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

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Abstract. In this study, airborne measurements of the sum of hydroperoxyl (HO_2) and organic peroxy (RO_2) radicals that react with NO to produce NO_2, i.e. RO_2^*, 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 (**E**ffect of **M**egacities on the transport and transformation of pollutants on the **R**egional to **G**lobal scal**e**s) project in Europe on-board the **H**igh **A**ltitude **Lo**ng range research aircraft (HALO). The on-board measurements of RO_2^* were made using the in-situ instrument **P**eroxy **R**adical **C**hemical **E**nhancement and **A**bsorption **S**pectrometer (PeRCEAS). RO_2^* 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 RO_2^* measurements agree reasonably well with radical production rates estimated using photolysis frequencies and RO_2^* precursor concentrations measured on-board. RO_2^* is primarily produced following the photolysis of ozone (O_3), formaldehyde (HCHO), glyoxal (CHOCHO), and nitrous acid (HONO) in the airmasses investigated. The suitability of **p**hotostationary **s**teady-**s**tate (PSS) assumptions to estimate the mixing ratios and the variability of RO_2^* during the airborne observations is investigated. The PSS assumption is robust enough to calculate RO_2^* mixing rations for most conditions encountered in air masses measured. The similarities and discrepancies between measured and calculated RO_2^* mixing ratios are analysed stepwise. The parameters, which predominantly control the RO_2^* mixing ratios under different chemical and physical regimes, are identified during the analysis. The dominant removal processes of RO_2^* in the airmasses measured up to 2000 m are the loss of OH and RO through the reaction with NO_x during the radical interconversion. Above 2000 m, $HO_2 - HO_2$ and $HO_2 - RO_2$ reactions dominate RO_2^* loss reactions. RO_2^* 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 RO_2^* through oxidation and photolysis of the OVOCs not measured during EMeRGe.

1. Introduction

Hydroperoxyl (HO_2) and organic peroxy (RO_2, 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, HO_2 and RO_2 take part in rapid
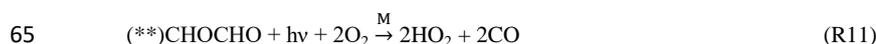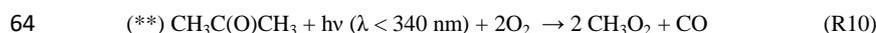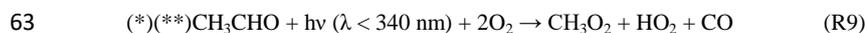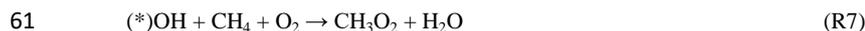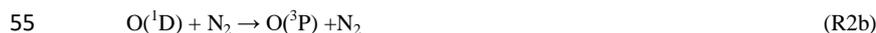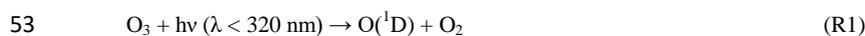
38 chemical processes that control the lifetime of many key trace constituents in the troposphere. Examples of key tropospheric

39 processes involving HO_2 and RO_2 are as follows:

40 • the catalytic cycles, which produce and destroy ozone (O_3)

41 • the generation of key inorganic acids, which are precursors of aerosol (e.g. sulphuric acid, H_2SO_4) and important

42 chemical constituents (e.g. nitric acid, HNO_3) in both summer and winter smog

43 • the generation of organic acids; the production of hygroscopic hydrogen peroxide (H_2O_2) and organic peroxides

44 (ROOH), which enter aerosol and cloud droplets

45 • the generation of organic peroxy nitrates (RO_2NO_2), peroxyacetyl nitrate ($CH_3COO_2NO_2$, PAN) and other summer
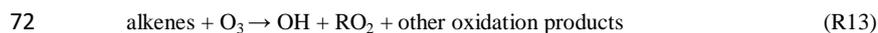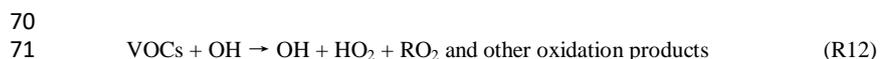
46 smog constituents.

47 The abundance of HO_2 and RO_2 in the free troposphere has a non-linear and complex dependency on photochemistry, initiated

48 by solar actinic radiation, and on the concentration of the precursors, such as carbon monoxide (CO), **v**olatile **o**rganic **c**ompounds

49 (VOCs), and peroxides. It also strongly depends on the amounts of nitrogen monoxide (NO) and nitrogen dioxide (NO_2) due to

50 the gas-phase reactions of NO and NO_2 with the OH and organic oxy (RO) radicals formed during the radical interconversion.

51 The main production and loss processes of HO_2 and RO_2 in the troposphere are summarised as follows:

52 a) Production processes of HO_2 and RO_2 through photolysis and oxidation by OH formed through photolysis
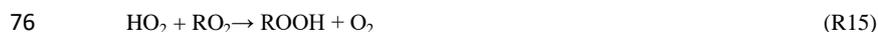
53 $\quad$ $O_3 + h\nu\ (\lambda < 320\ nm) \rightarrow O(^1D) + O_2$ $\qquad$ (R1)

54 $\quad$ $O(^1D) + H_2O \rightarrow 2OH$ $\qquad$ (R2a)

55 $\quad$ $O(^1D) + N_2 \rightarrow O(^3P) + N_2$ $\qquad$ (R2b)

56 $\quad$ $O(^1D) + O_2 \rightarrow O(^3P) + O_2$ $\qquad$ (R2c)

57 $\quad$ $HONO + h\nu\ (\lambda \leq 400\ nm) \rightarrow OH + NO$ $\qquad$ (R3)

58 $\quad$ $H_2O_2 + h\nu \rightarrow 2OH$ $\qquad$ (R4)

59 $\quad$ $OH + O_3 \rightarrow HO_2 + O_2$ $\qquad$ (R5)

60 $\quad$ $OH + CO + O_2 \rightarrow HO_2 + CO_2$ $\qquad$ (R6)

61 $\quad$ (*)$OH + CH_4 + O_2 \rightarrow CH_3O_2 + H_2O$ $\qquad$ (R7)

62 $\quad$ (**)$HCHO + h\nu\ (\lambda < 340\ nm) + 2O_2 \rightarrow 2HO_2 + CO$ $\qquad$ (R8)

63 $\quad$ (*)(**)$CH_3CHO + h\nu\ (\lambda < 340\ nm) + 2O_2 \rightarrow CH_3O_2 + HO_2 + CO$ $\qquad$ (R9)

64 $\quad$ (**) $CH_3C(O)CH_3 + h\nu\ (\lambda < 340\ nm) + 2O_2 \rightarrow 2\ CH_3O_2 + CO$ $\qquad$ (R10)

65 $\quad$ (**)$CHOCHO + h\nu + 2O_2 \xrightarrow{M} 2HO_2 + 2CO$ $\qquad$ (R11)

66 (*) The CH_3 produced from the oxidation of CH_4 or the photolysis of VOCs further reacts with O_2 to form CH_3O_2. The net reaction is written since the formation
67 of CH_3O_2 is much faster than the CH_3 formation due to the high amount of O_2 present in the atmosphere.
68 (**) H and CHO formed through the VOC photolysis further react with O_2 to form HO_2. The net reaction is written since the formation of HO_2 is much faster
69 than the H and CHO formation due to the high amount of O_2 present in the atmosphere.

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71 $\quad$ VOCs + OH → OH + HO$_2$ + RO$_2$ and other oxidation products $\qquad$ (R12)

72 $\quad$ alkenes + O$_3$ → OH + RO$_2$ + other oxidation products $\qquad$ (R13)

73

74 $\quad$ b) Loss processes of HO$_2$ and RO$_2$

75 $\quad$ HO$_2$ + HO$_2$ → H$_2$O$_2$ + O$_2$ $\qquad$ (R14)

76 $\quad$ HO$_2$ + RO$_2$ → ROOH + O$_2$ $\qquad$ (R15)

77 $\quad$ RO$_2$ + RO$_2$ → ROOH + R$_{C-1}$CHO + O$_2$ $\qquad$ (R16a)

78 $\quad$ OH + HO$_2$ → H$_2$O + O$_2$ $\qquad$ (R17)

79 $\quad$ OH + OH $\overset{M}{\rightarrow}$ H$_2$O$_2$ $\qquad$ (R18)

80 $\quad$ OH + NO $\overset{M}{\rightarrow}$ HONO $\qquad$ (R19)

81 $\quad$ OH + NO$_2$ $\overset{M}{\rightarrow}$ HNO$_3$ $\qquad$ (R20)

82 $\quad$ OH + HONO → H$_2$O + NO$_2$ $\qquad$ (R21)

83 $\quad$ RO + NO $\overset{M}{\rightarrow}$ RONO $\qquad$ (R22)

84 $\quad$ In addition, HO$_2$ and RO$_2$ undergo radical interconversion processes through the following reactions:

85 $\quad$ RO$_2$ + RO$_2$ → RO + RO + O$_2$ $\qquad$ (R16b)

86 $\quad$ HO$_2$ + NO → OH + NO$_2$ $\qquad$ (R23)

87 $\quad$ HO$_2$ + O$_3$ → OH + 2O$_2$ $\qquad$ (R24)

88 $\quad$ RO$_2$ + NO → RO + NO$_2$ $\qquad$ (R25)

89 $\quad$ RO + O$_2$ → R$_{H-1}$O + HO$_2$ $\qquad$ (R26)

90 $\quad$ R23 is one of the most important reactions in the troposphere as it leads to O$_3$ formation through R27 and R28.

91 $\quad$ Provided that there is sufficient insolation to ensure rapid photochemical processing and all species involved are known, the sum

92 $\quad$ of HO$_2$ and RO$_2$ that react with NO to produce NO$_2$ can be estimated from a **p**hotochemical **s**teady-**s**tate (PSS) assumption in

93 $\quad$ which production and loss mechanisms are equally important. The HO$_2$ + RO$_2$ concentrations and mixing ratios can be estimated

94 $\quad$ using the PSS assumption for NO$_2$ by considering the following reactions:

95 $\quad$ HO$_2$ + NO → OH + NO$_2$ $\qquad$ (R23)

96 $\quad$ RO$_2$ + NO + O$_2$ → R$_{H-1}$O + NO$_2$ + HO$_2$ $\qquad$ (R25 + R26)

97 $\quad$ NO$_2$ + hv (λ < 400 nm) → NO + O $\qquad$ (R27)

98    $O + O_2 \xrightarrow{M} O_3$ (R28)

99    $NO + O_3 \rightarrow NO_2 + O_2$ (R29)
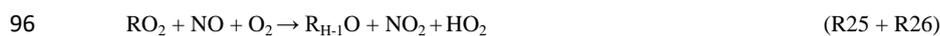
100   Assuming a PSS for NO_2, this leads to Eq. 1

101   $$[HO_2 + RO_2]_{PSS} = \frac{k_{NO+O_3}}{k_{NO+(HO_2+RO_2)}}\left(\frac{j_{NO_2}[NO_2]}{k_{NO+O_3}[NO]} - [O_3]\right)$$ (Eq.1)

102   where j_{NO_2} is the photolysis frequency of NO_2; k_{NO+O_3} (1.9×10^{-14} cm^3 molecules^{-1} s^{-1}) is the rate coefficient of the reaction of

103   NO with O_3 and $k_{NO+(HO_2+RO_2)}$ is the weighted average rate coefficient assumed for the reactions of peroxy radicals with NO.

104   The comparison of $[HO_2 + RO_2]_{PSS}$ calculated using Eq.1 with ground-based (e.g. Ridley et al., 1992; Cantrell et al., 1997;

105   Carpenter et al., 1998; Volz-Thomas et al., 2003), and airborne measurements, has shown in the past different degree of

106   agreement. The underestimations and overestimations found in air masses with different chemical compositions are not well

107   understood. In the case of airborne measurements, the PSS calculation generally overestimates that measured peroxy radicals

108   (Cantrell et al., 2003a, 2003b). The differences observed could not be attributed to systematic changes in NO, altitude, water

109   vapour and temperature, although these variables are often correlated.

110   Ground-based (Mihelcic et al., 2003; Kanaya et al., 2007, 2012; Elshorbany et al., 2012; Lu et al., 2012, 2013; Tan et al., 2017,

111   2018; Whalley et al., 2018, 2021; Lew et al., 2020) and airborne (Crawford et al., 1999; Tan et al., 2001; Cantrell et al., 2003b)

112   measurements have also been compared with model simulations of HO_2 and RO_2. The discrepancies encountered depend upon

113   the chemical composition of the air mass and the chemical mechanisms and constraints used in the model simulations. Tan et al.,

114   2019 and Whalley et al., 2021 reported experimental radical budget calculations based on the published reaction rate coefficients

115   of fundamental reactions (R1 to R26) controlling OH, HO_2 and RO_2 in the lower troposphere and ground-based measurements of

116   all relevant reactants and photolysis frequencies. In this study, a similar approach has been used to calculate the amount of

117   peroxy radicals in the air masses measured on-board of the **H**igh **A**ltitude **Lo**ng range (HALO) research aircraft over Europe

118   during the first campaign of the EMeRGe (**E**ffect of **Me**gacities on the transport and transformation of pollutants on the Regional

119   to Global scal**e**s) project. The available on-board measurements of RO_2^* are defined as the total sum of OH, RO and peroxy

120   radicals reacting with NO to produce NO_2 (i.e., $RO_2^* = OH + \sum RO + HO_2 + \sum RO_2$, where RO_2 are the organic peroxy radicals

121   reacting with NO to produce NO_2). Since the amount of OH and RO is much smaller, RO_2^* to a good approximation is the sum

122   of HO_2 and those RO_2 radicals that react with NO to produce NO_2. For the calculation, RO_2^* is assumed to be in PSS, and an

123   analytical expression is developed with a manageable degree of complexity to estimate the concentration and mixing ratios of

124   RO_2^*. The simultaneous on-board measurements of trace gases and photolysis frequencies are used to constrain the estimate of

125   the RO_2^* concentration.

126   In contrast to other experimental deployments, the concentrations and/or mixing ratios of the majority of the key species

127   involved in reactions R1 to R26 were continuously measured on-board HALO during the EMeRGe campaign. This minimises

128   the number of assumptions required for the calculations of RO_2^*. Consequently, this data set provides an excellent opportunity to

129   gain a deeper insight into the source and sink reactions of RO_2^* and the applicability of the PSS assumption for the different

130   pollution regimes and related weather conditions in the free troposphere.

131

2. EMeRGe field campaign in Europe

133 The overarching objective of the EMeRGe project is to test and improve the current understanding of the photochemical and

134 heterogeneous processing of pollution outflows from **m**ajor **p**opulation **c**entres (MPCs) and their impact on the atmosphere. Two

135 **i**ntensive **o**bservational **p**eriods (IOP) were carried out to investigate selected European and Asian MPC outflows. The European

136 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

137 and remote-sensing airborne measurements of trace gases and aerosol particles were made on-board the HALO aircraft (see

138 www.halo-spp.de) along flight tracks in the lower layers of the troposphere from northwest Europe to the Mediterranean region.

139 HALO carried out a total of 53 flight hours distributed over seven flights to investigate the chemical composition of the outflows

140 from the target MPCs: London, Paris, Benelux/ Ruhr metropolitan area, Po Valley, and urban agglomerations such as Rome,

141 Madrid, and Barcelona. The flight tracks are shown in Fig. 1. All HALO flights started from the HALO base at the DLR in

142 Oberpfaffenhofen, southwest of Munich, Germany. To achieve the scientific goals, 60 % of the flights were carried out below

143 3000 m. Vertical profiles of trace constituents were typically made in three stable flight levels upwind and downwind of the

144 target MPCs. The flights are named E-EU-FN, where E stands for EMeRGe, EU for Europe, and FN is the two-digit flight

145 number. More details about the EMeRGe IOP in Europe and the set of instruments deployed on-board the HALO aircraft are

146 described elsewhere (Andrés Hernández et al., 2021).
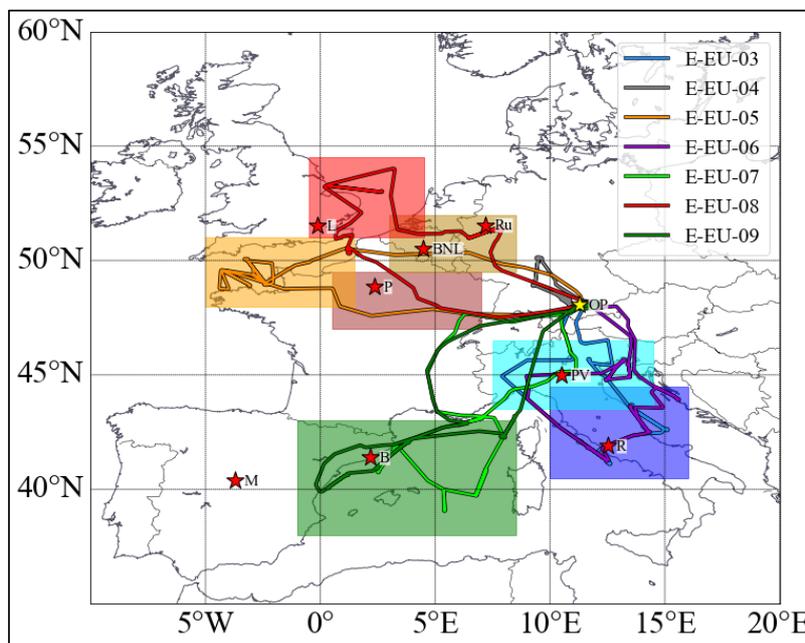
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148 Figure 1: The research flight tracks made by HALO during the EMeRGe-Europe campaign on 11, 13, 17, 20, 24, 26 and 28 July
149 2017 (E-EU-03 to E-EU-09, respectively, colour coded). MPC target areas are colour coded by shading, and the targeted
150 locations/regions are marked with red stars, M: Madrid, B: Barcelona, P: Paris, L: London; BNL: BeNeLux; Ru: Ruhr area; PV:
151 Po Valley, R: Rome. The location of the HALO base at the DLR in Oberpfaffenhofen, Germany (OP) is indicated by a yellow
152 star.

3. PeRCEAS and other instruments on-board

154 The RO_2^* measurements on-board the HALO research aircraft during EMeRGe were made using the **Pe**roxy **R**adical **C**hemical

155 **E**nhancement and **A**bsorption **S**pectrometer (PeRCEAS). PeRCEAS combines the **Pe**roxy **R**adical **C**hemical **A**mplification

156   (PeRCA) and **C**avity **R**ing-**D**own **S**pectroscopy (CRDS) techniques in a dual-channel instrument. Each channel has a separate

157   chemical reactor and detector, which operate alternatively in both background and amplification modes, i.e. without and with the

158   addition of CO, to account for the rapid background variations during airborne measurements. In the amplification mode, the

159   sum of the NO_2 produced from ambient RO_2^* through the chain reaction, the ambient NO_2, the NO_2 produced from the ambient

160   O_3 – NO reagent gas reaction and the NO_2 produced in the inlet from any other sources (e.g. thermal decomposition of PAN) is

161   measured. In the background mode, the sum of the ambient NO_2, the NO_2 produced from the ambient O_3 – NO reagent gas

162   reaction and NO_2 produced in the inlet from any other sources is measured. The RO_2^* is retrieved by dividing the difference in

163   NO_2 concentration (ΔNO_2) between amplification and background mode by the conversion efficiency of RO_2^* to NO_2, which is

164   referred to as eCL (**e**ffective **c**hain **l**ength). The PeRCEAS instrument and its specifications have been described in detail

165   elsewhere (Horstjann et al., 2014, George et al., 2020).

166   The two chemical reactors for sampling the ambient air are part of the **DU**al channel **A**irborne peroxy radical Chemica**l**

167   Amplifi**er** (DUALER) inlet installed inside a pylon located on the outside of the HALO fuselage. During the EMeRGe campaign

168   in Europe, a reagent gas mixing ratio of 30 ppmv NO ([NO] = 1.46×10^{14} molecules cm^{-3} at 296 K) and of 9 % CO ([CO] = 4.4

169    $\times 10^{17}$ molecules cm^{-3} at 296 K) were added to the sample flow for the chemical conversion of RO_2^* to NO_2. The DUALER inlet

170   was operated at an internal pressure of 200 mbar to achieve stable chemical conversion. The average eCL under these operational

171   conditions was determined to be 50 ± 8 from laboratory calibrations, where the error is the standard deviation estimated from the

172   reproducibility of the experimental determinations. The HO_2 and RO_2 detection sensitivity depends on the reagent gas NO

173   concentration due to the rate coefficient of reaction R22 being larger than that for R19. For the measurement conditions used

174   during the IOP in Europe, the ratio $\alpha = eCL_{CH_3O_2}/eCL_{HO_2}$ is 65% (George et al., 2020).

175   Although the DUALER pressure is kept constant below the ambient pressure, variations in dynamical pressure > 10 mbar during

176   the flight can change the residence time and induce turbulences inside the inlet (Kartal et al., 2010; George et al., 2020). These

177   may lead to different physical losses of radicals before amplification and affect the eCL. In the measurements presented in this

178   study, variations in dynamical pressure of this magnitude were only encountered during flight level changes of the aircraft. When

179   used during the analysis, these data sets are either excluded or flagged (P_flag). The effect of the ambient air humidity on eCL

180   (Mihele and Hastie, 1998; Mihele et al., 1999; Reichert et al., 2003) has been accounted for by a calibration procedure reported

181   in George et al. (2020).

182   In addition to the measurement of RO_2^* from PeRCEAS, other in-situ and remote-sensing measurements and basic aircraft data

183   from HALO are used in this study. Details of the corresponding instruments are summarised in Table 1. Concerning the data

184   obtained by the remote sensing instruments, the miniDOAS retrieves the Slant Column Density (SCD) of the target gas and a

185   scaling gas (O_4) towards the horizon at the flight altitude. From this, mixing ratios of the targeted gas within the line of sight is

186   estimated using RT modelling (Stutz et al., 2017; Hüneke et al., 2017; Kluge et al., 2020; Rotermund et al., 2021). The HAIDI

187   instrument retrieves SCDs below the aircraft. The SCDs from HAIDI are then converted to mixing ratios using the

188   corresponding geometric Air Mass Factor (AMF) under a well-mixed NO_2 layer assumption. As a result of this assumption, the

189   calculated mixing ratios for HAIDI target gases are lower limits and close to the actual values while flying within and close to a

190   well-mixed boundary layer. Despite the differences in sampling volume and temporal and spatial resolution in the in-situ and

191   remote sensing measurement techniques, the concentration of common and related species obtained are in reasonable agreement

192   (Schumann, 2020).

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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: Flugexperimente.

Trace gas-in situ measurements				
Species/parameters	Acronym	Institution	Technique/Instrument	Reference
$RO_2^* = HO_2 + \sum RO_2$	PeRCEAS	Univ. Bremen	PeRCA + CRDS	George et al., 2020
OVOC	HKMS	KIT Karlsruhe	PTR-MS	Brito and Zahn, 2011
O_3	FAIRO	KIT Karlsruhe	UV-Photometry/ Chemiluminescence	Zahn et al., 2012
O_3, CO	AMTEX	DLR-IPA	UV-Photometry/ VUV-Fluorimetry	Gerbig et al., 1996
NO, NO_y	AENEAS	DLR-IPA	Chemiluminescence/ Gold converter	Ziereis et al., 2004
CO_2, CH_4	CATS	DLR-IPA	CRDS	Chen et al., 2010
Trace gas- remote sensing measurements				
Species/parameters	Acronym	Institution	Technique/Instrument	Reference
NO_2, HONO, CH_2O, $C_2H_2O_2$, $C_3H_4O_2$	miniDOAS	Univ. Heidelberg	DOAS / UV-nIR; 2D optical spectrometer	Hüneke et al., 2017
NO_2	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 RO_2^* measurements during EMeRGe in Europe

RO_2^* mixing ratios up to 120 pptv were measured during the campaign, as shown in Fig. 2. Typically, the highest RO_2^* mixing ratios were observed below 3000 m over Southern Europe. This is attributed to the higher insolation and temperatures favouring the rapid production of RO_2^* from the photochemical oxidations of CO and VOCs.
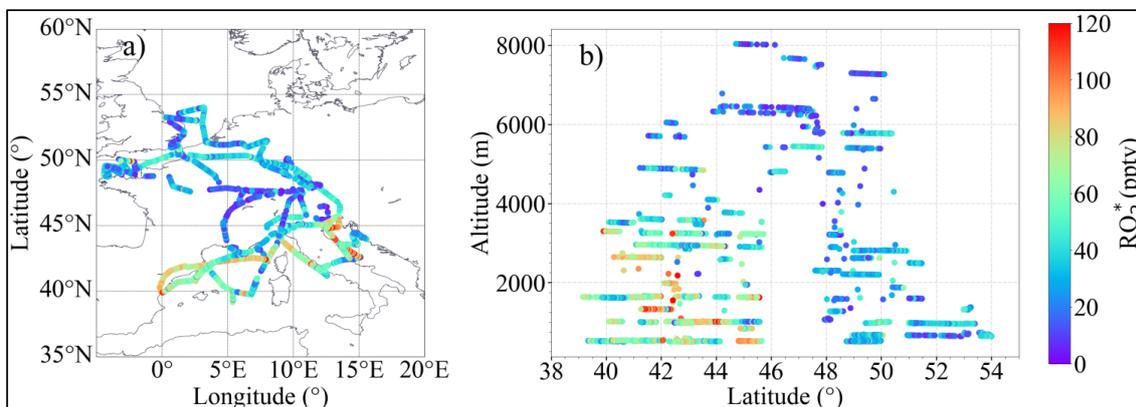
Figure 2: RO_2^* measured during EMeRGe-Europe: a) as a function of longitude and latitude, b) as a function of latitude and altitude.

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.

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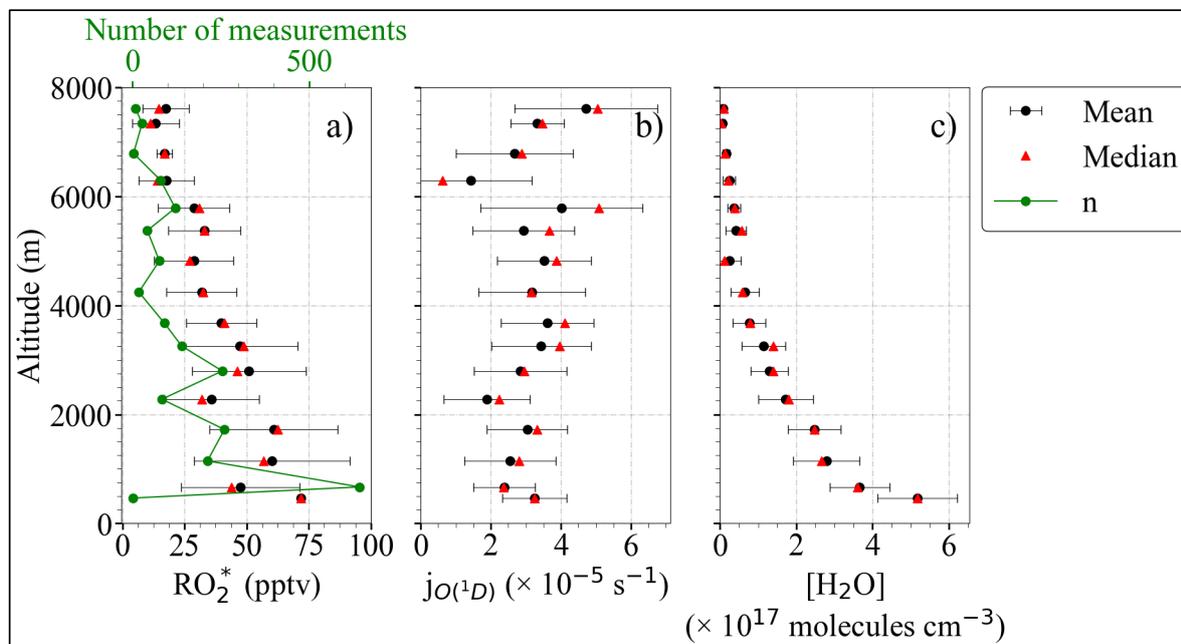
Figure 3: Composite average vertical profiles of a) RO_2^*, b) $j_{O(^1D)}$ and c) $[H_2O]$ observations. The measurements are binned over 500 m altitude. The error bars are the standard errors (i.e. $\pm 1\sigma$ standard deviation of each bin). Median values (red triangles) and the number of individual measurements, n, for each bin (in green) are additionally plotted.

Differences between mean and median values indicate less RO_2^* 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 RO_2^* precursors. HALO flew at the lowest altitudes over the English Channel, the Mediterranean and the North Sea. The H_2O concentration in the air masses decreases steadily with altitude as expected. The higher relative variability in H_2O observed at 3000 m and the increase at 5000 m is associated with measurements under stormy conditions, often over the Alps.

4.2. RO_2^* production rates

The total production rate of OH and RO_2^* ($P_{OH+HO_2+RO_2}$) can be estimated from the reactions R1 to R13 as follows:

$$P_{OH+HO_2+RO_2} = 2jO_D^1[O_3] \frac{k_{O_D^1+H_2O}[H_2O]}{k_{O_D^1+H_2O}[H_2O]+k_{O_D^1+O_2}[O_2]+k_{O_D^1+N_2}[N_2]} + j_{HONO}[HONO] + 2j_{H_2O_2}[H_2O_2] + 2\sum_i j_i[OVOC_i] +$$

$$\sum_j k_{OH+VOC_j}[OH][VOC_j] + \sum k_{O_3+alkenes_k}[O_3][alkenes_k] \qquad (Eq. 2)$$

In this work, Eq. 2 has been applied to the measurements taken within the EMeRGe campaign in Europe. There were no H_2O_2 measurements available for EMeRGe IOP. However, from the results reported by Tan et al. (2001), the OH production from the H_2O_2 photolysis become significant at low NO_x conditions. Since the $[NO_x] > 8 \times 10^{12}$ molecules cm^{-3} for 60 % of the measurements during the IOP, as a first approximation, the production of OH from H_2O_2 photolysis is assumed to be negligible for the dataset considered in this study. Similarly, the VOC photolysis was assumed to dominate the RO_2^* production over the oxidation by OH and ozonolysis of alkenes. The most abundant and reactive oxygenated volatile organic compounds (OVOCs)

239 measured have been taken as a surrogate for the sum of VOCs. These assumptions lead to Eq. 3, which estimates the RO_2^*

240 production rate ($P_{RO_2^*}$) as:

241 $P_{RO_2^*} = 2j_{O(^1D)}[O_3] \dfrac{k_{O_D^1 + H_2O}[H_2O]}{k_{O_D^1 + H_2O}[H_2O] + k_{O_D^1 + O_2}[O_2] + k_{O_D^1 + N_2}[N_2]} + j_{HONO}[HONO] + 2j_{HCHO}[HCHO] + 2j_{CH_3CHO}[CH_3CHO] +$

242 $2j_{CH_3C(O)CH_3}[CH_3C(O)CH_3] + 2j_{CHOCHO}[CHOCHO]$ (Eq.3)

243 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

244 dividing with the air concentration at each altitude, estimated from the pressure and temperature measurements. Figure 4 shows

245 the composite averaged vertical profile of all measured RO_2^* mixing ratios colour-coded with the estimated $P_{RO_2^*}$. Small circles

246 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

247 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

248 steps. The error bars are the standard errors for each altitude bin. For the sake of representativeness and comparability, the

249 number of measurements in each altitude bin is shown in Fig. 4b. Higher RO_2^* mixing ratios observed below 4000 m are

250 typically associated with $P_{RO_2^*} \geq$ 0.4 pptv s⁻¹. Above 4000 m both $P_{RO_2^*}$ and RO_2^* start to decrease with altitude, as expected. This

251 is related to the decrease in H_2O and other radical precursor concentrations with altitude, as detailed in Fig. 5 and Fig. 6. In

252 previous airborne campaigns at various parts of the world, RO_2^* vertical distributions showed a local maximum between 1500

253 and 4000 m, as reported by Tan et al. (2001), Cantrell et al. (2003a, 2003b), and Andrés-Hernández et al. (2009). In the present

254 work, this local maximum is more evident for measurements with $P_{RO_2^*} \geq$ 0.5 pptv s⁻¹.
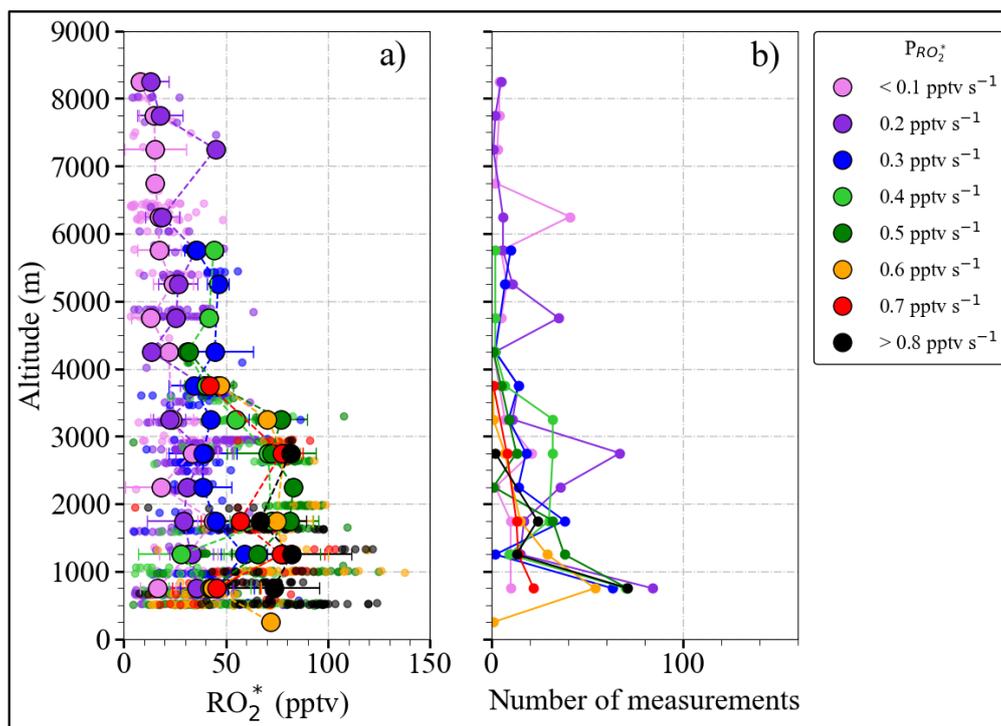
255

256 Figure 4: a) Composite averaged vertical distribution of measured RO_2^* colour-coded according to the value of $P_{RO_2^*}$, b) the

257 number of measurements in each altitude bin. Small circles are 1-minute individual measurements binned with $P_{RO_2^*}$ values in

258 0.1 ppts⁻¹ intervals. Larger circles result from a further binning over 500 m altitude steps. All the production rates below 0.1 pptv

259 s⁻¹ and above 0.8 pptv s⁻¹ are binned to 0.1 pptv s⁻¹ and 0.8 pptv s⁻¹, respectively.

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260   Figure 5 shows the fractional contribution of the production rate from each radical precursor reaction included in Eq. 3 as a
261   function of altitude. The data are classified into three groups according to the rate of change of production of the RO_2^* mixing
262   ratio $P_{RO_2^*} < 0.07$ pptv s^{-1} (5a), $0.07 < P_{RO_2^*} < 0.8$ pptv s^{-1} (5b), and $P_{RO_2^*} > 0.8$ pptv s^{-1} (5c) to show the lowest, most common,
263   and highest ranges, respectively, encountered during the IOP. For 89 % of the measurements, $0.07 < P_{RO_2^*} < 0.8$ pptv s^{-1} applies,
264   while the rest of the data are equally distributed in the other two $P_{RO_2^*}$ ranges. The data in each group are always binned over 500
265   m when available.

266   Typically, the high amount of H_2O in the air masses probed results in the O_3 photolysis and subsequent reaction of O^1D with
267   H_2O (R1-R2a) and is the highest RO_2^* radical production rate ($\geqslant$ 50 %) below 4000 m. As the amount of H_2O reduces with
268   altitude, the relative contribution from O_3 photolysis decreases. Above 4000 m, HCHO, HONO, and CHOCHO photolysis
269   contributions range between 20 % to 40 %, 2.5 % to 30 %, and 5 % to 25 %, respectively. The HCHO contribution increases up
270   to 80% during measurements above 6000 m. The contributions of CH_3CHO and $CH_3C(O)CH_3$ photolysis are, in contrast,
271   practically negligible (< 5 %).

272   The vertical changes of the precursor mixing ratios and photolysis frequencies used to calculate $P_{RO_2^*}$ in Fig. 5 are shown in Fig.
273   6a to 6f. $P_{RO_2^*} < 0.07$ pptv s^{-1} is associated with measurements under cloudy conditions, towards sunset where the photolysis
274   frequencies are low, or at altitudes above 5000 m in air masses with a low amount of RO_2^* precursors. $P_{RO_2^*} > 0.8$ pptv s^{-1} are
275   found for air masses, measured below 2000 m in the outflow of MPCs over the sea, for conditions having sufficient insolation
276   ($j_{O(^1D)} > 3 \times 10^{-5}$ S^{-1}) and a high content of RO_2^* precursors (HCHO > 1000 pptv and HONO >100 pptv). The increase in the
277   photolysis frequencies as a function of altitude is concurrent with decreases in precursor concentrations. As a result, the $P_{RO_2^*}$ do
278   not significantly vary with altitude in the air masses investigated.

279   In previous airborne campaigns, Tan et al. (2001) and Cantrell et al. (2003b) reported a reduction of the fractional contribution of
280   the reaction of $O(^1D)$ with H_2O as the $P_{RO_2^*}$ value decreases. At very low $P_{RO_2^*}$ values (< 0.03 pptv s^{-1}), the sum of all other
281   production terms exceeded the fraction from the $O(^1D) + H_2O$ term. For these conditions, H_2O_2 and VOCs photolysis dominated
282   the $P_{RO_2^*}$. In the case of the EMeRGe data set in Europe, only 6 % of $P_{RO_2^*}$ are below 0.06 pptv s^{-1}.

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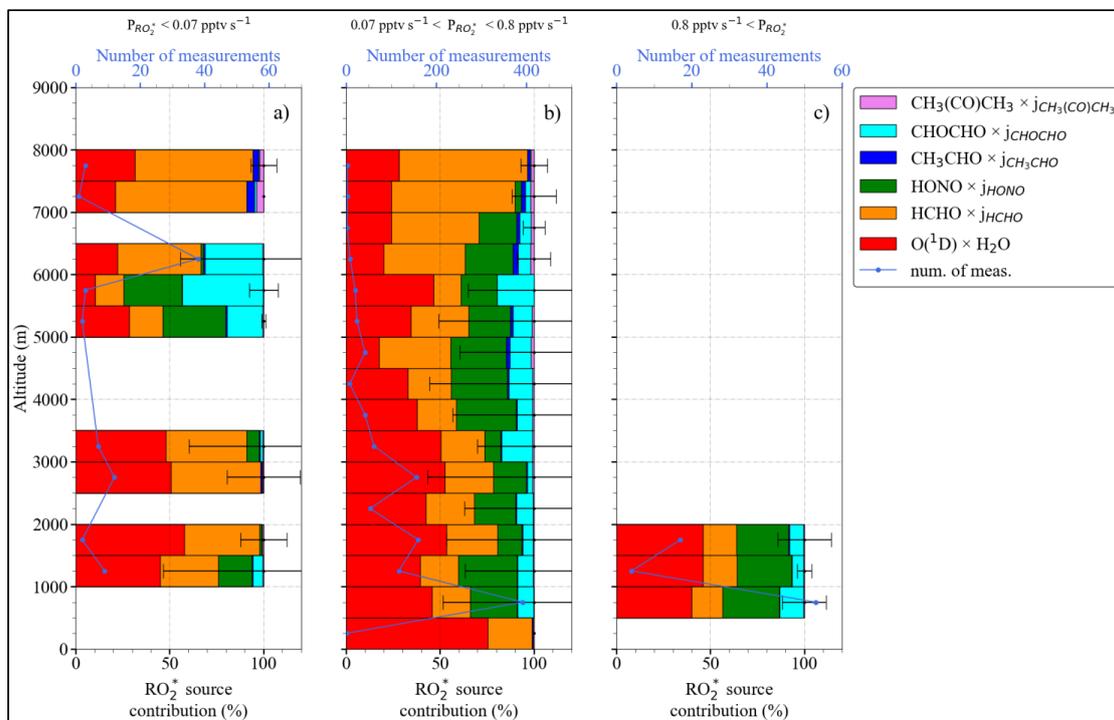
Figure 5: Total $P_{RO_2^*}$ and fractional precursor contributions estimated using Eq. 5 as a function of altitude, for: a) $P_{RO_2^*} < 0.07$ pptv s^{-1}, b) 0.07 pptv s^{-1} < $P_{RO_2^*}$ < 0.8 pptv s^{-1}, and c) $P_{RO_2^*} > 0.8$ pptv s^{-1}. Note the different scales in the number of measurements.
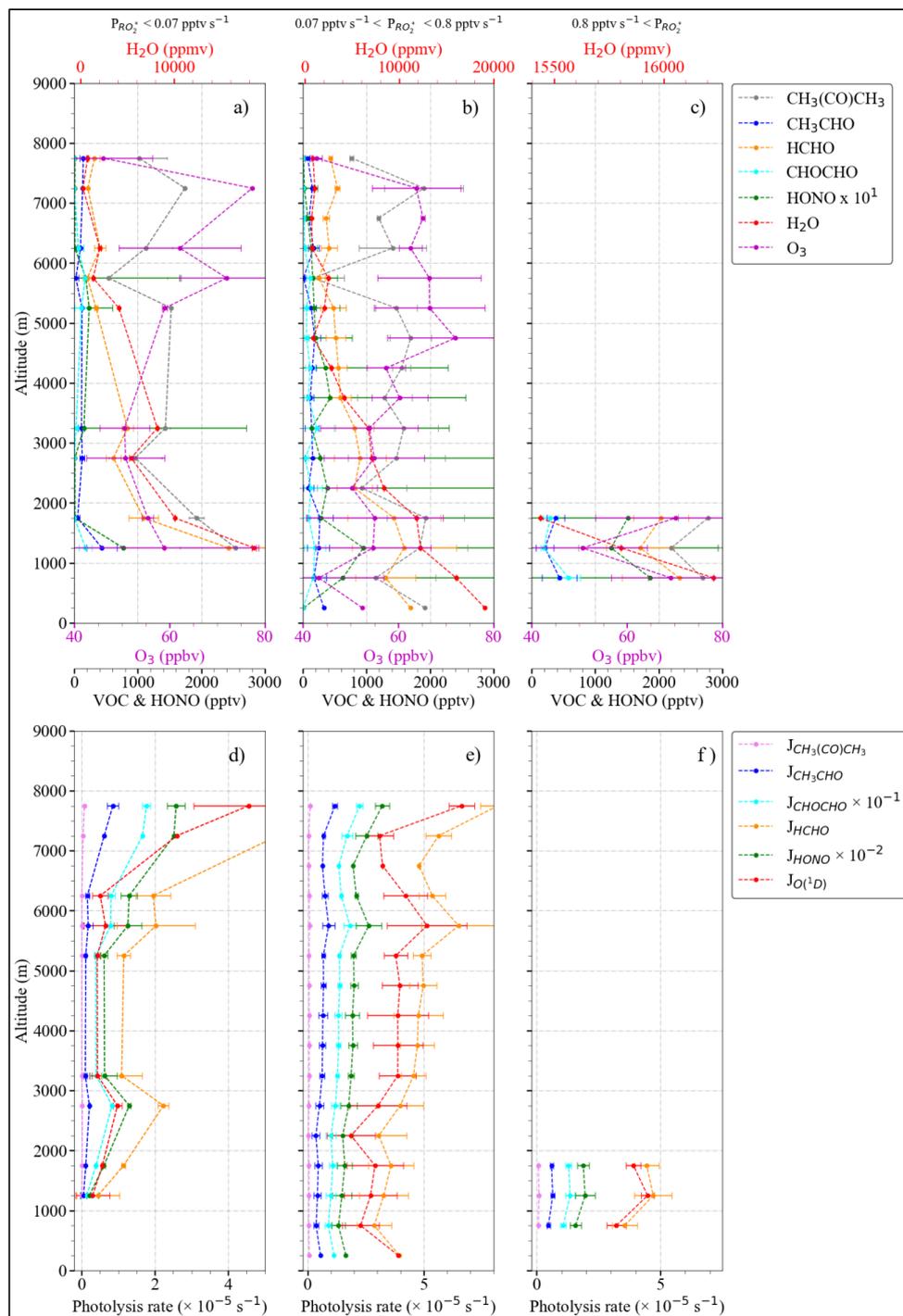
Figure 6: Vertical distribution and variation of a) to c) precursor mixing ratios; d) to f) photolysis frequencies for the $P_{RO_2^*}$ bins as in Fig. 5. Note the different scales in the H_2O concentration

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4.3. PSS estimation of RO_2^* mixing ratios

291

292 Under most ambient conditions in the troposphere, the RO_2^*, which to a first approximation is the sum of HO_2 and RO_2, are

293 short-lived, and the chemical lifetime of RO_2^* is much shorter than the chemical transport time into and out of an air mass being

294 probed. Consequently, pseudo-steady-state conditions prevail, and the radical production and loss rates are balanced:

295

296 $P_{HO_2+RO_2} = L_{HO_2+RO_2}$ (Eq.4)

297 If the interconversion reactions between OH, RO, HO_2 and RO_2 (R5 to R7, R12, R16b, and R23 to R26) occur without losses,

298 then the radical number concentrations are calculated by solving Eq. 4. If the $RO_2^* - RO_2^*$ reactions are assumed to be the

299 dominant radical loss processes, Eq. 4 leads to Eq. 5.

$$2j_{O(^1D)}[O_3]\frac{k_{O_D^1+H_2O}[H_2O]}{k_{O_D^1+H_2O}[H_2O] + k_{O_D^1+O_2}[O_2] + k_{O_D^1+N_2}[N_2]} + j_{HONO}[HONO] + 2j_{HCHO}[HCHO] + 2j_{CH_3CHO}[CH_3CHO]$$
$$+ 2j_{CH_3C(O)CH_3}[CH_3C(O)CH_3] + 2j_{CHOCHO}[CHOCHO] = k_{RO_2^*+RO_2^*}[RO_2^*]^2$$

300 (Eq. 5)

301 where $k_{RO_2^*+RO_2^*}$ is the effective RO_2^* self-reaction rate coefficient, which is defined as the weighted average rate coefficient

302 between $HO_2 - HO_2$, $HO_2 - RO_2$ and $RO_2 - RO_2$ reactions.

303 Consequently, the RO_2^* concentrations are expected to correlate with the square root of the $P_{RO_2^*}$.

304 Figure 7 shows the relationship between the measured $[RO_2^*]$ and the estimated $\sqrt[2]{P_{RO_2^*}}$. Generally, both $[RO_2^*]$ and $\sqrt[2]{P_{RO_2^*}}$

305 increase with the photolysis frequency of O_3 ($j_{O(^1D)}$). The $[RO_2^*] < 0.5 \times 10^{12}$ molecules cm⁻³ and $\sqrt[2]{P_{RO_2^*}} < 1000$ with $j_{O(^1D)} > 5$

306 $\times 10^{-5}$ belong to the measurements made above 6000 m, where the amount of RO_2^* precursors is low. The relatively weak

307 correlation observed between $[RO_2^*]$ and $\sqrt[2]{P_{RO_2^*}}$ indicates the presence of other radical loss processes and/or missing production

308 terms in the $P_{RO_2^*}$ calculation. Apart from this, the spread in the diagram confirms that the effective RO_2^* self-reaction rate

309 $k_{RO_2^*+RO_2^*}[RO_2^*]^2$ varies widely in the air masses probed due to the effect of changes in HO_2 and $\sum RO_2$ concentrations in the

310 individual loss reaction rate coefficients. As mentioned in section 4.1, photochemical processing was expected to be enhanced

311 over Southern Europe due to the prevailing high insolation and temperatures during the measurements. This is also reflected in

312 the higher $P_{RO_2^*}$ and $[RO_2^*]$ observed in Southern Europe as compared to those in Northern Europe (Fig. 7b).
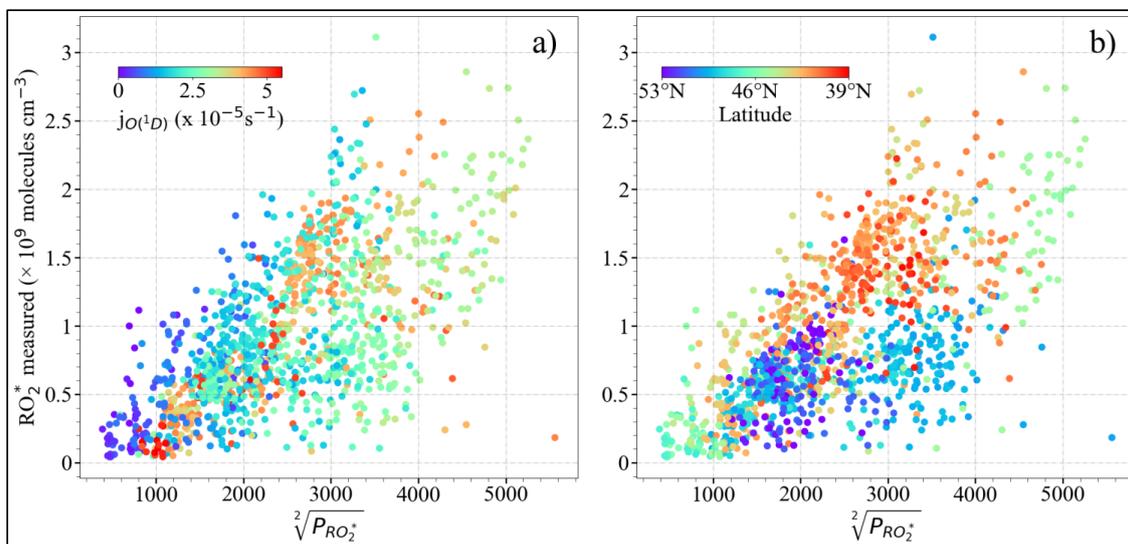
313

314 Figure 7: Plot of the measured $[RO_2^*]$ versus estimated $\sqrt[2]{P_{RO_2^*}}$ colour-coded for values of a) $j_{O(^1D)}$ and b) latitude.

315 The correlation between $[RO_2^*]$ and $\sqrt[2]{P_{RO_2^*}}$ improves when the measurements south and north of 47°N are separately analysed

316 (Fig. 8). For a given $[RO_2^*]$, the $P_{RO_2^*}$ calculated is higher for the measurements north of 47°N than south of 47°N. The lowest

317 $[RO_2^*]$ to $\sqrt[2]{P_{RO_2^*}}$ ratios are associated with higher NO_x (NO + NO_2), especially north of 47°N, indicating the urban character and

318 higher content in RO_2^* precursors of the air probed (Fig. 8d). Note that these results are only valid for the data set acquired over

319 Europe during EMeRGe and do not yield a relationship between $[RO_2^*]$ and $\sqrt[2]{P_{RO_2^*}}$, which is generally applicable for these two

320 latitude windows.
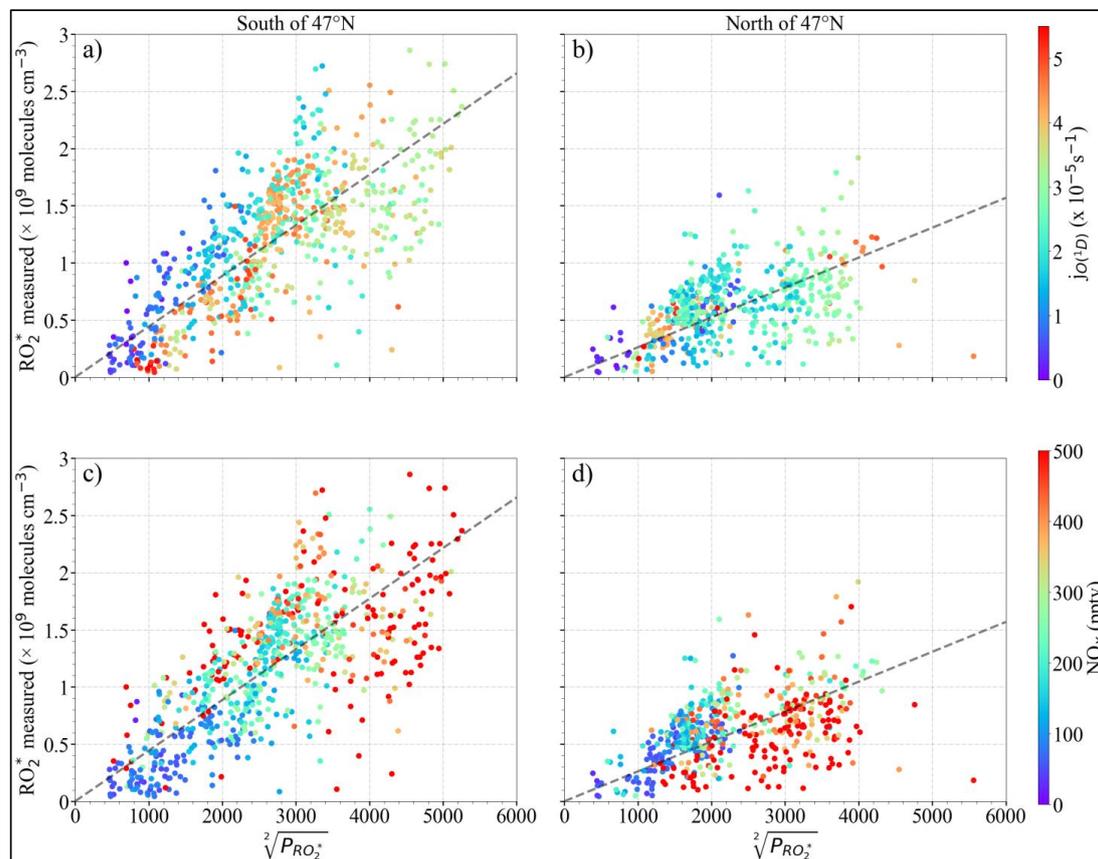
Figure 8: Plots of the measured $[RO_2^*]$ vs $\sqrt[2]{P_{RO_2^*}}$ for the following latitudes: a) and c) south of 47°N; b) and d) north of 47°N. Note that a) and b) are colour-coded with $j_{O(^1D)}$; c) and d) are colour-coded by NO_x mixing ratio. The dashed lines indicate the linear fit for visual support.

The relationship between RO_2^* and $P_{RO_2^*}$ is further investigated to identify the dominant RO_2^* 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 RO_2^* by the PeRCEAS instrument. So, the effect of changes in the HO_2 to the total RO_2^* ratios, represented by δ, i.e., $[HO_2] = δ[RO_2^*]$ and $[CH_3O_2] = (1- δ) [RO_2^*]$, is investigated. As a first approach, CH_3O_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:

$$2j_1[O_3]β + j_3[HONO] + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = 2k_{15}δ(1 - δ)[RO_2^*]^2 + 2k_{16a}((1 - δ)[RO_2^*])^2 + 2k_{14}(δ[RO_2^*])^2 \qquad \text{(Eq. 6)}$$

where β is the effective yield of OH production in the reaction of $O(^1D)$ with H_2O given by:

$$β = \left(\frac{k_{2a}[H_2O]}{k_{2a}[H_2O] + k_{2b}[O_2] + k_{2c}[N_2]}\right)$$

From Eq. 6, $[RO_2^*]$ can be calculated as

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335 $$[RO_2^*] = \sqrt[2]{P_{RO_2^*}/2k_{RO_2^*}}$$ (Eq. 7)

336 where

337 $$k_{RO_2^*} = (k_{15}\delta(1-\delta) + k_{16a}(1-\delta)^2 + k_{14}\delta^2)$$

$$P_{RO_2^*} = 2j_1[O_3]\beta + j_3[HONO] + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO]$$

338 The second solution gives negative values for $[RO_2^*]$, therefore has no physical meaning. A more detailed derivation of Eq. 6 and

339 Eq. 7 are given in the supplementary information.

340 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-

341 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.

342 $RO_2^* = HO_2$ 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

343 determined in laboratory experiments, as reported by George et al. (2020). The small circles represent 1-minute $RO_{2\,m}^*$, whereas

344 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

345 loss processes considered, $RO_{2\,c}^*$ reasonably agrees with $RO_{2\,m}^*$ as indicated by the fit parameters (Table 2). $RO_{2\,c}^*$ often

346 overestimates $RO_{2\,m}^*$ for NO mixing ratios above 250 pptv. The overestimation is also evident for $RO_{2\,m}^*$ below 40 pptv. This

347 may be due to the HO and RO losses during the radical interconversion by reacting with NO_x producing HONO, HNO_3 and
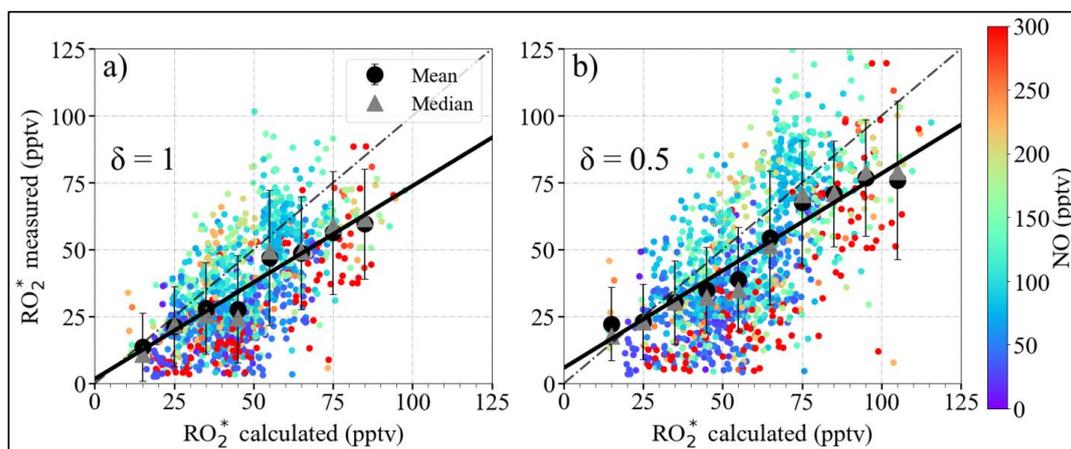
348 organic nitrate.

349

350 Figure 9: RO_2^* measured ($RO_{2\,m}^*$) versus PSS RO_2^* calculated ($RO_{2\,c}^*$) using Eq. 7 for a) $\delta = 1$, b) $\delta = 0.5$ by assuming only RO_2^*
351 – 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),
352 and the median of each bin (grey triangles) are shown. The error bars indicate the standard error of each bin. The linear
353 regression for the binned values (solid line) and the 1:1 relation (dashed line) are also plotted for reference. The fit parameters
354 are given in Table 2.

355 The PSS data presented in Fig, 9 are calculated assuming interconversion reactions between OH, RO and RO_2^* occur without

356 losses and the limiting case of $[OH] \lll [HO_2 + RO_2]$ in the case of a low amount of NO and NO_2. Furthermore, VOC oxidation

357 processes are not considered as a source of radicals. To identify other major loss processes, Eq. 6 is extended with radical

358 conversion reactions between oxy and peroxy radicals and OH and RO losses through HONO, HNO_3, and organic nitrate

359   formation. In the resulting Eq. 8, CH_4, HCHO, CH_3CHO, CHOCHO, CH_3OH, and $CH_3C(O)CH_3$ measured on-board HALO are

360   taken as surrogates for the dominant VOC acting as RO_2^* precursors through oxidation:

361    $(2j_1[O_3]\beta + j_3[HONO])(1-\rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] =$

362    $\delta[RO_2^*](k_{23}[NO] + k_{24}[O_3])\rho + \left(2k_{16b}((1-\delta)[RO_2^*])^2 + k_{25}(1-\delta)[RO_2^*][NO]\right)\left(\frac{k_{22}[NO]}{(k_{22}[NO]+k_{26}[O_2])}\right) + 2k_{15}\delta(1-$

363    $\delta)[RO_2^*]^2 + 2k_{16a}\left((1-\delta)[RO_2^*]\right)^2 + 2k_{14}(\delta[RO_2^*])^2$ (Eq. 8)

364   where β is the OH production efficiency of the O_3 photolysis and δ is the HO_2 to RO_2^* ratio as in Eq. 6, ρ is the OH loss during

365   the OH – RO_2^* interconversion. As in Eq. 6, CH_3O_2 is taken as a surrogate for all RO_2. The detailed derivation of Eq. 8 is given

366   in the supplementary information.

367   During the IOP in Europe, HCHO and CH_3CHO are the dominant radical precursors from OVOC oxidations. Their impact on

368   the radical budget is similar because their respective concentrations compensate the difference in the rate coefficients of their

369   reactions with OH ($k_{OH+HCHO} = 8.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and $k_{OH+CH_3CHO} = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}). Despite the

370   high mixing ratios measured, $CH_3C(O)CH_3$ is a less important source of RO_2^*. This is because the rate coefficient

371    $k(T)_{OH+CH_3C(O)CH_3}$ is significantly slower than $k_{OH+HCHO}$ and k_{OH+CH_3CHO} (see Table S1 in the supplement). Similarly, the

372   RO_2^* production rate of CHOCHO and CH_3OH through oxidation is an order of magnitude lower than that of HCHO and

373   CH_3CHO. Since $k_{HO_2+O_3}$ is almost four orders of magnitude smaller than k_{HO_2+NO} and the NO concentrations remained about

374   three orders of magnitude smaller than the O_3 measured, the HO_2 reaction with O_3 had a negligible effect in Eq. 8.

375   The impact of the methylglyoxal ($CH_3C(O)C(O)H$) photolysis was also investigated by using the $CH_3C(O)C(O)H^*$

376   measurements provided by the miniDOAS instrument. The $CH_3C(O)C(O)H^*$ measured is the sum of $CH_3C(O)C(O)H$, and a

377   fraction of other substituted dicarbonyls (mainly 2,3-butanedione, $C_3H_6O_2$), with similar visible absorption spectra. For the

378   calculation, $CH_3C(O)C(O)H$ was assumed to be half of $CH_3C(O)C(O)H^*$ as recommended by Zarzana et al. (2017) and Kluge et

379   al. (2020). The RO_2^* calculated by including $CH_3C(O)C(O)H$ photolysis systematically overestimated the measurements. Since

380   the adequacy of the recommended factor of 0.5 varies with the actual air mass composition, $CH_3C(O)C(O)H$ was not included in

381   the calculations.

382   The revised PSS $[RO_2^*]$ is then calculated from Eq. 8, as:

383    $[RO_2^*] = \dfrac{-\left(-L_{RO_2^*}\right) - \sqrt[2]{L_{RO_2^*}^2 - 4\left(-2k_{RO_2^*}\right)P_{RO_2^*}}}{2\left(-2k_{RO_2^*}\right)}$ (Eq. 9)

384   where

385    $k_{RO_2^*} = \left(\left(k_{16b}\left(\frac{k_{22}[NO]}{(k_{22}[NO]+k_{26}[O_2])}\right)\right) + k_{16a}\right)(1-\delta)^2 + k_{15}\delta(1-\delta) + k_{14}\delta^2\right)$

$L_{RO_2^*} = \left(\delta(k_{23}[NO] + k_{24}[O_3])\rho + \left(\frac{k_{22}[NO]}{(k_{22}[NO]+k_{26}[O_2])}\right)k_{25}(1-\delta)[NO]\right)$

$P_{RO_2^*} = (2j_1[O_3]\beta + j_3[HONO])(1-\rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO]$

386   Applying Eq. 9 to the measured dataset reduces the overestimation of $RO_{2\ m}^*$ by $RO_{2\ c}^*$ at NO mixing ratios higher than 250 pptv

387   (Fig. 10), especially for $RO_{2\ m}^* < 40$ pptv but does not introduce significant changes in the overall correlations (Table 2). As in

388   Fig. 9, plots of the 1-minute $RO_2^*{}_m$ and the average of $RO_2^*{}_m$ binned over 10 pptv $RO_2^*{}_c$ intervals versus $RO_2^*{}_c$ are depicted for δ

389   = 1 and δ = 0.5 in Fig. 10. The RO_2^* data are colour-coded with the on-board NO measurements. The linear regression slopes are

390   around 0.7 (R^2= 0.96), indicating an overall 25 – 30 % underestimation of the $RO_2^*{}_m$. However, the $RO_2^*{}_m$ are mostly

391   overestimated 4000 m under low insolation and underestimated in polluted plumes measured below 2000 m with NO mixing

392   ratios approximately above 50 pptv (see Fig. 11 for δ = 0.5). The y-axis intercept is below the instrumental detection limit for

393   most measurement conditions.

394   Table 2: Linear regression parameters from $RO_2^*{}_m$ versus $RO_2^*{}_c$ using Eq. 7 and Eq. 9 from Fig. 9 and Fig.10, respectively.

Formula used to calculate RO_2^*	δ	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
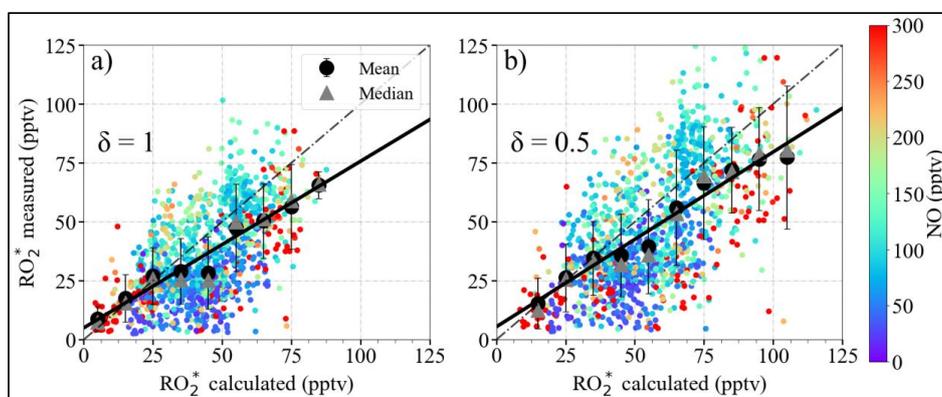
395

396 Figure 10: $RO_2^*{}_m$ versus $RO_2^*{}_c$ calculated using Eq. 9 for a) δ = 1 and b) δ = 0.5. The data are colour-coded with the measured
397 NO mixing ratios. The 1-minute (small circles), the mean of the binned $RO_2^*{}_m$ over 10 pptv $RO_2^*{}_c$ intervals (large circles), and
398 the median of each bin (grey triangles) are shown. The error bars indicate the standard error of each bin. The linear regression for
399 the binned values (solid line) and the 1:1 relation (dashed line) are also depicted for reference.

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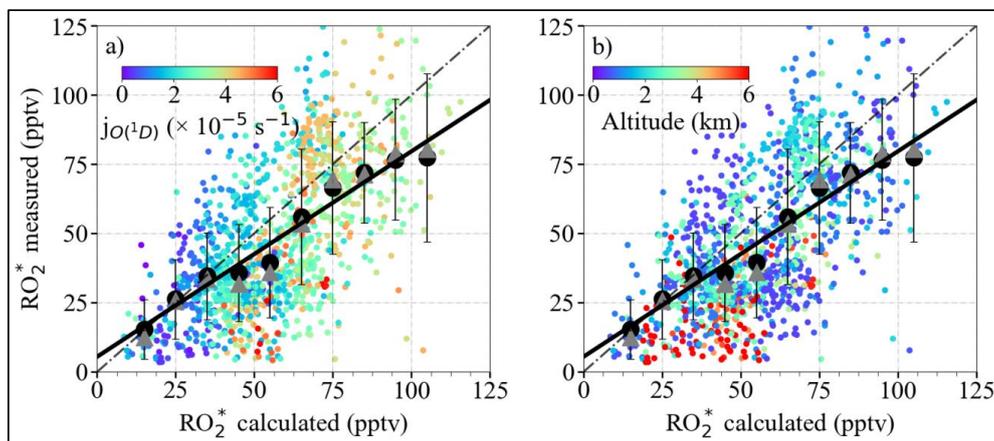
Figure 11: $RO_2^*{}_m$ versus $RO_2^*{}_c$ calculated using Eq. 9 for $\delta = 0.5$. The data points are colour-coded for a) photolysis frequency of O_3; b) altitude. The 1-minute (small circles), the mean of the binned $RO_2^*{}_m$ over 10 pptv $RO_2^*{}_c$ intervals (large circles), and the median 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 depicted for reference.

Figure 12 shows the data for $\delta = 0.5$ colour-coded with NO, NO_x, the sum of HCHO, CH_3CHO, CHOCHO, CH_3OH, and $CH_3C(O)CH_3$ (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 $RO_2^*{}_m$ and $RO_2^*{}_c$ is observed for the bins around 50 pptv. The $RO_2^*{}_m < 25$ pptv observed above 4000 m are overestimated for air masses with low insolation, i.e. $j_{O(^1D)} < 2 \times 10^{-5}$ s^{-1} (Fig. 11), NO < 50 pptv, $\sum VOCs$ 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_2O_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 $RO_2^*{}_m$ 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_2O 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).

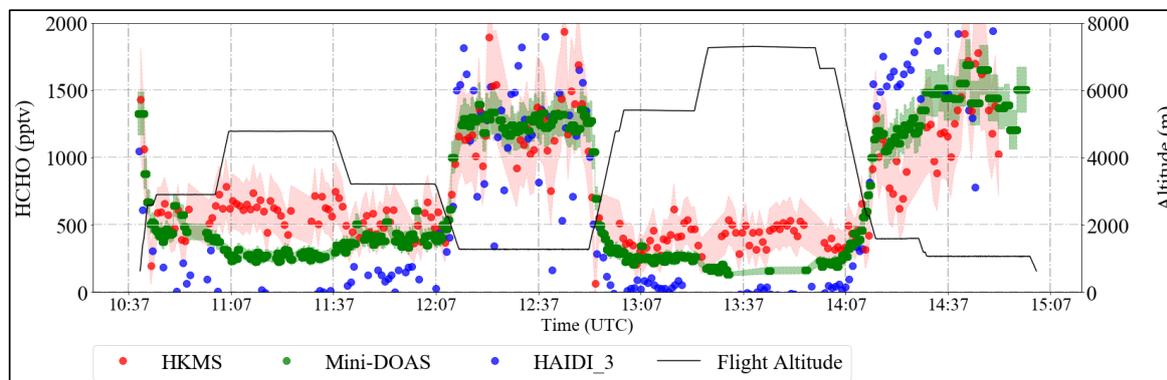$RO_2^*{}_m$ is systematically underestimated for $\sum VOCs$ greater than 7 ppbv. The composition of these air masses is quite different, as reflected by the $\Sigma VOCs/NO$ ratios. This implies that Eq. 9 does not capture the peroxy radical production adequately from VOCs in these cases. The underestimation of $RO_2^*{}_m$ 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.
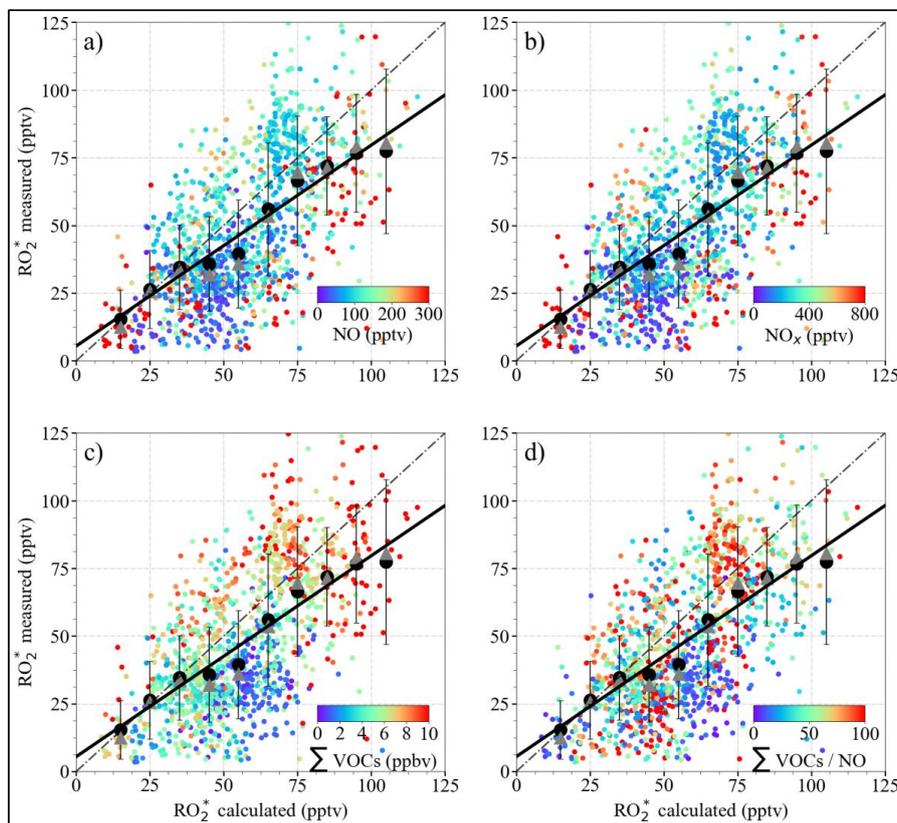
Figure 12: $RO_2^*{}_m$ versus $RO_2^*{}_c$ using Eq. 9 for $\delta = 0.5$ colour-coded with the measured a) NO mixing ratio, b) NO_x mixing ratio, c) $\Sigma VOCs$ mixing ratio, where $\Sigma VOCs = HCHO + CH_3CHO + (CHO)_2 + CH_3OH + CH_3C(O)CH_3$, and d) $\Sigma VOCs/NO$ ratio. The 1-minute (small circles), the mean of the binned $RO_2^*{}_m$ over 10 pptv $RO_2^*{}_c$ intervals (large circles), and the median of each bin (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_3, NO, H_2O, CO, CH_4, VOCs) with respect to remote sensing observations (NO_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_2O, $\Sigma VOCs$, and NO_x. The air masses probed at altitudes above 2000 m are close to the PSS assumptions used to develop Eq. 9, and consequently, the $RO_2{}^*{}_m/RO_2{}^*{}_c$ remains ≤ 1. In contrast, $RO_2{}^*{}_m/RO_2{}^*{}_c$ is at its highest value below 2000 m, reaching up to 3. At these altitudes, most of the flights in Europe were carried out in pollution plumes, in which both the amount of NO_x and $RO_2{}^*$ precursors are high. 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. $\Sigma VOCs > 7$ 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 $\Sigma VOCs$ and NO_x mixing ratio > 7 ppbv and 1000 pptv, respectively.
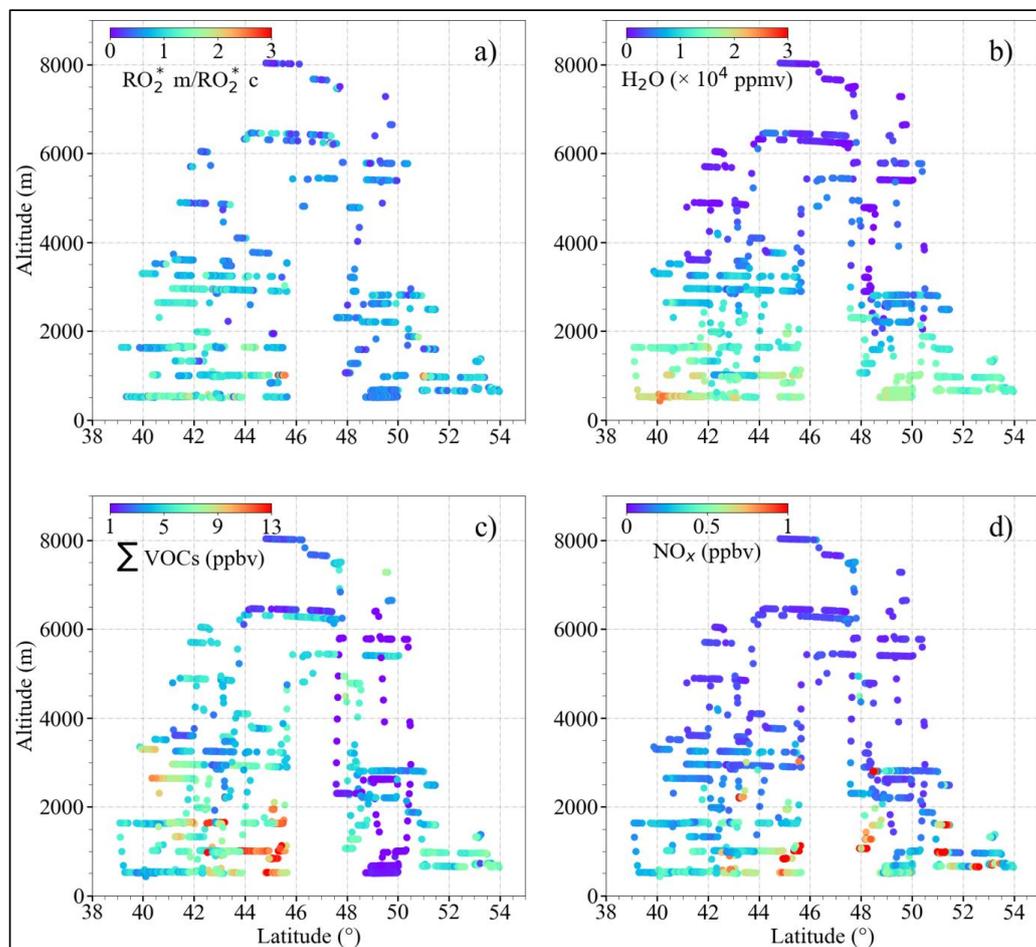
Figure 14: Plots of a) the ratio of $RO_2^{*}{}_{m}$ to $RO_2^{*}{}_{c}$ ($RO_2^{*}{}_{m}/RO_2^{*}{}_{c}$) assuming that δ = 0.5; b) H_2O; c) ∑VOCs; d) NO_x as a function of latitude and altitude for the EMeRGe measurements in Europe.

The applicability of Eq. 9 for calculating the in-flight measurements of RO_2^{*} 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 $j_{O(^1D)}$, cloudless conditions dominated throughout the flight track. The $RO_2^{*}{}_{c}$ agree reasonably well with $RO_2^{*}{}_{m}$ throughout this period except in the pollution plume measured from 12:05 to 12:25 UTC. In this plume, CO, NO, NO2, HONO, NOy, and HCHO reached 100 ppbv, 180 pptv, 150 pptv, 120 pptv, 1ppbv and 2 ppbv, respectively. The RO_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.
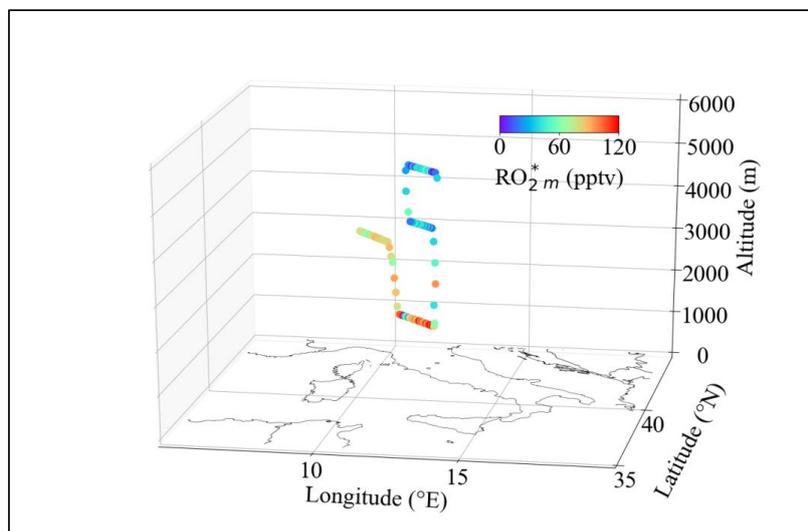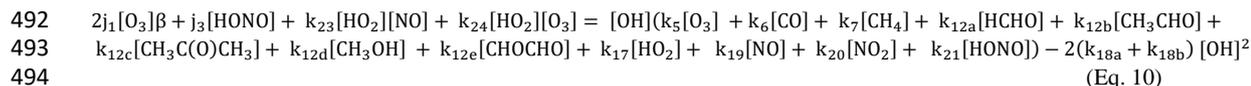
Figure 15: Maps of the flight track of E-EU-03 11 July 2017 along the western coast of Italy over the Tyrrhenian Sea colour-coded with RO_2^* measurements.

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_3O_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 $RO_2^* = HO_2 + 0.65 \times RO_2$, and the eCL is determined for a 1:1 mixture of $HO_2:CH_3O_2$, i.e. $\delta = 0.5$ is used for the RO_2^* retrieval. However, the HO_2 to CH_3O_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.
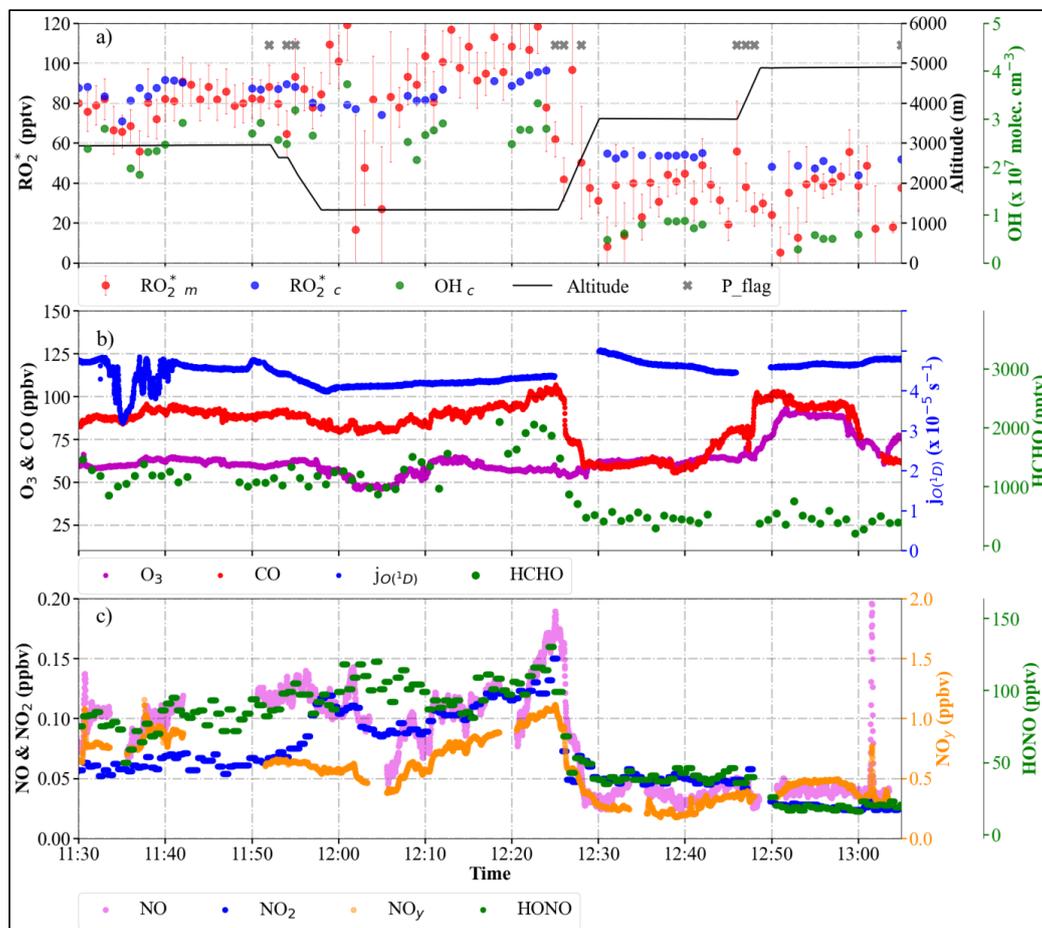
Figure 16: Temporal variation of $RO_2^*{}_m$ and $RO_2^*{}_c$, selected radical precursors and $j_{O(^1D)}$ along the E-EU-03 flight track: a) $RO_2^*{}_m$, $RO_2^*{}_c$ and calculated OH (OH_c) mixing ratios. The flight altitude is indicated in black. The P_flag indicates RO_2^* measurements affected by dynamical pressure variation in the inlet; b) O_3, CO, HCHO mixing ratios, and $j_{O(^1D)}$; c) NO, NO_2, NO_y, 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:

$$2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3] = [OH](k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO]) - 2(k_{18a} + k_{18b})[OH]^2$$

(Eq. 10)

The OH calculated from Eq. 10 assuming δ = 0.5 is much higher than the OH concentration reported in the previous airborne (Crawfor 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 EMeRGe data set is insufficient to calculate the OH reactivity. The overestimation of OH agrees with the underestimation of $RO_2^*{}_m$ in airmasses with a high amount of OVOCs ($\sum$VOCs > 7 ppbv) as the missing OH – OVOCs reactions in Eq. 8 should reduce ρ (the OH loss during the OH – RO_2^* interconversion) and thereby increase the $RO_2^*{}_c$. Due to the direct reaction of OH

502 with most of the gases emitted in the atmosphere, OH budget calculations in airmasses of complex chemistry are challenging and

503 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 RO_2^* production rate

506 Cantrell et al. (2003b) proposed $P_{RO_2^*}$ to be equal to the sum of two terms representing $RO_2^* - RO_2^*$ reactions and the $RO_2^* -$

507 NO_x reactions in the troposphere. As a result of this assumption, the relationship between HO_2, RO_2, $P_{RO_2^*}$ and NO_x is described

508 by Eq.11:

509 $$P_{RO_2^*} = k_{RR} [HO_2 + RO_2]^2 + k_{RN} [HO_2 + RO_2] [NO_x] \qquad (Eq. 11)$$

510 where k_{RR} and k_{RN} refer to effective rate coefficients for $RO_2^* - RO_2^*$ and $RO_2^* - NO_x$ reactions, and are calculated as fit

511 parameters. Solving Eq. 11 for $[HO_2 + RO_2]^2$ leads to:

512 $$[HO_2 + RO_2] = \sqrt[2]{A + B^2} - B \qquad (Eq. 12)$$

513 where $A = \frac{P_{RO_2^*}}{k_{RR}}$ and $B = \frac{k_{RN}[NO_x]}{2\,k_{RR}}$. For low NO_x and/or high $P_{RO_2^*}$, B becomes negligible compared to A. Then $[HO_2 + RO_2]$

514 approaches $\sqrt[2]{A}$ and is independent of NO_x. For high NO_x and /or low $P_{RO_2^*}$, $[HO_2 + RO_2]$ approaches zero.

515 The least-square fitting in Eq. 12 is applied to $RO_{2\,m}^*$ and $RO_{2\,c}^*$ from the EMeRGe measurements in Europe binned in 0.1 pptv s^{-1}

516 $P_{RO_2^*}$ intervals as shown in Fig. 17. The fit parameters for Fig. 17a and Fig. 18b are $k_{RR} = 7 \times 10^{-5}$; $k_{RN} = 9 \times 10^{-6}$. The RO_2^*

517 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

518 et al. (2003b), a decrease of RO_2^* with NO_x is identified for $NO_x > 1000$ pptv, although only for $P_{RO_2^*} < 0.7$ pptv s^{-1}. In the study

519 of Cantrell et al. (2003b), $P_{RO_2^*}$ only reached values up to 0.275 pptv s^{-1}.

520 Despite the low agreement of the fitted lines with the $RO_{2\,m}^*$, a decrease of the $RO_{2\,m}^*$ as a function of NO_x is still observed. The

521 disagreement between the $RO_{2\,m}^*$ and the curves estimated using Eq. 12 implies that the simplified Eq. 11 is insufficient to

522 adequately describe the chemical and physical processes occurring in the troposphere. Part of the disagreement might arise from

523 missing terms in the $P_{RO_2^*}$ calculation or inaccuracies related to the NO to NO_2 ratio in the air mass, which are more evident at

524 higher $P_{RO_2^*}$. As expected, the ratio of calculated $[RO_{2\,c}^*]$ to $\sqrt[2]{P_{RO_2^*}}$ has a negative linear dependency on the measured $[NO_x]$ (see

525 Fig. 17c). The comparable plot of $[RO_{2\,m}^*]$ to $\sqrt[2]{P_{RO_2^*}}$ is not linear. This indicates that more complex non-linear processes are

526 involved in the air masses investigated than those considered in Eq. 11 (see Fig.17d).

527
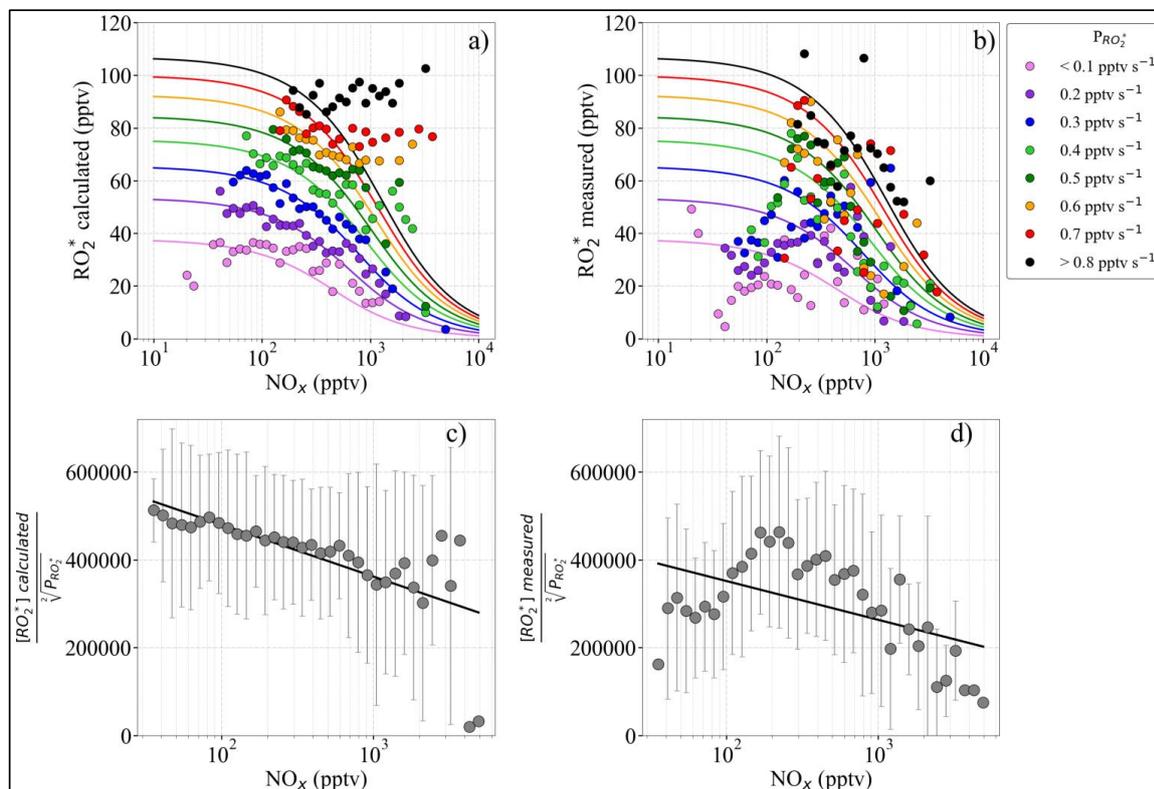
Figure 17: a) $RO_2^*{}_c$ binned with $P_{RO_2^*}$; b) $RO_2^*{}_m$ binned with $P_{RO_2^*}$; c) $[RO_2^*]_c$ to $\sqrt[2]{P_{RO_2^*}}$ ratio; and d) $[RO_2^*]_m$ to $\sqrt[2]{P_{RO_2^*}}$ ratio. The data in a) and b) are coloured with radical production rates. The RO_2^* for different $P_{RO_2^*}$ ranges are binned into 50 bins over NO_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 O₃ production rate

The O_3 production rate (P_{O_3}) is calculated from the EMeRGe Europe dataset using the reaction of RO_2^* 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).

$$P_{O_3} = k_{RO_2^*+NO}[RO_2^*][NO] \qquad \text{(Eq. 13)}$$

where $k_{RO_2^*+NO}$ is taken as the average of k_{HO_2+NO} and $k_{CH_3O_2+NO}$.

Figure 18 shows plots of the mean P_{O_3} calculated using Eq. 13 from the $RO_2^*{}_m$ and $RO_2^*{}_c$ 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_{O_3} using the $RO_2^*{}_m$ and $RO_2^*{}_c$ agree well within the standard deviation of the bins.

567 usually overestimated when NO is < 50 pptv in the air probed. This is attributed to RO_2^* loss processes involving reactions with

568 OH, which are not considered in the analytical expression. The reactions are excluded from the analytical expression to constrain

569 it with on-board measurements. These reactions become significant RO_2^* loss processes at low NO concentrations.

570 The results indicate that the steady-state calculations mostly underestimated the RO_2^* measurements in polluted plumes of urban

571 origin at altitudes below 2000 m. Changes in the HO_2 to RO_2 ratios in different plumes partly account for the disagreement in

572 particular cases. In pollution plumes with the sum of the OVOCs measured mixing ratios > 7 ppbv, the underestimation of the

573 measurements can reach up to 80 %. In these plumes, the oxidation and/or photolysis of non-measured VOCs and the ozonolysis

574 of alkenes might be significant, limiting the accuracy of the analytical expression. The overestimation of the OH concentration

575 calculated based on the measured reactants also indicates missing oxy–peroxy radical interconversion reactions in the analytical

576 PSS expression. More information about peroxy radical speciation and VOC partitioning is required to better describe the fast

577 photochemistry in these pollution plumes.

578 The analytical expression developed is robust enough to simulate the radical chemistry in most of the conditions in the free

579 troposphere encountered during EMeRGe IOP in Europe. Speciated radical and VOC measurements in future campaigns would

580 facilitate the estimation of radical loss reactions in air masses with NO < 50 pptv and improve radical production rates

581 estimations in pollution plumes with a high amount of VOCs, where non-linear complex chemistry is involved. Comparing RO_2^*

582 measurements with RO_2^* calculations from the analytical expression helps to identify different chemical and physical regimes,

583 which can be used to constrain future model studies.

584 The calculated O_3 production rates for NO < 1 ppbv are in the same order of magnitude as those previously reported for urban

585 environments. This indicates that the selected RO_2^* production and loss processes and observations of the radical precursors on-

586 board are, to a good approximation, adequate for the estimation of the O_3 production in the measured airmasses in the free

587 troposphere over Europe.

Author contribution:

599 MG, VN, and YL undertook the RO_2^* measurements, flying as key scientists on-board HALO. VN led the deployment of

600 PeRCEAS in the HALO aircraft. MG led the analysis of the PeCEAS measurements and prepared the manuscript with

601 contributions from all co-authors. MDAH and JPB initiated the EMeRGe research project and consortium, acted as co-principal

602 and principal investigators, and participated in the measurement campaigns. They developed the overarching EMeRGe scientific

603 objectives and the required measurement portfolio, directed the EMeRGe research campaigns, and participated in the data

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604   analysis presented. AZ, BB, BS, EF, FO, FK, HS, HZ, KB, KP, and TH have contributed by providing their measurements made

605   on-board HALO during the campaign and participated in the discussion of results.

606   **Competing interests**:

607   The authors declare that they have no conflict of interest.

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