text{RO}_2^*$ using Eq. 7 and Eq. 9 from Fig. 9 and Fig. 10, respectively.

| Formula used to calculate $\text{RO}_2^*$ | $\delta$ | slope | $y$-intercept (pptv) | $R^2$ |
|----------------------------------------|---------|-------|----------------------|-------|
| Eq. 7                                  | 1.00    | 0.72  | 2                    | 0.96  |
|                                        | 0.50    | 0.73  | 6                    | 0.96  |
| Eq. 9                                  | 1.00    | 0.71  | 5                    | 0.96  |
|                                        | 0.50    | 0.74  | 6                    | 0.97  |

Figure 10: $\text{RO}_2^*$ versus $\text{RO}_2^*$, calculated using Eq. 9 for a) $\delta = 1$ and b) $\delta = 0.5$. The data are colour-coded with the measured NO mixing ratios. The 1-minute (small circles), the mean of the binned $\text{RO}_2^*$ over 10 pptv $\text{RO}_2^*$ intervals (large circles), and the median of each bin (grey triangles) are shown. The error bars indicate the standard error of each bin. The linear regression for the binned values (solid line) and the 1:1 relation (dashed line) are also depicted for reference.
Figure 11: RO$_2^*$ versus RO$_2^*$ calculated using Eq. 9 for \( \delta = 0.5 \). The data points are colour-coded for a) photolysis frequency of O$_3$; b) altitude. The 1-minute (small circles), the mean of the binned RO$_2^*$ over 10 pptv RO$_2^*$ intervals (large circles), and the median of each bin (grey triangles) are shown. The error bars indicate the standard error of each bin. The linear regression for the binned values (solid line) and the 1:1 relation (dashed line) are also depicted for reference.

Figure 12 shows the data for \( \delta = 0.5 \) colour-coded with NO, NO$_x$, the sum of HCHO, CH$_3$CHO, CHOCHO, CH$_3$OH, and CH$_3$C(O)CH$_3$ (from now on referred to as \( \Sigma \) VOCs), as a surrogate for the amount of OVOCs acting as RO$_2^*$ precursors, and the \( \Sigma \) VOCs to NO ratio. The largest differences between RO$_2^*$ and RO$_2^*$, is observed for the bins around 50 pptv. The RO$_2^*$ < 25 pptv observed above 4000 m are overestimated for air masses with low insolation, i.e. \( J_{O(1D)} > 2 \times 10^{-3} \text{s}^{-1} \) (Fig. 11), NO < 50 pptv, \( \Sigma \) VOCs typically below 4 ppbv, and high \( \Sigma \) VOCs/NO ratios ( > 50). Under these insolation conditions, the radical production rate is expected to be low, and the RO$_2^*$ - RO$_2^*$ reactions are expected to dominate the RO$_2^*$ loss processes. Since OH and H$_2$O$_2$ were not measured during the EMERGe campaign in Europe, Eq. 9 does not include the loss reactions R17 and R18, which might be significant under such conditions and explain the RO$_2^*$ overestimation. This is also the case for the overestimations observed below 40 pptv RO$_2^*$ at other altitudes, where NO < 50 pptv but the \( \Sigma \) VOCs/NO ratios remain low.

The overestimation may therefore be independent of the \( \Sigma \) VOCs/NO ratios. For NO \( \leq 50 \) pptv, NO$_2$ \( \leq 100 \) pptv, RO$_2^*$ \( \leq 40 \) pptv and HCHO \( \leq 1 \) ppbv, the rate of reaction R18, which forms H$_2$O and O$_2$ from OH and HO$_2$, is about 4 times faster than the rate of the OH oxidation reaction of the dominant OVOCs (R12) considered in this study or the rate of formation of HONO (R19).

RO$_2^*$ is systematically underestimated for \( \Sigma \) VOCs greater than 7 ppbv. The composition of these air masses is quite different, as reflected by the \( \Sigma \) VOCs/NO ratios. This implies that Eq. 9 does not capture the peroxy radical production adequately from VOCs in these cases. The underestimation of RO$_2^*$ may be explained in part by a) OH recycling through additional VOC oxidation processes, which are not in Eq. 9 and/or b) RO$_2^*$ production from the photolysis of carbonyls, which were not measured and/or c) RO$_2^*$ production from the ozonolysis of alkenes.
Figure 12: RO2\textsuperscript{*}m versus RO2\textsuperscript{*}c using Eq. 9 for $\delta = 0.5$ colour-coded with the measured a) NO mixing ratio, b) NO\textsubscript{x} mixing ratio, c) $\Sigma$VOCs mixing ratio, where $\Sigma$VOCs = HCHO + CH\textsubscript{3}CHO + (CHO)\textsubscript{2}+ CH\textsubscript{2}OH+ CH\textsubscript{3}C(O)CH\textsubscript{3}, and d) $\Sigma$VOCs/NO ratio. The 1-minute (small circles), the mean of the binned RO2\textsuperscript{*}m over 10 pptv RO2\textsuperscript{*}c intervals (large circles), and the median of each bin (triangles) are shown. The error bars represent the standard error of each bin. The linear regression for the binned values (solid line) and the 1:1 relationship (dashed line) are plotted for reference.

Spatial and temporal differences in the in-situ measurements of the key trace gases (O\textsubscript{3}, NO, H\textsubscript{2}O, CO, CH\textsubscript{4}, VOCs) with respect to remote sensing observations (NO\textsubscript{2} and HONO) used in Eq. 9 may also contribute to the overall spread observed in Fig. 12. Although the temporal evolution and the amount of the trace gases measured using in-situ and remote sensing instruments agree reasonably well, as shown for HCHO in Fig.13, the remote sensing instruments have, in general, larger air sampling volumes compared to that of in-situ instruments. This may occasionally lead to significant differences depending on the location of the pollutant layers with respect to HALO. In addition, PTR-MS measurements of HCHO might include interferences from molecular fragments of other compounds in the sample air (Inomata et al., 2008). Further details about the accuracy and comparability of the instrumentation on-board during the campaign can be found elsewhere (Schumann, 2020).
Figure 13: An example of the time series of the measured HCHO mixing ratios retrieved from the remote sensing (HAIDI in blue and miniDOAS in green) and in-situ (HKMS in red) instruments during the E-EU-04 flight on 14.07.2017. The shaded region shows ± 1σ uncertainties of the HKMS and miniDOAS instruments. The flight altitude is depicted in black.

In summary, the differences between RO$_2^*$$_m$ and RO$_2^*$$_c$ might be caused by a combined effect of the limitations of the analytical expression to simulate complex non-linear chemistry and the measurement uncertainties arising from the spatial heterogeneity of the plume for the remote sensing instruments. Consequently, individual analysis of the pollution events encountered along the flights is required to quantify limiting factors in Eq. 9.

The ratio of RO$_2^*$$_m$ to RO$_2^*$$_c$ (RO$_2^*$$_m$/RO$_2^*$$_c$) has been used to assess the applicability of Eq. 9 for the calculation of RO$_2^*$ in the air masses probed (Fig. 14). In Fig. 14, the data are colour-coded with respect to RO$_2^*$$_m$/RO$_2^*$$_c$, H$_2$O, ΣVOCs, and NO$_x$. The analytical expression does not capture the RO$_2^*$ variations resulting from fast non-linear photochemistry present in these pollution plumes. This is the case for the measurements made between 42°N and 46°N in the outflow of Po Valley and Rome. ΣVOCs > 7 ppbv and NO$_x$ mixing ratios > 500 pptv indicate high radical precursor loading and relatively fresh emissions. The RO$_2^*$$_m$/RO$_2^*$$_c$ is also > 2 in the measurements over the English Channel (between 50°N and 52°N) with ΣVOCs and NO$_x$ mixing ratio > 7 ppbv and 1000 pptv, respectively.
The applicability of Eq. 9 for calculating the in-flight measurements of RO\textsubscript{2} throughout the flight track along the track of the E-EU-03 flight on 11 July 2017 is shown in Fig. 16. The E-EU-03 flight investigated the outflow of selected MPCs in Italy (i.e., Po Valley and Rome). Consequently, the flight track was routed along the western coast of Italy and included vertical profiling over the Tyrrhenian Sea upwind of Rome (Fig. 15). As can be seen in Fig. 1D, cloudless conditions dominated throughout the flight track. The RO\textsubscript{2} measurements are approximately 20 % underestimated during this period. Backward trajectories calculated using FLEXTRA indicate the transport of pollution through the Mediterranean mixed with dust plumes originating from Tunisia. The NO mixing ratios observed indicate the proximity to emission sources.
Figure 15: Maps of the flight track of E-EU-03 11 July 2017 along the western coast of Italy over the Tyrrhenian Sea color-coded with RO$_2^*$ measurements.

The measurements of VOCs used in Eq. 9 may not be representative of the actual complex VOC composition in the plume measured from 12:05 to 12:25 UTC. Consequently, the RO$_2$ to HO$_2$ ratio and the RO intermediates involved in the radical interconversion processes, the branching ratios and effective rate coefficients for RO$_2^*$ – RO$_2$ reactions might not be well represented in Eq. 9. Taking CH$_3$O$_2$ as a surrogate for all RO$_2$ might lead to uncertainties in the RO$_2^*$ calculations in the presence of OVOCs with larger organic chains. On the experimental side, changes in the HO$_2$ to RO$_2$ ratio affect the accuracy of the PeRCEAS retrieval of the total sum of radicals. As noted in section 3, in this study RO$_2^*$ = HO$_2$ + 0.65 × RO$_2$, and the eCL is determined for a 1:1 mixture of HO$_2$:CH$_3$O$_2$, i.e. δ = 0.5 is used for the RO$_2^*$ retrieval. However, the HO$_2$ to CH$_3$O$_2$ ratio is not expected to remain constant in all the air masses probed. For a 3:1 ratio of HO$_2$:RO$_2$, the RO$_2^*$$_m$ would decrease by 10%.

Similarly, a HO$_2$:RO$_2$ ratio of 1:3 would lead to an increase of 10% in the reported RO$_2^*$$_m$. This uncertainty is well below the in-flight uncertainty of the PeRCEAS instrument indicated by the error bars in Fig. 16 (George et al., 2020), and cannot account for the overall 20% underestimations. However, it might reduce the differences observed between RO$_2^*$$_m$ and RO$_2^*$$_c$ in particular cases. A complete explanation of the variability of RO$_2^*$ in the pollution plumes measured within the IOP in Europe is beyond the scope of this analysis and requires an investigation by high-resolution chemical models.
Figure 16: Temporal variation of $\text{RO}_2^*$, selected radical precursors and $j_{\text{O}(1\text{D})}$ along the E-EU-03 flight track: a) $\text{RO}_2^*$, $\text{RO}_2^*_{\text{c}}$ and calculated OH (OH$_c$) mixing ratios. The flight altitude is indicated in black. The P_flag indicates $\text{RO}_2^*$ measurements affected by dynamical pressure variation in the inlet; b) $\text{O}_3$, CO, HCHO mixing ratios, and $j_{\text{O}(1\text{D})}$; c) NO, NO$_2$, NO$_p$, and HONO mixing ratios.

The OH concentrations in Fig. 16 are upper limits calculated by assuming pseudo-steady-state for the OH production (R1- R3, R24 and R26) and loss (R4 to R6, R13 and R15 to R19) reactions as described by Eq. 10:

$$2\Delta[\text{O}_3] + j_3[\text{HONO}] + k_{23}[\text{HO}_2][\text{NO}] + k_{24}[\text{HO}_2][\text{O}] = [\text{OH}](k_5[\text{O}] + k_6[\text{CO}] + k_7[\text{CH}_4] + k_{12a}[\text{HCHO}] + k_{12b}[\text{CH}_3\text{CHO}] + k_{12c}[\text{CH}_3\text{C(O)CH}_3] + k_{12d}[\text{CH}_3\text{OH}] + k_{12e}[\text{CHOCHO}] + k_{17}[\text{HO}_2] + k_{19}[\text{NO}] + k_{20}[\text{NO}_2] + k_{21}[\text{HONO}] - 2(k_{18a} + k_{18b})[\text{OH}])^2 \quad \text{(Eq. 10)}$$

The OH calculated from Eq. 10 assuming $\delta = 0.5$ is much higher than the OH concentration reported in the previous airborne (Crawford et al., 1999; Tan et al. 2001) and ground-based measurements (Mihelcic et al., 2003; Kanaya et al., 2007, 2012; Hofzumahaus et al., 2009; Elshorbany et al., 2012; Lu et al., 2012, 2013; Tan et al., 2017, 2018; Whalley et al., 2018, 2021; Michelle et al., 2020) in different urban environments. This indicated that the limited number of OVOCs measurements available for the EME-RGe data set is insufficient to calculate the OH reactivity. The overestimation of OH agrees with the understimation of $\text{RO}_2^*$ in airmasses with a high amount of OVOCs ($\sum$OVOCs $> 7 \text{ ppbv}$) as the missing OH – OVOCs reactions in Eq. 8 should reduce $\rho$ (the OH loss during the OH – $\text{RO}_2^*$ interconversion) and thereby increase the $\text{RO}_2^*_{\text{c}}$. Due to the direct reaction of OH
with most of the gases emitted in the atmosphere, OH budget calculations in airmasses of complex chemistry are challenging and require the experimental determination of the OH reactivity, as described by Tan et al. 2019 and Whalley et al., 2021.

4.4. Comparison of results with other studies

4.4.1 $\text{RO}_2^-$ production rate

Cantrell et al. (2003b) proposed $P_{\text{RO}_2^+}$ to be equal to the sum of two terms representing $\text{RO}_2^+ - \text{RO}_2^-$ reactions and the $\text{RO}_2^+ - \text{NO}_x$ reactions in the troposphere. As a result of this assumption, the relationship between HO$_2$, RO$_2$, $P_{\text{RO}_2^+}$ and NO$_x$ is described by Eq. 11:

$$P_{\text{RO}_2^+} = k_{\text{RR}} [\text{HO}_2 + \text{RO}_2]^2 + k_{\text{RN}} [\text{HO}_2 + \text{RO}_2] [\text{NO}_x]$$  \hspace{1cm} (Eq. 11)

where $k_{\text{RR}}$ and $k_{\text{RN}}$ refer to effective rate coefficients for $\text{RO}_2^+ - \text{RO}_2^-$ and $\text{RO}_2^+ - \text{NO}_x$ reactions, and are calculated as fit parameters. Solving Eq. 11 for $[\text{HO}_2 + \text{RO}_2]^2$ leads to:

$$[\text{HO}_2 + \text{RO}_2] = \sqrt{A + B^2} - B$$  \hspace{1cm} (Eq. 12)

where $A = \frac{P_{\text{RO}_2^+}}{k_{\text{RR}}}$ and $B = \frac{k_{\text{RN}} [\text{NO}_x]}{2 k_{\text{RR}}}$. For low NO$_x$ and/or high $P_{\text{RO}_2^+}$, B becomes negligible compared to A. Then $[\text{HO}_2 + \text{RO}_2]$ approaches $\sqrt{A}$ and is independent of NO$_x$. For high NO$_x$ and/or low $P_{\text{RO}_2^+}$, $[\text{HO}_2 + \text{RO}_2]$ approaches zero.

The least-square fitting in Eq. 12 is applied to $\text{RO}_2^+_{\text{m}}$ and $\text{RO}_2^+_{\text{c}}$ from the EMeRGGe measurements in Europe binned in 0.1 pptv s$^{-1}$$P_{\text{RO}_2^+}$ intervals as shown in Fig. 17. The fit parameters for Fig. 17a and Fig. 18b are $k_{\text{RR}} = 7 \times 10^6$; $k_{\text{RN}} = 9 \times 10^6$. The $\text{RO}_2^-$

calculated by Eq. 9 appears to be close to the linear function of the NO$_x$ measured. Similar to the results of the study of Cantrell et al. (2003b), a decrease of $\text{RO}_2^-$ with NO$_x$ is identified for NO$_x > 1000$ pptv, although only for $P_{\text{RO}_2^+} < 0.7$ pptv s$^{-1}$. In the study of Cantrell et al. (2003b), $P_{\text{RO}_2^+}$ only reached values up to 0.275 pptv s$^{-1}$.

Despite the low agreement of the fitted lines with the $\text{RO}_2^+_{\text{m}}$ a decrease of the $\text{RO}_2^+_{\text{m}}$ as a function of NO$_x$ is still observed. The disagreement between the $\text{RO}_2^+_{\text{m}}$ and the curves estimated using Eq. 12 implies that the simplified Eq. 11 is insufficient to adequately describe the chemical and physical processes occurring in the troposphere. Part of the disagreement might arise from missing terms in the $P_{\text{RO}_2^+}$ calculation or inaccuracies related to the NO to NO$_2$ ratio in the air mass, which are more evident at higher $P_{\text{RO}_2^+}$. As expected, the ratio of calculated $[\text{RO}_2^+_{\text{c}}]$ to $\sqrt[3]{P_{\text{RO}_2^+}}$ has a negative linear dependency on the measured [NO$_x$] (see Fig. 17c). The comparable plot of $[\text{RO}_2^+_{\text{m}}]$ to $\sqrt[3]{P_{\text{RO}_2^+}}$ is not linear. This indicates that more complex non-linear processes are involved in the air masses investigated than those considered in Eq. 11 (see Fig.17d).
Figure 17: a) $\text{RO}_2^\ast$ binned with $P_{\text{RO}_2^\ast}$; b) $\text{RO}_2^\ast_m$ binned with $P_{\text{RO}_2^\ast}$; c) $[\text{RO}_2^\ast]_c$ to $\sqrt{P_{\text{RO}_2^\ast}}$ ratio; and d) $[\text{RO}_2^\ast]_m$ to $\sqrt{P_{\text{RO}_2^\ast}}$ ratio. The data in a) and b) are coloured with radical production rates. The $\text{RO}_2^\ast$ for different $P_{\text{RO}_2^\ast}$ ranges are binned into 50 bins over NO\textsubscript{x} in the logarithmic scale from 10 to 10000 pptv. The solid lines are the least square fits obtained using Eq. 11. Error bars indicate $\pm 1 \sigma$ of the bins.

4.4.2 O\textsubscript{3} production rate

The O\textsubscript{3} production rate ($P_{\text{O}_3}$) is calculated from the EMeRGe Europe dataset using the reaction of $\text{RO}_2^\ast$ with NO in a similar manner to that used in previous studies of photochemical processes in urban environments (e.g. Kleinman et al., 1995; Volz-Thomas et al., 2003; Mihelcic et al., 2003; Cantrell et al., 2003b; and references herein).

$$P_{\text{O}_3} = k_{\text{RO}_2^\ast + \text{NO}}[\text{RO}_2^\ast][\text{NO}]$$  \hspace{1cm} (Eq. 13)

where $k_{\text{RO}_2^\ast + \text{NO}}$ is taken as the average of $k_{\text{HO}_2 + \text{NO}}$ and $k_{\text{CH}_3\text{O}_2 + \text{NO}}$.

Figure 18 shows plots of the mean $P_{\text{O}_3}$ calculated using Eq. 13 from the $\text{RO}_2^\ast_m$ and $\text{RO}_2^\ast_c$ as a function of NO. The measurements are binned into 50 NO mixing ratio bins. The bin size increases with NO to keep the points equidistant in the logarithmic scale. The calculated $P_{\text{O}_3}$ using the $\text{RO}_2^\ast_m$ and $\text{RO}_2^\ast_c$ agree well within the standard deviation of the bins.
Figure 18: Calculated O₃ production (Pₒ₃) determined using RO₂⁺ (red dots) and RO₂⁻ (blue dots) as a function of: a) NO mixing ratio; b) NO number concentration. The 1-minute measurements are binned into 50 bins over NO in the logarithmic scale from 10 to 10000 pptv and from 5 × 10⁹ to 3.5 × 10¹⁰ molecules cm⁻³ in 15a and 15b, respectively. The shaded area shows ± 1σ standard deviation of each bin. For comparison with ground-based measurements, the number concentration corresponding to 1 ppbv NO at 1000 mbar and 25°C has been marked by the solid black line in plot b).

Similar Pₒ₃ values have been reported for ground-based measurements in polluted areas such as Wangdu (Tan et al., 2017) and Beijing (Whalley et al., 2021) and similar ranges of peroxy radicals and NO mixing ratios. In previous work, Whalley et al. (2018) calculated Pₒ₃ to be about an order of magnitude lower than that found in this study from observations in central London for about an order of magnitude lower amount of HO₂ + RO₂. For NO > 1 ppbv, the Pₒ₃ estimated from the measurement of HO₂ and RO₂, or from the assumptions of an HO₂ to RO₂ ratio were underestimated by the models in other studies in the urban atmosphere (e.g. Martinez et al., 2003; Ren et al., 2003; Kanaya et al., 2008; Mao et al., 2010; Kanaya et al., 2012; Ren et al., 2013; Brune et al., 2016; Griffith et al., 2016). This is generally attributed to underestimating large RO₂ concentrations, which likely undergo multiple bimolecular reactions with NO before forming an HO₂ radical.

During the EMcRGe IOP in Europe, the NO mixing ratios were < 1 ppbv (approximately < 3 × 10¹⁰ molecules cm⁻³). The ozone production rates obtained for both measured and calculated RO₂⁺ are in reasonable agreement with other modelling studies in urban environments where the mixing ratio of NO is < 1 ppbv.

5. Summary and conclusions

This study exploits the airborne measurements of various atmospheric constituents on-board the HALO research aircraft over Europe in summer 2017 to investigate radical photochemistry in the probed airmasses. RO₂⁺ are calculated by assuming a photostationary steady-state (PSS) of RO₂⁺ and compared with the actual measurements. The calculation is constrained by the simultaneous airborne measurements of radical precursors, photolysis frequencies and reactants of RO₂⁺ such as NOₓ and O₃.

The significance and the importance of selected production and loss processes in the RO₂⁺ chemistry are investigated by gradually increasing the complexity of the analytical expression. The agreement of the calculations with the measurements over a wide range of chemical composition and insolation conditions improves when the analytical expression is extended to account for oxy–peroxy radical interconversion reactions and loss of OH and RO during the interconversion. The RO₂⁺ measured is
usually overestimated when NO is < 50 pptv in the air probed. This is attributed to RO$_2^*$ loss processes involving reactions with OH, which are not considered in the analytical expression. The reactions are excluded from the analytical expression to constrain it with on-board measurements. These reactions become significant RO$_2^*$ loss processes at low NO concentrations.

The results indicate that the steady-state calculations mostly underestimated the RO$_2^*$ measurements in polluted plumes of urban origin at altitudes below 2000 m. Changes in the HO$_2$ to RO$_2$ ratios in different plumes partly account for the disagreement in particular cases. In pollution plumes with the sum of the OVOCs measured mixing ratios > 7 ppbv, the underestimation of the measurements can reach up to 80%. In these plumes, the oxidation and/or photolysis of non-measured VOCs and the ozonolysis of alkenes might be significant, limiting the accuracy of the analytical expression. The overestimation of the OH concentration calculated based on the measured reactants also indicates missing oxy–peroxy radical interconversion reactions in the analytical PSS expression. More information about peroxy radical speciation and VOC partitioning is required to better describe the fast photochemistry in these pollution plumes.

The analytical expression developed is robust enough to simulate the radical chemistry in most of the conditions in the free troposphere encountered during EMeRGe IOP in Europe. Speciated radical and VOC measurements in future campaigns would facilitate the estimation of radical loss reactions in air masses with NO < 50 pptv and improve radical production rates estimations in pollution plumes with a high amount of VOCs, where non-linear complex chemistry is involved. Comparing RO$_2^*$ measurements with RO$_2^*$ calculations from the analytical expression helps to identify different chemical and physical regimes, which can be used to constrain future model studies.

The calculated O$_3$ production rates for NO < 1 ppbv are in the same order of magnitude as those previously reported for urban environments. This indicates that the selected RO$_2^*$ production and loss processes and observations of the radical precursors on-board are, to a good approximation, adequate for the estimation of the O$_3$ production in the measured airmasses in the free troposphere over Europe.

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

Financial support. The study was funded in part by the German Research Foundation (Deutsche Forschungsgemeinschaft; DFG) HALO-SPP 1294, the University and the State of Bremen, IPA, DLR, Oberpfaffenhofen, Germany. The contributions from BS, FK, and KP were supported via the DFG grants PF 384/16, PF 384/17 and PF 384/19. KB was granted funding via the DFG grant PI 193/21/1 and acknowledges additional financial from the Heidelberg Graduate School for Physics. EF was supported via the DFG grant NE 2150/1-1 and acknowledges additional financial support from the Karlsruhe Institute of Technology. MG, YL, MDAH and JPB acknowledge financial support from the University of Bremen.

Acknowledgements: MG, MDAH, YL and JPB thank Wilke Thomssen for support during the preparation and integration phases of EMeRGe.

Author contribution: MG, VN, and YL undertook the RO$_2^*$ measurements, flying as key scientists on-board HALO. VN led the deployment of PeRCEAS in the HALO aircraft. MG led the analysis of the PeRCEAS measurements and prepared the manuscript with contributions from all co-authors. MDAH and JPB initiated the EMeRG research project and consortium, acted as co-principal and principal investigators, and participated in the measurement campaigns. They developed the overarching EMeRG scientific objectives and the required measurement portfolio, directed the EMeRG research campaigns, and participated in the data.
analysis presented. AZ, BB, BS, EF, FO, FK, HS, HZ, KB, KP, and TH have contributed by providing their measurements made on-board HALO during the campaign and participated in the discussion of results.

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

6. References

Andreae, M. O., Afcine, A., Albrecht, R., Holanda, B. A., Artaxo, P., Barbosa, H. M. J., Borrmann, S., Cecchini, M. A., Costa, A., Dollner, M., Fütterer, D., Järvinen, E., Jurkat, T., Klimach, T., Konemann, T., Krone, C., Krämer, M., Krisna, T., Machado, L. A. T., Mertes, S.; Minikin, A., Pöhlker, C., Pöhlker, M. L., Pöschl, U. Rosenfeld, D., Sauer, D., Schlager, H., Schnaiter, M., Schneider, J., Schulz, C., Spanu, A., Sperling, V. B., Voigt, C., Walser, A., Wang, J., Weinzierl, B., Wendisch, M., Ziereis, H.: Aerosol characteristics and particle production in the upper troposphere over the Amazon Basin. Atmos. Chem. Phys., 18, 921–961, https://doi.org/10.5194/acp-18-921-2018, 2018.

Andrés Hernández, M. D., Kartal, D., Reichert, L., Burrows, J. P., Meyer Arnek, J., Lichtenstern, M., Stock, P., and Schlager, H.: Peroxy radical observations over West Africa during AMMA 2006: photochemical activity in the outflow of convective systems, Atmos. Chem. Phys., 9, 3681–3695, https://doi.org/10.5194/acp-9-3681-2009, 2009.

Andrés Hernández, M. D., Hilboll, A., Ziereis, H., Förster, E., Krüger, O. O., Kaiser, K., Schneider, J., Barnaba, F., Vrekoussis, M., Schmidt, J., Huntrieser, H., Blechschmidt, A.-M., George, M., Nenakhov, V., Klausner, T., Holanda, B. A., Wolf, J., Eirenschmalz, L., Krebsbach, M., Pöhlker, M. L., Hedegaard, A. B., Mei, L., Pfeilsticker, K., Liu, Y., Koppmann, R., Schlager, H., Bohn, B., Schumann, U., Richter, A., Schreiner, B., Sauer, D., Baumann, R., Mertens, M., Jöckel, P., Kihain, M., Stratmann, G., Pöhlker, C., Campanelli, M., Pandolfi, M., Sicard, M., Gomez-Amo, J. L., Pujadas, M., Bigge, K., Kluge, F., Schwarz, A., Daskalakis, N., Walter, D., Zahn, A., Pöschl, U., Bönisch, H., Borrmann, S., Platt, U., and Burrows, J. P.: Overview: On the transport and transformation of pollutants in the outflow of major population centres – observational data from the EMeRGe European intensive operational period in summer 2017, Atmos. Chem. Phys. Discuss. [preprint], https://doi.org/10.5194/acp-2021-500, in review, 2021.

Brito, J., and Zahn, A.: An unheated permeation device for calibrating atmospheric VOC measurements, Atmos. Meas. Tech., 4(10), 2143–2152, https://doi.org/10.5194/amt-4-2143-2011, 2011.

Brune, W. H., Baier, B. C., Thomas, J., Ren, X., Cohen, R. C., Pusede, S. E., Browne, E. C., Goldstein, A. H., Gentner, D. R., Keutsch, F. N., Thornton, J. A., Harrold, S., Lopez-Hilfiker, F. D., and Wennberg, P. O.: Ozone production chemistry in the presence of urban plumes, Faraday Discuss., 189, 169–189, https://doi.org/10.1039/c5fd00204d, 2016.

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, available at: http://jpldataeval.jpl.nasa.gov (last access: 7 April 2020), 2015.

Cantrell, C. A. and Stedman, D. H.: A possible technique for the measurement of atmospheric peroxy radicals, Geophys. Res. Lett., 9, 846–849, 1982.
Cantrell, C. A., Stedman, D. H., and Wendel, G. J.: Measurement of atmospheric peroxy radicals by chemical amplification, Anal. Chem., 56, 1496–1502, 1984.

Cantrell, C. A., Shetter, R. E., Calvert, J. G., Eisele, F. L., Williams, E., Baumann, K., Brune, W. H., Stevens, P. S., Mather J. H.: Peroxy radicals from photostationary state deviations and steady state calculations during the Tropospheric OH Photochemistry Experiment at Idaho Hill, Colorado, 1993, J. Geophys. Res., 102(D5), 6369, https://doi.org/10.1029/96JD01703, 1997.

Cantrell, C. A., Edwards, G. D., Stephens, L. Mauldin, E. Kosciuch, M. Zondlo, and F. Eisele: Peroxy radical observations using chemical ionisation mass spectrometry during TOPSE, J. Geophys. Res., 108(D6), 8381, https://doi.org/10.1029/2002JD002715, 2003a.

Cantrell, C. A., Edwards, G. D., Stephens, S., Mauldin, R. L., Zondlo. M.A., Kosciuch, E., Eisele, F. L., Shetter, R. E., Lefer, B. L., Hall, S., Flocke, F., Weinheimer, A., Fried, A., Apel, E., Kondo, Y., Blake, D. R., Blake, N. J., Simpson, I. J., Bandy, A. R., Thornton, D. C., Heikes, B. G., Singh, H. B., Brune, W. H., Harder, H., Martinez, M., Jacob, D. J., Avery, M. A., Barrick, J. D., Sachse, G. W., Olson, J. R., Crawford, J. H., and Clarke, A. D.: Peroxy radical behaviour during the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign as measured aboard the NASA -3B aircraft, J. Geophys. Res., 108(D20), 8797, https://doi.org/10.1029/2003JD003674, 2003b.

Chen H., Winderlich, J., Gerbig, C., Hoefer, A., Rella, C. W., Crosson, E. R., Van Pelt, A. D., Steinbach, J., Kolle, O., Beck, V., Daube, B. C., Gottlieb, E. W., Chow, V. Y., Santoni, G. W., and S. C. Wofsy, High-accuracy continuous airborne measurements of greenhouse gases (CO2 and CH4) using the cavity ring-down spectroscopy (CRDS) technique, Atmos. Mes. Tech., 3, 375-386, 2010.

Crawford, J., Davis, D., Olson, J., Chen, G., Liu, S., Gregory, G., Barrick, J., Sachse, G., Sandholm, S., Heikes, B., Singh, H., and Blake, D.: Assessment of upper tropospheric HOx sources over the tropical Pacific based on NASA GTE/PEM data: Net effect on HOx and other photochemical parameters, J. Geophys. Res., 104, 16255–16273, https://doi.org/10.1029/1999JD900106, 1999.

Elshorbany, Y. F., Kleffmann, J., Hofzumahaus, A., Kurtenbach, R., Wiesen, P., Brauers, T., Bohn, B., Dorn, H.-P., Fuchs, H., Holland, F., Rohrer, F., Tillmann, R., Wegener, R., Wahner, A., Kanaya, Y., Yoshino, A., Nishida, S., Kajii, Y., Martinez, M., Kubistin, D., Harder, H., Lelieveld, J., Elste, T., Plass-Dülmer, C., Stange, G., Berresheim, H., Schurath, U.: HOx budgets during HOxComp: A case study of HOx chemistry under NOx-limited conditions, J. Geophys. Res., 117, D03307, https://doi.org/10.1029/2011JD017008. 2014.

Fisher, R., Lowry, D., Wilkin, O., Sriskantharajah, S., and Nisbet, E. G.: High-precision, automated stable isotope analysis of atmospheric methane and carbon dioxide using continuous-flow isotope-ratio mass spectrometry, Rapid communications in mass spectrometry: RCM, 20 (2), 200–208. https://doi.org/10.1002/rcm.2300, 2006.

Fricke, C., Ehrlich, A., Jäkel, E., Bohn, B., Wirth, M., and Wendisch, M.: Influence of local surface albedo variability and ice crystal shape on passive remote sensing of thin cirrus, Atmos. Chem. Phys.,14, 1943-1958, https://doi.org/10.5194/acp-14-1943-2014, 2014.
General, S., Pöhler, D., Sihler, H., Bobrowski, N., Frieß, U., Zielcke, J., Horbanski, M., Shepson, P. B., Stirm, B. H., Simpson, W. R., Weber, K., Fischer, C., and Platt, U.: The Heidelberg Airborne Imaging DOAS Instrument (HAIDI) – a novel Imaging DOAS device for 2-D and 3-D imaging of trace gases and aerosols, Atmos. Meas. Tech., 7, 3459-3485, 2014, https://doi.org/10.5194/amt-7-3459-2014.

George, M., Andrés-Hernández, M. D., Nenakhov, V., Liu, Y., and Burrows, J. P.: Airborne measurement of peroxy radicals using chemical amplification coupled with cavity ring-down spectroscopy: the PeRCEAS instrument, Atmos. Meas. Tech. 13, 2577–2600, https://doi.org/10.5194/amt-13-2577-2020.

Gerbig, C., Kley, D., Volz-Thomas, A., Kent, J., Dewey, K., and McKenna, D. S.: Fast response resonance fluorescence CO measurements aboard the C-130: Instrument characterisation and measurements made during North Atlantic Regional Experiment 1993, J. Geophys. Res., 101, 29229-29238, 1996.

Griffith, S. M., Hansen, R. F., Dusanter, S., Michoud, V., Gilman, J. B., Kuster, W. C., Veres, P. R., Graus, M., de Gouw, J. A., Roberts, J., Young, C., Washenfelder, R., Brown, S. S., Thalmann, R., Wexman, E., Volkamer, R., Tsai, C., Stutz, J., Flynn, J. H., Grossberg, N., Lefer, B., Alvarez, S. L., Rappenglueck, B., Mielke, L. H., Osthoff, H. D., and Stevens, P. S.: Measurements of Hydroxyl and Hydroperoxy Radicals during CalNexLA: Model Comparisons and Radical Budgets, J. Geophys. Res.-Atmos., 121, 4211–4232, https://doi.org/10.1002/2015JD024358, 2016.

Hofzumahaus, A., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.-C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S., Shao, M., Zeng, L., Wahner, A., and Zhang, Y.: Amplified trace gas removal in the troposphere, Science, 324, 1702–1704, https://doi.org/10.1126/science.1164566, 2009.

Horstjann, M., Andrés Hernández, M. D., Nenakhov, V., Chrobry, A., and Burrows, J. P.: Peroxy radical detection for airborne atmospheric measurements using absorption spectroscopy of NO2, Atmos. Meas. Tech. 7, 1245-1257, https://doi.org/10.5194/amt-7-1245-2014.

Hüneke, T., Aderhold, O.-A., Bounin, J., Dorf, M., Gentry, E., Grossmann, K., Grooß, J.-U., Hoor, P., Jöckel, P., Kenntner, M., Knapp, M., Knecht, M., Lücks, D., Ludmann, S., Matthes, S., Raaecke, R., Reichert, M., Weimar, J., Werner, B., Zahn, A., Ziereis, H., and Pfeilsticker, K.: The novel HALO mini-DOAS instrument: inferring trace gas concentrations from airborne UV/visible limb spectroscopy under all skies using the scaling method, Atmos. Meas. Tech., 10, 4209–4234, https://doi.org/10.5194/amt-10-4209-2017, 2017.

Inomata, S., Tanimoto, H., Kameyama, S., Tsunogai, U., Irie, H., Kanaya, Y., and Wang, Z.: Technical Note: Determination of formaldehyde mixing ratios in air with PTR-MS: laboratory experiments and field measurements, Atmos. Chem. Phys., 8, 273–284, https://doi.org/10.5194/acp-8-273-2008, 2008.

Kanaya, Y., Cao, R., Akimoto, H., Fukuda, M., Komazaki, Y., Yokouchi, Y., Koike, M., Tanimoto, H., Takegawa, N., and Kondo, Y.: Urban photochemistry in central Tokyo: 1. Observed and modelled OH and HO2 radical concentrations during the winter and summer of 2004, J. Geophys. Res., 112, D21312, https://doi.org/10.1029/2007JD008670, 2007.
Kanaya, Y., Fukuda, M., Akimoto, H., Takegawa, N., Komazaki, Y., Yokouchi, Y., Koike, M., and Kondo, Y.: Urban photochemistry in central Tokyo: 2. Rates and regimes of oxidant \((O_3 + NO_2)\) production, \emph{J. Geophys. Res.}, 113, D06301, https://doi.org/10.1029/2007JD008671, 2008.

Kanaya, Y., Hofzumahaus, A., Dorn, H.-P., Brauers, T., Fuchs, H., Holland, F., Rohrer, F., Bohn, B., Tillmann, R., Wegener, R., Wahner, A., Kajii, Y., Miyamoto, K., Nishida, S., Watanabe, K., Yoshino, A., Kubistin, D., Martinez, M., Rudolf, M., Harder, H., Berresheim, H., Elste, T., Plass-Dülmer, C., Stange, G., Kleffmann, J., Elshorbany, Y., and Schurath, U.: Comparisons of observed and modeled \(OH\) and \(HO_2\) concentrations during the ambient measurement period of the HOxComp field campaign, \emph{Atmos. Chem. Phys.}, 12, 2567–2585, https://doi.org/10.5194/acp-12-2567-2012, 2012.

Kartal, D., Andrés-Hernández, M. D., Reichert, L., Schlager, H., and Burrows, J. P.: Technical Note: Characterisation of a DUALER instrument for the airborne measurement of peroxy radicals during AMMA 2006, \emph{Atmos. Chem. Phys.}, 10, 3047–3062, https://doi.org/10.5194/acp-10-3047-2010, 2010.

Kleinman, L., Y.-N. Lee, S. R. Springston, J. H. Lee, L. Nunnermacker, J. Weinstein-Lloyd, X. Zhou, and L. Newman, Peroxy radical concentration and ozone formation rate at a rural site in southeastern United States, \emph{J. Geophys. Res.}, 100, 7263–7273, 1995.

Kluge, F., Hünke, T., Knecht, M., Lichtenstern, M., Rotermund, M., Schlager, H., Schreiner, B., and Pfeilsticker, K.: Profiling of formaldehyde, glyoxal, methylglyoxal, and CO over the Amazon: normalized excess mixing ratios and related emission factors in biomass burning plumes, \emph{Atmos. Chem. Phys.}, 20, 12363–12389, https://doi.org/10.5194/acp-20-12363-2020, 2020.

Lew, M. M., Rickly, P. S., Bottorff, B. P., Reidy, E., Sklaveniti, S., Léonardis, T., Locoge, N., Dusanter, S., Kundu, S., Wood, E., and Stevens, P. S.: \(OH\) and \(HO_2\) radical chemistry in a midlatitude forest: measurements and model comparisons, \emph{Atmos. Chem. Phys.}, 20, 9209–9230, https://doi.org/10.5194/acp-20-9209-2020, 2020.

Lu, K. D., Rohrer, F., Holland, F., Fuchs, H., Bohn, B., Brauers, T., Chang, C. C., Häselar, R., Hu, M., Kita, K., Kondo, Y., Li, X., Lou, S. R., Nehr, S., Shao, M., Zeng, L. M., Wahner, A., Zhang, Y. H., and Hofzumahaus, A.: Observation and modelling of \(OH\) and \(HO_2\) concentrations in the Pearl River Delta 2006: a missing \(OH\) source in a VOC rich atmosphere, \emph{Atmos. Chem. Phys.}, 12, 1541–1569, https://doi.org/10.5194/acp-12-1541-2012, 2012.

Lu, K. D., Hofzumahaus, A., Holland, F., Bohn, B., Brauers, T., Fuchs, H., Hu, M., Häselar, R., Kita, K., Kondo, Y., Li, X., Lou, S. R., Oebel, A., Shao, M., Zeng, L. M., Wahner, A., Zhu, T., Zhang, Y. H., and Rohrer, F.: Missing \(OH\) source in a suburban environment near Beijing: observed and modelled \(OH\) and \(HO_2\) concentrations in summer 2006, \emph{Atmos. Chem. Phys.}, 13, 1057–1080, https://doi.org/10.5194/acp-13-1057-2013, 2013.

Mallaun, C., Giez, A. and Baumann, R.: Calibration of 3-D wind measurements on a single engine research aircraft Atmos. Meas. Tech., 8, 3177-3196, https://doi.org/10.5194/amt-8-3177-2015, 2015.

Mihelcic, D., Holland, F., Hofzumahaus, A., Hoppe, L., Konrad, S., Müggen, P., Pätz, H.-W., Schäfer, H.-J., Schmitz, T., Volz-Thomas, A., Bächmann, K., Schlomski, S., Platt, U., Geyer, A., Alcie, B., and Moortga, G. K.: Peroxy radicals during BERLIOZ at Pabstthum: Measurements, radical budgets and ozone production, \emph{J. Geophys. Res.}, 108, 8254, https://doi.org/10.1029/2001JD001014, 2003.
Mao, J., Jacob, D. J., Evans, M. J., Olson, J. R., Ren, X., Brune, W. H., Clair, J. M. St., Crounse, J. D., Spencer, K. M., Beaver, M. R., Wennberg, P. O., Cubison, M. J., Jimenez, J. L., Fried, A., Weibring, P., Walega, J. G., Hall, S. R., Weinheimer, A. J., Cohen, R. C., Chen, G., Crawford, J. H., McNaughton, C., Clarke, A. D., Jaeglé, L., Fisher, J. A., Yantosca, R. M., Le Sager, P., and Carouge, C.: Chemistry of hydrogen oxide radicals (HOx) in the Arctic troposphere in spring, Atmos. Chem. Phys., 10, 5823–5838, https://doi.org/10.5194/acp-10-5823-2010, 2010.

Ren, X., Harder, H., Martinez, M., Lesher, R. L., Oliger, A., Shirley, T., Adams, J., Simpas, J. B., and Brune, W. H.: HOX concentrations and OH reactivity observations in New York City during PMTACS-NY2001, Atmos. Environ., 37, 3627–3637, 2003.

Ren, X., van Duin, D., Cazorla, M., Chen, S., Mao, J., Zhang, L., Brune, W. H., Flynn, J. H., Grossberg, N., Lefer, B. L., Rappenglück, B., Wong, K. W., Tsai, C., Stutz, J., Dibb, J. E., Thomas Jobson, B., Luke, W. T., and Kelley, P.: Atmospheric oxidation chemistry and ozone production: Results from SHARP 2009 in Houston, Texas, J. Geophys. Res., 118, 5770–5780, https://doi.org/10.1002/jgrd.50342, 2013.

Ren, Y., Baumann, R., Schlager, H.: An airborne perfluorocarbon tracer system and its first application for a Lagrangian experiment. Atmos. Meas. Tech., 8, 69–80. https://doi.org/10.5194/amt-8-69-2015, 2015.

Ridley, B.A., Madronich, S., Chatfield, R. B., Walega, J. G., and Shetter, R. E.: Measurements and model simulations of the photostationary state during the Mauna Loa observatory photochemistry experiment: Implications for radical concentrations and ozone production and loss rates, J. Geophys. Res. 97, 10375–10388 (1992).

Rotermund, M. K., Bense, V., Chipperfield, M. P., Engel, A., Grooß, J.-U., Hoor, P., Hünke, T., Keber, T., Kluge, F., Schreiner, B., Schuck, T., Vogel, B., Zahn, A., and Pfeilsticker, K.: Organic and inorganic bromine measurements around the extratropical tropopause and lowermost stratosphere: Insights into the transport pathways and total bromine, Atmos. Chem. Phys. Discuss. [preprint], https://doi.org/10.5194/acp-2021-202, in review, 2021.

Stutz, J., Werner, B., Spolaor, M., Scalone, L., Festa, J., Tsai, C., Cheung, R., Colosimo, S. F., Tricoli, U., Raecke, R., Hossaini, R., Chipper1180, Field, M. P., Feng, W., Gao, R.-S., Hintsa, E. J., Elkins, J. W., Moore, F. L., Daube, B., Pittman, J., Wofsy, S., and Pfeilsticker, K.: A new Differential Optical Absorption Spectroscopy instrument to study atmospheric chemistry from a high-altitude unmanned aircraft, Atmos. Meas. Tech., 10, 1017–1042, https://doi.org/10.5194/amt-10-1017-2017, 2017.

Schulz, C., Schneider, J., Holanda, B. A., Appel, O., Costa, A., de Sá, S.S., Dreiling, V. Fütterer, D., Jurkat-Witschas, T., Klimach, T., Knote, C., Krümer, M., Martin, S.T., Mertes, S., Pöhler, M.L., Sauer, D., Voigt, C., Walser, A., Weinzierl, A.B., Ziereis, H., Zöger, M., Andreae, M.O., Artaxo, P., Machado, L.A.T., Pöschl, U., Wendisch, M., and S. Borrmann, Aircraft-based observations of isoprene-epoxydiol-derived secondary organic aerosol (IEPOX-SOA) in the tropical upper troposphere over the Amazon region. Atmos. Chem. Phys., 18, 14979–15001, 2018, https://doi.org/10.5194/acp-18-14979-2018.

Schumann, U.: Measurement and model data comparisons for the HALO-FAAM formation flight during EMeRGe on 17 July 2017, doi:10.5281/zenodo.4427965, 2020.
Speidel, M., Nau, R., Arnold, F., Schlager, H., A. Stohl, Sulfur dioxide measurements in the lower, middle and upper troposphere: Deployment of an aircraft-based chemical ionisation mass spectrometer with permanent in-flight calibration, Atmospheric Environment, 41, 2427-2437, https://doi.org/10.1016/j.atmosenv.2006.07.047, 2007.

Tan, D., Faloon, I., Simpas, J. B., Brune, W., Olson, J., Crawford, J., Avery, M., Sachse, G., Vay, S., Sandholm, S., Guan, H.-W., Vaughn, T., Mastromarino, J., Heikes, B., Snow, J., Podolske, J., and Singh, H.: OH and HO2 in the tropical Pacific: Results from PEMTropics B, J. Geophys. Res., 106, 32,667–32,681, 2001.

Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Häselar, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO2 and RO2 radicals, Atmos. Chem. Phys., 17, 663–690, https://doi.org/10.5194/acp-17-663-2017, 2017.

Tan, Z., Rohrer, F., Lu, K., Ma, X., Bohn, B., Broch, S., Dong, H., Fuchs, H., Gkatzelis, G. I., Hofzumahaus, A., Holland, F., Li, X., Liu, Y., Liu, Y., Novelli, A., Shao, M., Wang, H., Wu, Y., Zeng, L., Hu, M., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Wintertime photochemistry in Beijing: observations of ROx radical concentrations in the North China Plain during the BEST-ONE campaign, Atmos. Chem. Phys., 18, 12391–12411, https://doi.org/10.5194/acp-18-12391-2018, 2018.

Tyndall, G. S.; Cox, R. A.; Granier, C.; Lesclaux, R.; Moortgat, G. K.; Ravishankara, A. R.; Wallington, T. J. Atmospheric chemistry of small organic peroxy radicals. J. Geophys. Res. 2001, 106, 12157-12182, https://doi.org/10.1029/2000JD900746.

Volz-Thomas, A., Xueref, I., and Schmitt, R.: Automatic gas chromatograph and calibration system for ambient measurements of PAN and PPN, Environ. Sci. Poll. Res., 9, 72-76, 2001.

Volz-Thomas, A., Pätz, H.-W., Houben, N., Konrad, S., Mihelcic, D., Klüpfel, T., Perner, D.: Inorganic trace gases and peroxy radicals during BERLIOZ at Pabstthum: An investigation of the photostationary state of NOx and O3, J. Geophys. Res., 108(D4), PHO 4-1, https://doi.org/10.1029/2001JD001255, 2003.

Wendisch, M., Pöschl, U., Andreae, M. O., Machado, L. A. T., Albrecht, R., Schlager, H., Rosenfeld, D., Martin, S. T., Abdelmonem, A. Afchine, A., Araújo, A. C., Artaxo, P., Aufmhooff, H. Barbosa, H. M. J., Borrmann, S., Braga, R., Buchholz, B., Cecchini, M. A., Costa, A. Curtius, J., Dollner, M., Dorf, M., Dreiling, V., Ebert, V., Ehrlich, A., Ewald, F., Fisch, G., Fix, A., Frank, F., Füterer, D., Heckl, C., Heidelberg, F., Hünke, T., Jäkel, E., Järvinen, E., Jurkat, T., Kanter, S., Kästner, M., Kenntner, M., Kesselmeier, J., Klimach, T., Knecht, M., Kohl, R., Köling, T., Krämer, M., Krüger, M., Krisna, T. C., Lavric, J. V., Longo, K., Mahnke, C., Manzi, A. O., Mayer, B., Mertes, S., Minikin, A., Molleker, S., Münch, S., Nillius, B., Pfeilsticker, K., Pöhlker, C., Roiger, A., Rose, D., Rosenow, D., Sauer, D., Schneider, M., Schneider, J., Schulz, C., de Souza, R. A. F. Spanu, A., Stock, P., Vila, D., Voigt, C., Walser, A., Walter, D., Weigel, R., Weinzierl, B., Werner, F., Yamase, M. A., Ziereis, H., Zinner, T., and Zöger, M.: The ACRIDICON-CHUVA campaign: Studying tropical deep convective clouds and precipitation over Amazonia using the new German research aircraft HALO, Bull. Amer. Meteorol. Soc., 97, 1885-1908, https://doi.org/10.1175/BAMS-D-14-00255. 2016.
Whalley, L. K., Stone, D., Dunmore, R., Hamilton, J., Hopkins, J. R., Lee, J. D., Lewis, A. C., Williams, P., Kleffmann, J., Laufs, S., Woodward-Massey, R., and Heard, D. E.: Understanding in situ ozone production in the summertime through radical observations and modelling studies during the Clean air for London project (ClearfLo), Atmos. Chem. Phys., 18, 2547–2571, https://doi.org/10.5194/acp-18-2547-2018, 2018.

Whalley, L. K., Slater, E. J., Woodward-Massey, R., Ye, C., Lee, J. D., Squires, F., Hopkins, J. R., Dunmore, R. E., Shaw, M., Hamilton, J. F., Lewis, A. C., Mehra, A., Worrall, S. D., Bacak, A., Bannan, T. J., Coe, H., Percival, C. J., Ouyang, B., Jones, L., Crilley, L. R., Kramer, L. J., Bloss, W. J., Vu, T., Kotthaus, S., Grimmond, S., Sun, Y., Xu, W., Yue, S., Ren, L., Acton, W. J. F., Hewitt, C. N., Wang, X., Fu, P., and Heard, D. E.: Evaluating the sensitivity of radical chemistry and ozone formation to ambient VOCs and NOx in Beijing, Atmos. Chem. Phys., 21, 2125–2147, https://doi.org/10.5194/acp-21-2125-2021, 2021.

Wintel, J., Hösen, E., Koppmann, R., Krebsbach, M., Hofzumahaus, A., and Rohrer, F.: Stable carbon isotope ratios of toluene in the boundary layer and the lower free troposphere, Atmos. Chem. Phys., 13, 11059-11071, https://doi.org/10.5194/acp-13-11059-2013, 2013.

Zahn, A., Weppner, J., Widmann, H., Schlote-Holubek, K., Burger, B., Kühner, T., Franke, H.: A fast and precise chemiluminescence ozone detector for eddy flux and airborne application, Atmos. Meas. Tech., 5 (2), 363–375. https://doi.org/10.5194/amt-5-363-2012, 2012.

Zarzana, K. J., Min, K.-E., Washenfelder, R. A., Kaiser, J., Krawiec-Thayer, M., Peischl, J., Neuman, J. A., Nowak, J. B., Wagner, N. L., Dubè, W. P., St. Clair, J. M., Wolfe, G. M., Hanisco, T. F., Keutsch, F. N., Ryerson, T. B., and Brown, S. S.: Emissions of Glyoxal and Other Carbonyl Compounds from Agricultural Biomass Burning Plumes Sampled by Aircraft, Environ. Sci. Technol., 51, 11761–11770, https://doi.org/10.1021/acs.est.7b03517, 2017.

Ziereis, H., Minikin, A., Schlager, H., Gayet, J.F., Auriol, F., Stock, P., Baehr, J., Petzold, A., Schumann, U., Weinheimer, A., Ridley, B., and Ström, J.: Uptake of reactive nitrogen on cirrus cloud particles during INCA, Geophys. Res. Lett., 31(5), 2004.