



*Supplement of*

## **Airborne observations of peroxy radicals during the EMeRGe campaign in Europe**

**Midhun George et al.**

*Correspondence to:* Midhun George (m.george@leeds.ac.uk) and Maria Dolores Andrés Hernández (lola@iup.physik.uni-bremen.de)

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# Supplementary information

## I. Reactions and rate coefficients used in the current study

The temperature dependent rate coefficients of the bimolecular reactions are calculated using the Arrhenius expression:

$$k(T) = A \times e^{(-E/RT)} \quad \text{Eq. S1}$$

5 The low-pressure-limiting rate coefficients for termolecular reactions are given in the form:

$$k_0(T) = k_{0,298} \times (T/298)^{-n} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} \quad \text{Eq. S2}$$

The high-pressure-limiting rate coefficients for termolecular reactions are given in the form:

$$k_{\infty}(T) = k_{\infty,298} \times (T/298)^{-m} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \quad \text{Eq. S3}$$

The following formula calculates the effective second-order rate coefficients for a given condition of temperature and pressure (altitude) (Burkholder et al., 2019).

$$10 \quad k_f(T, [M]) = \frac{\{k_{\infty}(T)k_0(T)[M]\}}{\{k_{\infty}(T) + k_0(T)[M]\}} 0.6 \left\{ 1 + \left[ \log_{10} \left( \frac{k_0(T)[M]}{k_{\infty}(T)} \right) \right]^2 \right\}^{-1} \quad \text{Eq. S4}$$

Where [M] is the total gas concentration.

All the reaction rate constants used in this work were calculated for the ambient temperature and pressure measured on-board during the flights.

Table S1: Reactions and corresponding rate coefficients taken from Burkholder et al., 2019. The radical intermediate formed during OVCO oxidation and photolysis are assumed to be converted to  $\text{RO}_2^*$ , and the oxidation reaction or the photolysis is taken as the rate-determining step.

Number	Reaction	A-Factor	E/R	k (298 K) or k <sub>total</sub> (298K, 1 atm)	k <sub>0</sub> (T) = k <sub>0,298</sub> × (T/298) <sup>-n</sup>		k <sub>∞</sub> (T) = k <sub>∞,298</sub> × (T/298) <sup>-m</sup>	
					k <sub>0,298</sub>	n	k <sub>∞,298</sub>	m
R1	<sup>(a)</sup> O <sub>3</sub> + hv → O( <sup>1</sup> D) + O <sub>2</sub>							
R2a	O( <sup>1</sup> D) + H <sub>2</sub> O → 2OH	1.63 × 10 <sup>-10</sup>	-60	2.0 × 10 <sup>-10</sup>				

Number	Reaction	A-Factor	E/R	k (298 K) or k <sub>total</sub> (298K, 1atm)	k <sub>0</sub> (T) = k <sub>0</sub> <sup>298</sup> × (T/298) <sup>-n</sup>		k <sub>∞</sub> (T) = k <sub>∞</sub> <sup>298</sup> × (T/298) <sup>-m</sup>	
					k <sub>0</sub> <sup>298</sup>	n	k <sub>∞</sub> <sup>298</sup>	m
R2b	O( <sup>1</sup> D) + O <sub>2</sub> → O( <sup>3</sup> P) + O <sub>2</sub>	3.3 × 10 <sup>-11</sup>	-55	3.95 × 10 <sup>-11</sup>				
R2c	O( <sup>1</sup> D) + N <sub>2</sub> → O( <sup>3</sup> P) + N <sub>2</sub>	2.15 × 10 <sup>-11</sup>	-110	3.1 × 10 <sup>-11</sup>				
R3	HONO + hv → OH + NO							
R4	H <sub>2</sub> O <sub>2</sub> + hv → 2OH							
R5	OH + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>	1.7 × 10 <sup>-12</sup>	940	7.3 × 10 <sup>-14</sup>				
R6	OH + CO + O <sub>2</sub> <sup>M</sup> → HO <sub>2</sub> + CO <sub>2</sub>			2.4 × 10 <sup>-13</sup>	6.9 × 10 <sup>-33</sup>	2.1	1.1 × 10 <sup>-12</sup>	-1.3
R7	<sup>(b)</sup> OH + CH <sub>4</sub> + O <sub>2</sub> → CH <sub>3</sub> O <sub>2</sub> + H <sub>2</sub> O	2.45 × 10 <sup>-12</sup>	1775	6.3 × 10 <sup>-15</sup>				
R8	<sup>(c)</sup> HCHO + hv + 2O <sub>2</sub> → 2HO <sub>2</sub> + CO							
R9	<sup>(d)</sup> CH <sub>3</sub> CHO + hv + 2O <sub>2</sub> → CH <sub>3</sub> O <sub>2</sub> + HO <sub>2</sub> + CO							
R10a	<sup>(e)</sup> CH <sub>3</sub> C(O)CH <sub>3</sub> + hv + 2O <sub>2</sub> → CH <sub>3</sub> C(O)O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub>							
R10b	CH <sub>3</sub> C(O)CH <sub>3</sub> + hv + 2O <sub>2</sub> → 2 CH <sub>3</sub> O <sub>2</sub> + CO							
R11	CHOCHO + hv + 2O <sub>2</sub> → 2HO <sub>2</sub> + 2CO							
R12a	OH + HCHO + O <sub>2</sub> → HO <sub>2</sub> + CO + H <sub>2</sub> O	5.5 × 10 <sup>-12</sup>	-125	8.5 × 10 <sup>-12</sup>				
R12b	<sup>(f)</sup> OH + CH <sub>3</sub> CHO + O <sub>2</sub> <sup>M</sup> → CH <sub>3</sub> C(O)O <sub>2</sub> + H <sub>2</sub> O	4.63 × 10 <sup>-12</sup>	-350	1.5 × 10 <sup>-11</sup>				
R12c	<sup>(g)</sup> OH + CH <sub>3</sub> C(O)CH <sub>3</sub> → H <sub>2</sub> O + CH <sub>3</sub> C(O)CH <sub>2</sub>			See note				
R12d	OH + CH <sub>3</sub> OH + O <sub>2</sub> → CH <sub>2</sub> O + HO <sub>2</sub> + H <sub>2</sub> O	2.9 × 10 <sup>-12</sup>	345	9.1 × 10 <sup>-13</sup>				
R12e	OH + CHOCHO + O <sub>2</sub> → HO <sub>2</sub> + H <sub>2</sub> O + 2CO	1.15 × 10 <sup>-11</sup>	0	1.15 × 10 <sup>-11</sup>				
R13	<sup>(h)</sup> O <sub>3</sub> + CH <sub>2</sub> =C(CH <sub>3</sub> )CH=CH <sub>2</sub> → products	1.1 × 10 <sup>-14</sup>	2000	1.3 × 10 <sup>-17</sup>				

Number	Reaction	A-Factor	E/R	k (298 K) or k <sub>total</sub> (298K, 1atm)	k <sub>0</sub> (T) = k <sub>0</sub> <sup>298</sup> × (T/298) <sup>-n</sup>		k <sub>∞</sub> (T) = k <sub>∞</sub> <sup>298</sup> × (T/298) <sup>-m</sup>	
					k <sub>0</sub> <sup>298</sup>	n	k <sub>∞</sub> <sup>298</sup>	m
R14	<sup>(i)</sup> HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	3.0 × 10 <sup>-13</sup>	-460	1.4 × 10 <sup>-12</sup>	See note			
	$\xrightarrow{M}$ H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	2.1 × 10 <sup>-33</sup> [M]	-920	4.6 × 10 <sup>-32</sup> [M]				
R15	HO <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub> → CH <sub>3</sub> OOH + O <sub>2</sub>	4.1 × 10 <sup>-13</sup>	-750	5.2 × 10 <sup>-12</sup>				
R16a	<sup>(i)</sup> CH <sub>3</sub> O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub> → CH <sub>3</sub> OH + HCHO + O <sub>2</sub>	9.5 × 10 <sup>-14</sup>	-390	3.5 × 10 <sup>-13</sup>				
R16b	CH <sub>3</sub> O <sub>2</sub> + CH <sub>3</sub> O <sub>2</sub> → 2CH <sub>3</sub> O + O <sub>2</sub>	9.5 × 10 <sup>-14</sup>	-390	3.5 × 10 <sup>-13</sup>				
R17	OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	4.8 × 10 <sup>-11</sup>	-250	1.1 × 10 <sup>-10</sup>				
R18a	OH + OH $\xrightarrow{M}$ H <sub>2</sub> O <sub>2</sub>			6.3 × 10 <sup>-12</sup>	6.9 × 10 <sup>-31</sup>	1.0	2.6 × 10 <sup>-11</sup>	0
R18b	OH + OH → H <sub>2</sub> O + O( <sup>3</sup> P)	1.8 × 10 <sup>-12</sup>	0	1.8 × 10 <sup>-12</sup>				
R19	OH + NO $\xrightarrow{M}$ HONO			7.4 × 10 <sup>-12</sup>	7.1 × 10 <sup>-31</sup>	2.6	3.6 × 10 <sup>-11</sup>	0.1
R20	OH + NO <sub>2</sub> $\xrightarrow{M}$ HNO <sub>3</sub>			1.1 × 10 <sup>-11</sup>	1.8 × 10 <sup>-30</sup>	3.0	2.8 × 10 <sup>-11</sup>	0
R21	OH + HONO → H <sub>2</sub> O + NO <sub>2</sub>	3.0 × 10 <sup>-12</sup>	-250	6.9 × 10 <sup>-12</sup>				
R22	CH <sub>3</sub> O + NO $\xrightarrow{M}$ CH <sub>3</sub> ONO			2.9 × 10 <sup>-11</sup>	2.3 × 10 <sup>-29</sup>	2.8	3.8 × 10 <sup>-11</sup>	0.6
R23	<sup>(k)</sup> HO <sub>2</sub> + NO → OH + NO <sub>2</sub>	3.44 × 10 <sup>-12</sup>	-260	8.2 × 10 <sup>-12</sup>				

Number	Reaction	A-Factor	E/R	k (298 K) or k <sub>total</sub> (298K, 1 atm)	k <sub>0</sub> (T) = k <sub>0</sub> <sup>298</sup> × (T/298) <sup>-n</sup>		k <sub>∞</sub> (T) = k <sub>∞</sub> <sup>298</sup> × (T/298) <sup>-m</sup>	
					k <sub>0</sub> <sup>298</sup>	n	k <sub>∞</sub> <sup>298</sup>	m
R24	HO <sub>2</sub> + O <sub>3</sub> → OH + 2O <sub>2</sub>	1.0 × 10 <sup>-14</sup>	490	1.9 × 10 <sup>-15</sup>				
R25	<sup>(1)</sup> CH <sub>3</sub> O <sub>2</sub> + NO → CH <sub>3</sub> O + NO <sub>2</sub>	2.8 × 10 <sup>-12</sup>	-300	7.7 × 10 <sup>-12</sup>				
R26	CH <sub>3</sub> O + O <sub>2</sub> → CH <sub>2</sub> O + HO <sub>2</sub>	3.9 × 10 <sup>-14</sup>	900	1.9 × 10 <sup>-15</sup>				

- 15 (a) The O<sub>3</sub> photolysis has a second channel O<sub>3</sub> + hv (λ < 320 nm) → O(<sup>3</sup>P) + O<sub>2</sub>. So, only the photolysis rate for R1 is used in the calculation.  
 (b) Reaction OH with CH<sub>4</sub> produces CH<sub>3</sub> and H<sub>2</sub>O. The CH<sub>3</sub> formed further reacts with O<sub>2</sub> to form CH<sub>3</sub>O<sub>2</sub>. The formation of CH<sub>3</sub>O<sub>2</sub> is assumed to be much faster than the CH<sub>3</sub> formation due to the high amount of O<sub>2</sub> present in the atmosphere. So the reaction of OH with CH<sub>3</sub> is taken as the rate-determining step for R7.  
 (c) The HCHO photolysis has a second channel, HCHO + hv (λ < 320 nm) → H<sub>2</sub> + CO. So, only the photolysis rate for R8 is used in the calculation.  
 (d) The CH<sub>3</sub>CHO photolysis has a second channel CH<sub>3</sub>CHO + hv (λ < 320 nm) → CH<sub>4</sub> + CO. So, only the photolysis rate for R9 is used in the calculation.
- 20 (e) To simplify the calculation, the CH<sub>3</sub>C(O)O<sub>2</sub> produced is treated as a CH<sub>3</sub>O<sub>2</sub> molecule during the calculation.  
 (f) The reaction of OH with CH<sub>3</sub>CHO produces CH<sub>3</sub>C(O) and H<sub>2</sub>O. The CH<sub>3</sub>C(O) formed reacts with O<sub>2</sub> in a three-body reaction to form CH<sub>3</sub>C(O)O<sub>2</sub>. The formation of CH<sub>3</sub>C(O)O<sub>2</sub> is assumed to be much faster than the CH<sub>3</sub>C(O) formation due to the high amount of O<sub>2</sub> present in the atmosphere. So the reaction of OH with CH<sub>3</sub>CHO is taken as the rate-determining step for R12b. To simplify the calculation, the CH<sub>3</sub>C(O)O<sub>2</sub> produced is treated as a CH<sub>3</sub>O<sub>2</sub> molecule during the calculation.
- 25 (g) The temperature-dependent reaction rate coefficient is given by: k<sub>12c</sub>(T) = 1.33 × 10<sup>-13</sup> + 3.82 × 10<sup>-11</sup> × e<sup>(-2000/T)</sup> cm<sup>3</sup>molecules<sup>-1</sup>s<sup>-1</sup>. CH<sub>3</sub>C(O)CH<sub>2</sub> formed reacts with O<sub>2</sub> in a three-body reaction to form CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub>. The formation of CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> is assumed to be much faster than the CH<sub>3</sub>C(O)CH<sub>2</sub> formation due to the high amount of O<sub>2</sub> present in the atmosphere. So the reaction of OH with CH<sub>3</sub>C(O)CH<sub>3</sub> is taken as the rate-determining step for R12c. To simplify the calculation, the CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub> produced is treated as a CH<sub>3</sub>O<sub>2</sub> molecule during the calculation.  
 (h) The reaction R13 shows an example of an ozonolysis reaction. To simplify the calculation, the ozonolysis reactions are not considered in this study.  
 (i) Reaction R14 exhibits a dependence on H<sub>2</sub>O concentration. So the overall rate coefficient is given by the sum of the bimolecular component and a pressure-dependent termolecular component multiplied by the H<sub>2</sub>O enhancement term. i.e.,
- 30  $(1.4 \times 10^{-12} + 4.6 \times 10^{-32}[\text{M}])(1 + 1.4 \times 10^{-21}[\text{H}_2\text{O}]\text{exp}^{(2200/T)})$ .
- (j) The CH<sub>3</sub>O<sub>2</sub> self-reaction has a second channel with relative product yield,  $\frac{k_{16b}}{k_{16a}} = (26.2 \pm 6.6) e^{(-1130 \pm 240)/T}$  (Tyndall et al., 2001).  
 (k) Note that the HO<sub>2</sub> + NO reaction have another channel producing HNO<sub>3</sub>. The probability of this channel is less than 1% and therefore negligible.  
 (l) Note that the CH<sub>3</sub>O<sub>2</sub> + NO reaction have another channel producing CH<sub>3</sub>ONO<sub>2</sub>. The probability of this channel is less than 0.5% and therefore negligible.

## 35 II. Derivation of Eq. 5

An analytical equation to calculate  $RO_2^*$  was derived, assuming the primary source of  $RO_2^*$  production is precursor photolysis and the loss of  $RO_2^*$  is only through  $RO_2^* - RO_2^*$  reactions. The production of  $RO_2^*$  from the photolysis of  $H_2O_2$  and ozonolysis of alkenes were excluded from this study because  $H_2O_2$  and alkenes were not measured. As a first approach,  $RO_2$  is assumed to consist only of  $CH_3O_2$  to reduce the complexity of the calculations by considering only  $CH_3O_2$  reaction rate constants.

40 Under these assumptions and based on the reactions in Table S1

- The rate of change of  $[RO_2^*]$  is given by

$$\frac{d}{dt}([RO_2^*]) = \frac{d}{dt}([OH] + [CH_3O] + [HO_2] + [CH_3O_2])$$

$$\frac{d}{dt}([RO_2^*]) = 2j_1[O_3]\beta + j_3[HONO] + 2j_8[HCHO] + 2j_{11}[CHOCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] - 2k_{15}[HO_2][CH_3O_2] - 2k_{14}[HO_2]^2 - 2k_{16a}[CH_3O_2]^2$$

45

Eq. S5

Where  $\beta$  is the fraction of  $O(^1D)$  reacts with  $H_2O$  to form  $OH$  and is given by  $\beta = \left( \frac{k_{2a}[H_2O]}{k_{2a}[H_2O] + k_{2b}[O_2] + k_{2c}[N_2]} \right)$

Now substituting  $[HO_2] = \delta[RO_2^*]$  and  $[CH_3O_2] = (1 - \delta)[RO_2^*]$  in Eq. S5

$$\frac{d}{dt}([RO_2^*]) = 2j_1[O_3]\beta + j_3[HONO] + 2j_8[HCHO] + 2j_{11}[CHOCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] - 2k_{15}\delta(1 - \delta)[RO_2^*]^2 - 2k_{16a}((1 - \delta)[RO_2^*])^2 - 2k_{14}(\delta[RO_2^*])^2$$

50 Under photostationary steady-state (PSS)

$$\frac{d}{dt}([RO_2^*]) = 0$$

$$\Rightarrow 2j_1[O_3]\beta + j_3[HONO] + 2j_8[HCHO] + 2j_{11}[CHOCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] = 2k_{15}\delta(1 - \delta)[RO_2^*]^2 + 2k_{16a}((1 - \delta)[RO_2^*])^2 + 2k_{14}(\delta[RO_2^*])^2$$

Eq. S6

Eq. S6 is a quadratic equation of  $[RO_2^*]$  without a linear term. The solution is given by

$$55 \quad [RO_2^*]_c = \sqrt{\frac{P_{RO_2^*}}{2k_{RO_2^*}}}$$

Eq. S7

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

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

Since the amount of OH and RO is much smaller than that of HO<sub>2</sub> and RO<sub>2</sub> in the atmosphere, RO<sub>2</sub><sup>\*</sup> to a good approximation is the sum of HO<sub>2</sub> and RO<sub>2</sub> radicals.

### III. Derivation of Eq. 6 and Eq. 9

60 If the RO<sub>2</sub><sup>\*</sup> effective yields from VOC oxidation by OH and radical losses through HONO and HNO<sub>3</sub> formation are considered, then

- The rate of change of [OH] is given by

$$\frac{d}{dt}([OH]) = 2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3] - [OH](k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO]) - 2(k_{18a} + k_{18b})[OH]^2 \quad \text{Eq. S8}$$

Under photostationary steady-state

$$65 \quad \frac{d}{dt}([OH]) = 0$$

i.e.,

$$2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3] = [OH](k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{17}[HO_2] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO]) - 2(k_{18a} + k_{18b})[OH]^2 \quad \text{Eq. S9}$$

70 Since the atmospheric [OH] and [HO<sub>2</sub>] ≪ [NO] and [NO<sub>2</sub>], as a first approximation, the reactions R18 (OH – OH reaction) and R17 (OH – HO<sub>2</sub> reaction) are assumed to be negligible in the loss process of OH compared to the OH – NO<sub>x</sub> reactions. So Eq. S9 can be modified as:

$$[OH] = \frac{2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3]}{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO])} \quad \text{Eq. S10}$$

- The rate of change of [CH<sub>3</sub>O] is given by

$$\frac{d}{dt}([CH_3O]) = 2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO] - [CH_3O](k_{22}[NO] + k_{26}[O_2]) \quad \text{Eq. S11}$$

Under PSS

$$75 \quad \frac{d}{dt}([CH_3O]) = 0$$

$$\Rightarrow [CH_3O] = \frac{2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO] + k_{26}[O_2])} \quad \text{Eq. S12}$$

- The rate of change of  $[HO_2]$  is given by

$$\frac{d}{dt}([HO_2]) = 2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCHO] + [OH](k_5[O_3] + k_6[CO] + k_{12a}[HCHO] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]) + k_{26}[CH_3O][O_2] - [HO_2](k_{15}[CH_3O_2] + k_{17}[OH] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2$$

80 Based on the assumption made for Eq. S10, the reaction R17 (OH – HO<sub>2</sub> reaction) is assumed to have a negligible contribution in the HO<sub>2</sub> loss process. So

$$\frac{d}{dt}([HO_2]) = 2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCHO] + [OH](k_5[O_3] + k_6[CO] + k_{12a}[HCHO] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]) + k_{26}[CH_3O][O_2] - [HO_2](k_{15}[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2 \quad \text{Eq. S13}$$

- The rate of change of  $[CH_3O_2]$  is given by

$$85 \quad \frac{d}{dt}([CH_3O_2]) = j_9[CH_3CHO] + 2j_{11}[CH_3C(O)CH_3] + [OH](k_7[CH_4] + k_{12b}[CHOCHO] + k_{12c}[CH_3C(O)CH_3]) - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) - 2(k_{16a} + k_{16b})[CH_3O_2]^2 \quad \text{Eq. S14}$$

- If  $CH_3O_2$  is assumed as a surrogate for all  $RO_2^*$ , then the rate of change of  $[RO_2^*]$  is given by

$$\begin{aligned} \frac{d}{dt}([RO_2^*]) &= \frac{d}{dt}([HO_2] + [CH_3O_2]) \\ &= 2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCHO] + [OH](k_5[O_3] + k_6[CO] + k_{12a}[HCHO] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]) + k_{26}[CH_3O][O_2] - \\ &[HO_2](k_{15}[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2 + j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + [OH](k_7[CH_4] + k_{12b}[CHOCHO] + \\ 90 \quad &k_{12c}[CH_3C(O)CH_3]) - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) - 2(k_{16a} + k_{16b})[CH_3O_2]^2 \quad \text{Eq. S15} \end{aligned}$$

Since OH and CH<sub>3</sub>O are not measured on-board during EMerGe, Eq. S10 and Eq. S12 are substituted in Eq. S15 and on rearranging.

$$\begin{aligned} \frac{d}{dt}([RO_2^*]) &= 2j_8[HCHO] + j_9[CH_3CHO] + 2j_{11}[CHOCHO] + j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + \\ &\frac{2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + k_{24}[HO_2][O_3]}{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO])} (k_5[O_3] + k_6[CO] + k_7[CH_4] + \\ &k_{12a}[HCHO] + k_{12b}[CHOCHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]) + k_{26} \frac{2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO] + k_{26}[O_2])} [O_2] - \\ 95 \quad &[HO_2](k_{15}[CH_3O_2] + k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2 - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) - 2(k_{16a} + k_{16b})[CH_3O_2]^2 \quad \text{Eq. S16} \end{aligned}$$

Now substituting

$$(1 - \rho) = \frac{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CHOCHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO])}{(k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CH_3CHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO] + k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO])}$$
 in Eq. S16 gives

$$\begin{aligned} \frac{d}{dt}([RO_2^*]) = & 2j_8[HCHO] + 2j_9[CH_3CHO] + 2j_{11}[CHOCHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + (2j_1[O_3]\beta + j_3[HONO] + k_{23}[HO_2][NO] + \\ & k_{24}[HO_2][O_3])(1 - \rho) + k_{26} \frac{2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO] + k_{26}[O_2])} [O_2] - [CH_3O_2](k_{15}[HO_2] + k_{25}[NO]) - 2(k_{16a} + k_{16b})[CH_3O_2]^2 - [HO_2](k_{15}[CH_3O_2] + \\ & k_{23}[NO] + k_{24}[O_3]) - 2k_{14}[HO_2]^2 \end{aligned} \quad \text{Eq. S17}$$

Where  $\rho$  accounts for the effective yield of HONO, HNO<sub>3</sub> and H<sub>2</sub>O through reactions R19 to R21 and the HO<sub>2</sub> + NO and HO<sub>2</sub> + O<sub>3</sub> reactions (R23 and R24 respectively)

On rearranging

$$\begin{aligned} \frac{d}{dt}([RO_2^*]) = & (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] \\ & + [HO_2](k_{23}[NO] + k_{24}[O_3])(1 - \rho) + k_{26} \frac{2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]}{(k_{22}[NO] + k_{26}[O_2])} [O_2] - [HO_2](k_{23}[NO] + k_{24}[O_3]) - k_{15}[HO_2][CH_3O_2] \\ & - k_{15}[HO_2][CH_3O_2] - (2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]) - 2k_{16a}[CH_3O_2]^2 - 2k_{14}[HO_2]^2 \end{aligned}$$

Combining common terms indicated by the same colours gives

$$\begin{aligned} \frac{d}{dt}([RO_2^*]) = & (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] - \\ & [HO_2](k_{23}[NO] + k_{24}[O_3])\rho - (2k_{16b}[CH_3O_2]^2 + k_{25}[CH_3O_2][NO]) \left( \frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) - 2k_{15}[HO_2][CH_3O_2] - 2k_{16a}[CH_3O_2]^2 - 2k_{14}[HO_2]^2 \end{aligned}$$

110 Since the rate of R<sub>22</sub> in the atmosphere compared to that of R<sub>26</sub> is negligible, i.e.  $\left( \frac{k_{22}[NO]}{(k_{22}[NO] + k_{26}[O_2])} \right) \approx 0$ . Applying this gives

$$\begin{aligned} \frac{d}{dt}([RO_2^*]) = & (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] - \\ & [HO_2](k_{23}[NO] + k_{24}[O_3])\rho - 2k_{15}[HO_2][CH_3O_2] - 2k_{16a}[CH_3O_2]^2 - 2k_{14}[HO_2]^2 \end{aligned} \quad \text{Eq. S18}$$

Under steady-state

$$\frac{d}{dt}([RO_2^*]) = 0$$

$$115 \Rightarrow (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = [HO_2](k_{23}[NO] + k_{24}[O_3])\rho + 2k_{15}[HO_2][CH_3O_2] + 2k_{16a}[CH_3O_2]^2 + 2k_{14}[HO_2]^2 \quad \text{Eq. S19}$$

Now substituting  $[HO_2] = \delta [RO_2^*]$  and  $[CH_3O_2] = (1 - \delta) [RO_2^*]$  in Eq. S19

$$(2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO] = \delta[RO_2^*](k_{23}[NO] + k_{24}[O_3])\rho + 2k_{15}\delta(1 - \delta)[RO_2^*]^2 + 2k_{16a}((1 - \delta)[RO_2^*])^2 + 2k_{14}(\delta[RO_2^*])^2 \quad \text{Eq. S20}$$

120 Eq. S20 is a quadratic equation of  $[RO_2^*]$ . The solution is given by

$$[RO_2^*] = \frac{-(-L_{RO_2^*}) - \sqrt{L_{RO_2^*}^2 - 4(-2k_{RO_2^*})P_{RO_2^*g}}}{2(-2k_{RO_2^*})} \quad \text{Eq. S21}$$

Where

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

$$L_{RO_2^*} = (\delta(k_{23}[NO] + k_{24}[O_3])\rho)$$

$$125 P_{RO_2^*g} = (2j_1[O_3]\beta + j_3[HONO])(1 - \rho) + 2j_8[HCHO] + 2j_9[CH_3CHO] + 2(j_{10a} + j_{10b})[CH_3C(O)CH_3] + 2j_{11}[CHOCHO]$$

where  $k_{RO_2^*}$  is a weighed rate coefficient of  $RO_2^*$  self reactions for a 1:1 mixture of  $HO_2$  and  $CH_3O_2$ ,  $L_{RO_2^*}$  comprises the formation of HONO and  $HNO_3$  and  $P_{RO_2^*g}$  is the gross production of  $RO_2^*$ .

- **Special case I**

130 When  $k_{19}[NO] + k_{20}[NO_2] + k_{21}[HONO] \ll k_5[O_3] + k_6[CO] + k_7[CH_4] + k_{12a}[HCHO] + k_{12b}[CHOCHO] + k_{12c}[CH_3C(O)CH_3] + k_{12d}[CH_3OH] + k_{12e}[CHOCHO]$ , i.e.,  $\rho \approx 0$ , Eq. S20 becomes Eq. S6 and the solution is given by Eq. S7:

$$(2j_1[O_3]\beta + j_3[HONO]) + 2j_8[HCHO] + 2j_9[CH_3CHO]$$

#### IV. Figure S1: Ambient $[\text{H}_2\text{O}]$ versus $[\text{H}_2\text{O}]$ in the DUALER inlet during EMERGE in Europe

Figure S1 shows the humidity measured in the DUALER during the EMERGE campaign in Europe. As the pressure in the DUALER inlet is lower than the ambient,  $[\text{H}_2\text{O}]_{\text{inlet}} < [\text{H}_2\text{O}]_{\text{ambient}}$ . However, the humidity is still significant and affects the eCL in the DUALER. Therefore, the eCL was corrected using the equation  $\text{eCL}_{\text{wet}} = \text{eCL}_{\text{dry}} \times A^{([\text{H}_2\text{O}] \times 10^{-16})}$  obtained from the laboratory characterisation of the eCL water dependence, where  $A = 0.973$  for the NO number concentration added to the DUALER inlet during EMERGE campaign in Europe (George, 2022, PhD thesis).

The  $[\text{H}_2\text{O}]$  in the inlet was lower than  $1 \times 10^{17}$  molecules  $\text{cm}^{-3}$  for 60 % of measurements during EMERGE in Europe, for which the  $\text{eCL}_{\text{wet}} = 76 \%$  of  $\text{eCL}_{\text{dry}}$ . At the highest humidity observed during the campaign, i.e.,  $[\text{H}_2\text{O}]_{\text{inlet}} = 2 \times 10^{17}$  molecules  $\text{cm}^{-3}$ , the  $\text{eCL}_{\text{wet}}$  is 55 % of  $\text{eCL}_{\text{dry}}$ .

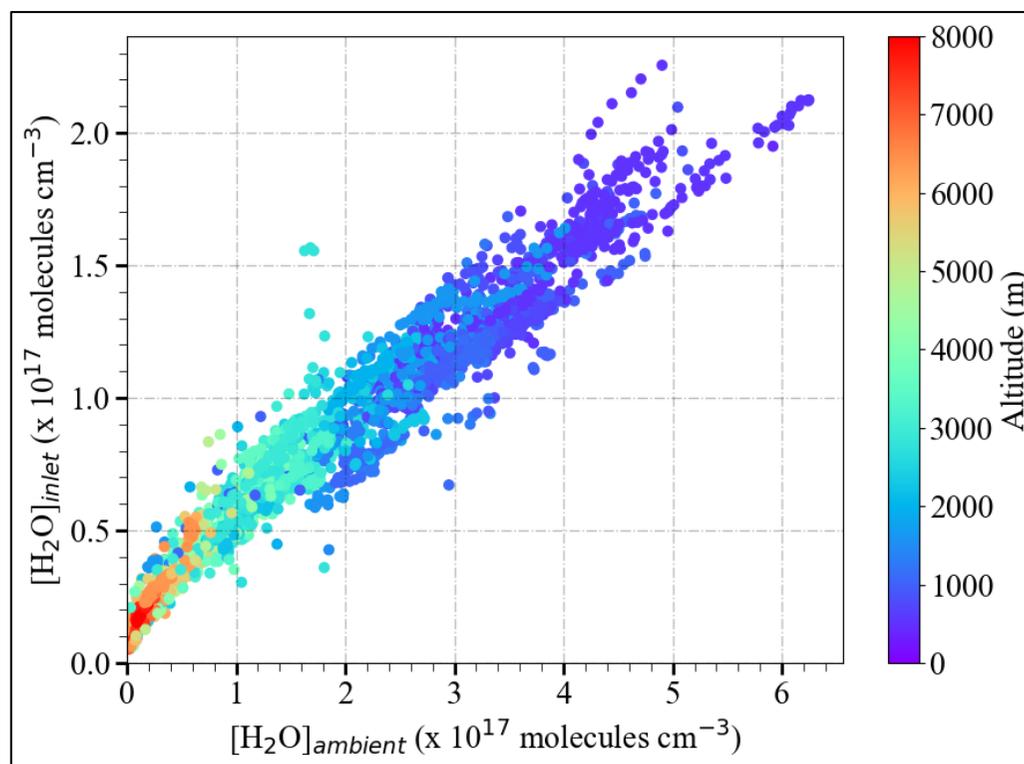
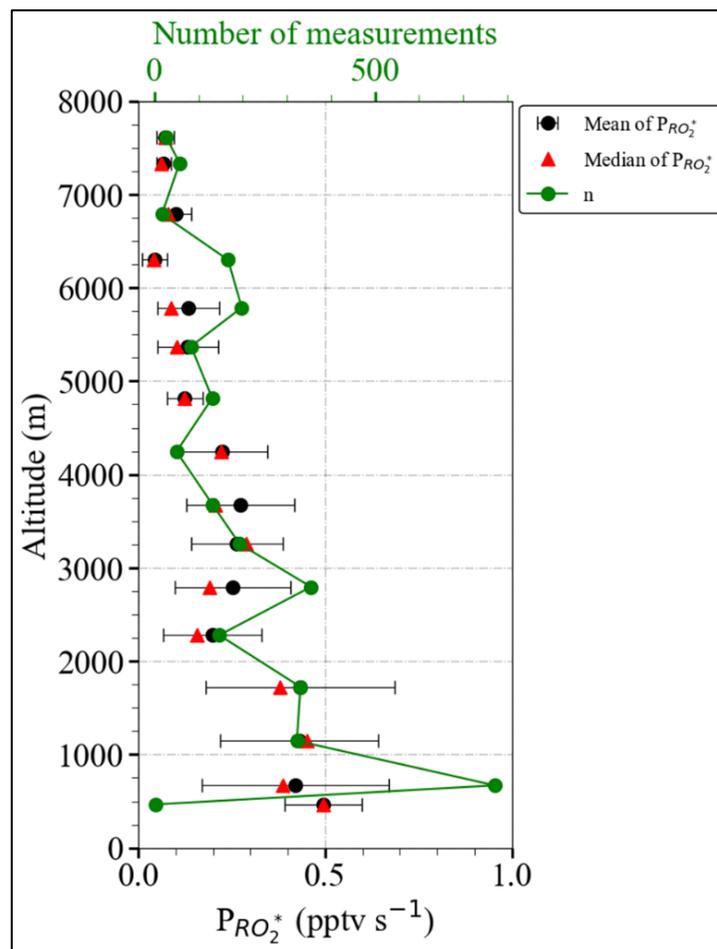


Figure S1: Ambient  $[\text{H}_2\text{O}]$  versus  $[\text{H}_2\text{O}]$  measured in the DUALER inlet during the EMERGE campaign in Europe, colour-coded with altitude.

## V. Figure S2: vertical profiles of $P_{RO_2^*}$



145 Figure S2: Composite average vertical profiles of  $P_{RO_2^*}$ . The measurements are binned over 500 m altitude. The error bars are the  $\pm 1\sigma$  standard deviation of each bin. Median values (red triangles) and the number of individual measurements,  $n$ , for each bin (in green) are additionally plotted.

The measurements below 2000 m were carried out in the outflow of MPCs, which are expected to contain significant amounts of  $RO_2^*$  precursors. As a result, the highest production rate is observed below 2000 m for the data considered in this study. As mentioned in Section 4.2, a decrease in  $P_{RO_2^*}$  with altitude is observed, as a consequence to the decrease in  $H_2O$  and other radical precursor concentrations with altitude.

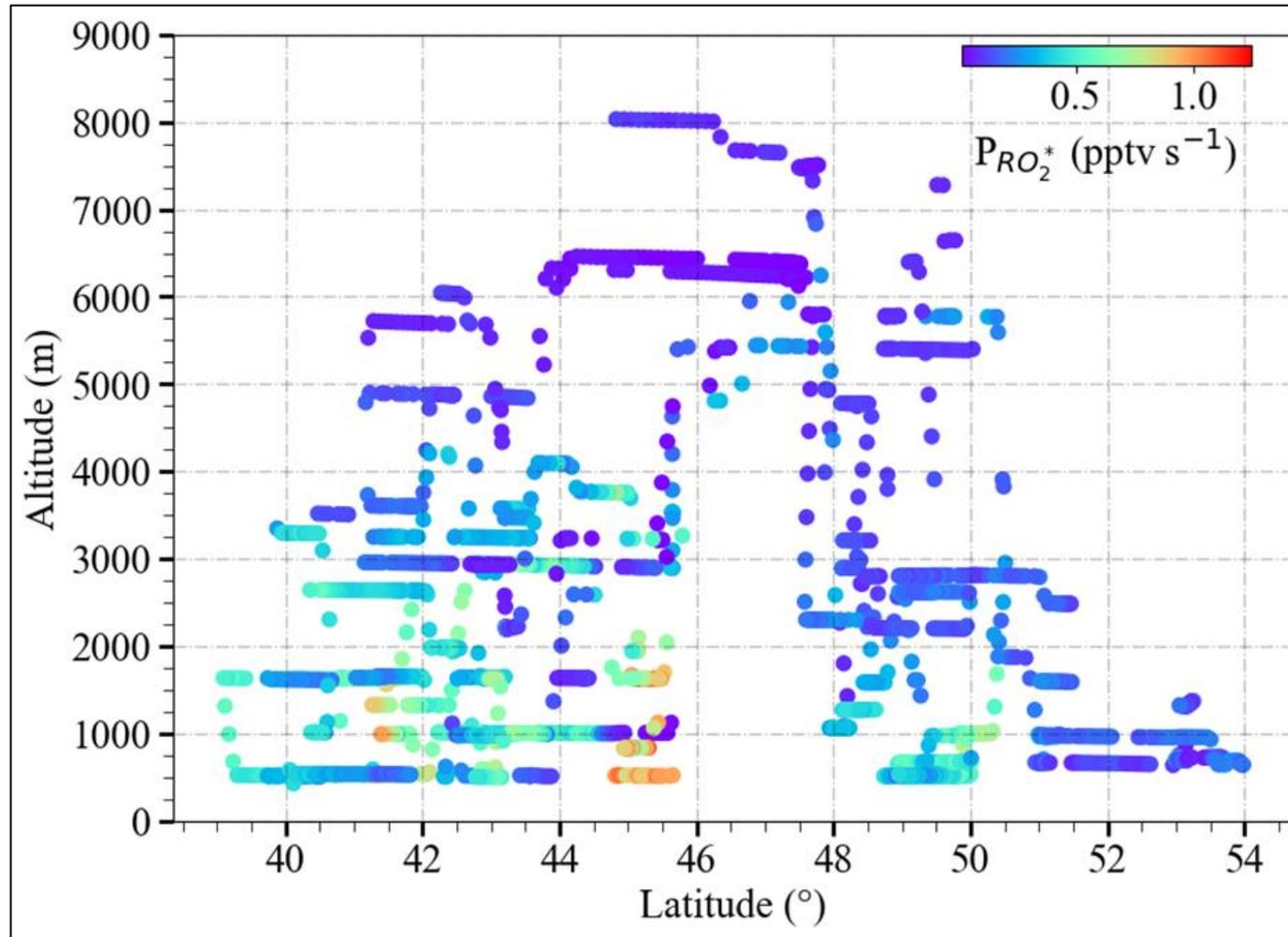
**VI. Figure S3: Latitudinal distribution of  $P_{RO_2^*}$  for the EMeRGe flights**

Figure S3:  $P_{RO_2^*}$  as a function of latitude and altitude for the EMeRGe measurements in Europe.

The  $P_{RO_2^*}$  latitudinal distribution shows higher production rates south of 47°N likely due to the higher insolation conditions during the measurement flights over southern Europe.

155 VII. Figure S4:  $RO_2^*_m$  and  $RO_2^*_c$  mixing ratios during EMERGE in Europe as a function of latitude and altitude

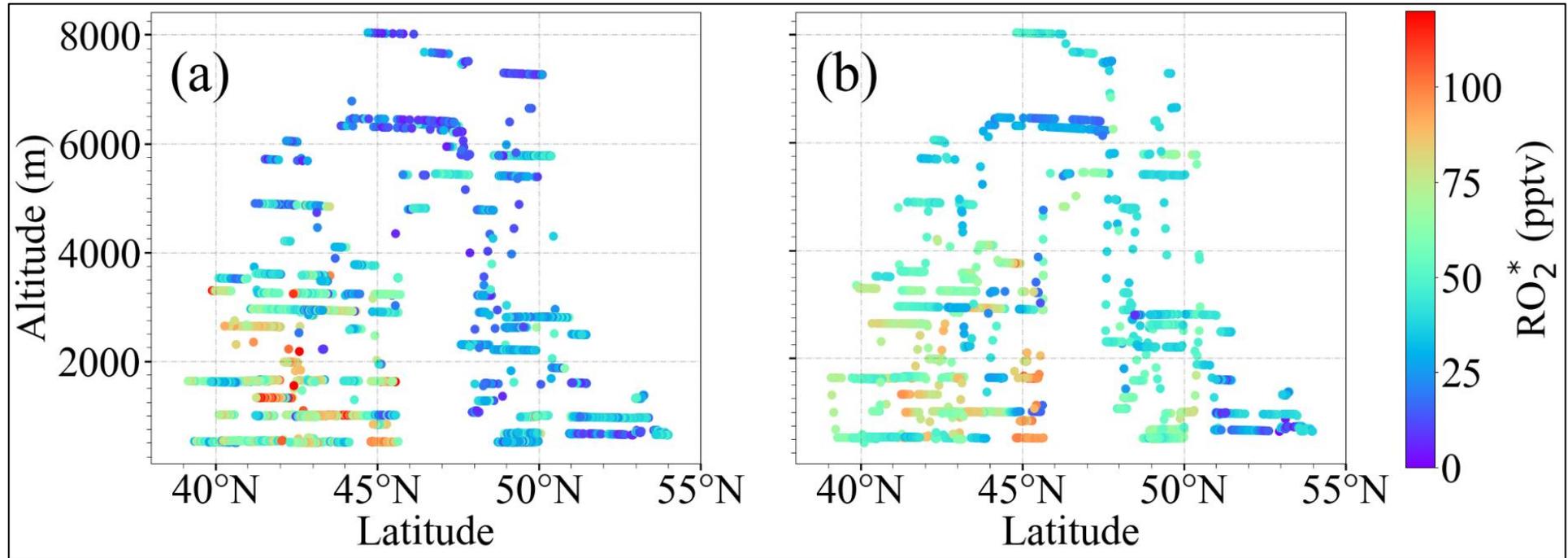


Figure S4: Latitudinal and altitudinal distribution of a)  $RO_2^*_m$  and b)  $RO_2^*_c$  mixing ratios calculated using Eq. 9 for  $\delta = 0.5$ .

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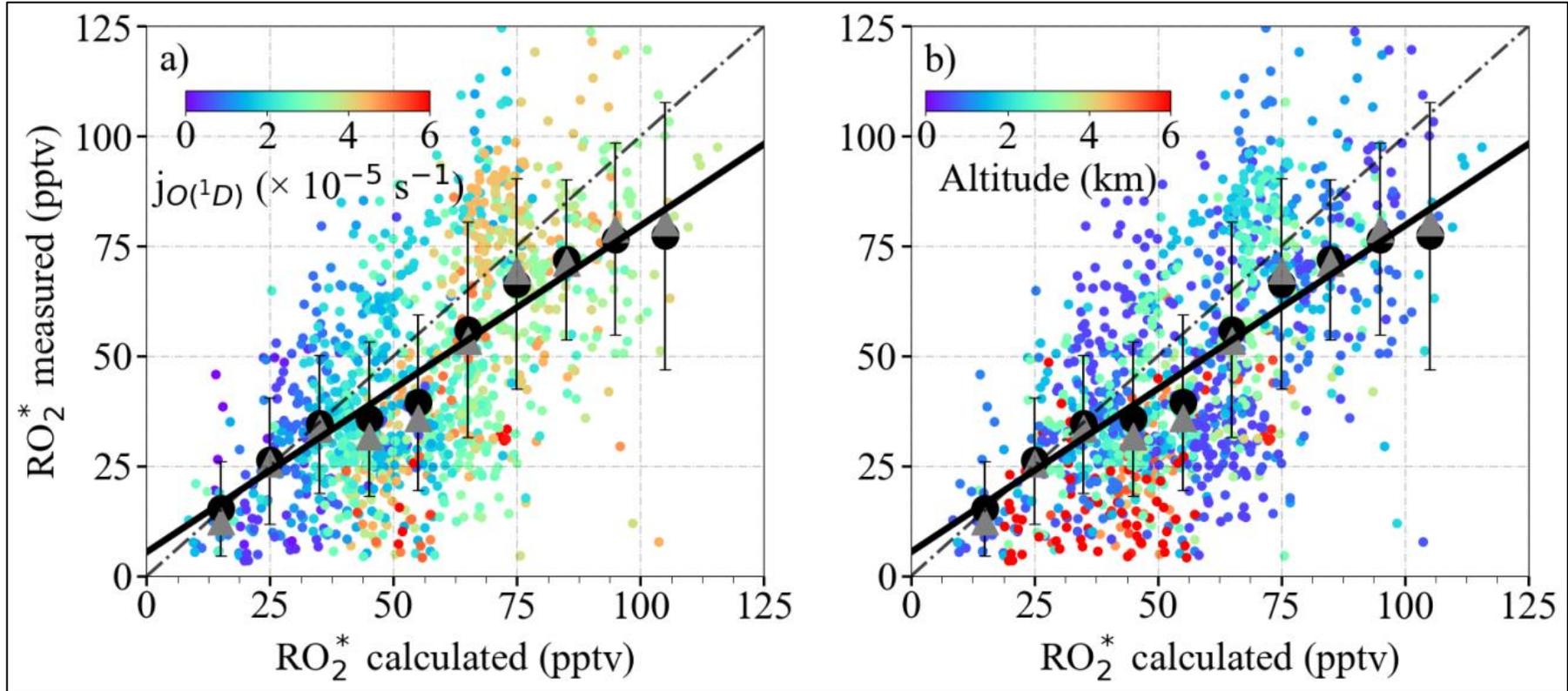
**VIII. Figure S5:  $RO_2^*_m$  versus  $RO_2^*_c$  for  $\delta = 0.5$** 


Figure S5:  $RO_2^*_m$  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.

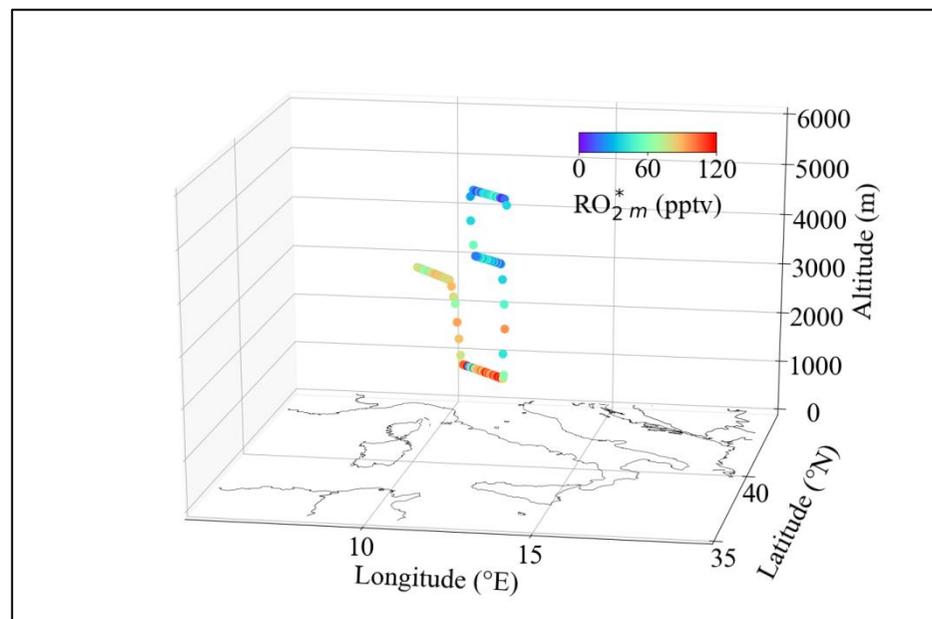
**IX. Figure S6:** flight track of E-EU-03 11 July 2017 along the western coast of Italy

Figure S6: Map 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.