



*Supplement of*

## **Impact of HO<sub>2</sub> / RO<sub>2</sub> ratio on highly oxygenated α-pinene photooxidation products and secondary organic aerosol formation potential**

**Yarê Baker et al.**

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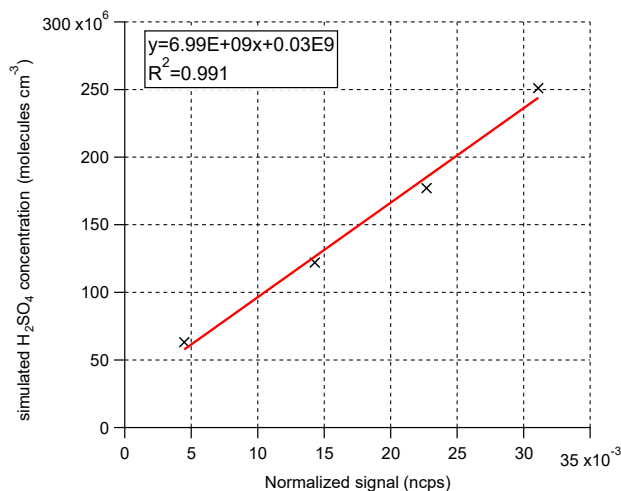
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## 9 S1 Sulfuric acid calibration for MION-API-LTOF

10 The calibration source setup used by us was described in detail by Kürten et al. (2012) and was recently applied to a newer  
11 model of the MION chemical ionization inlet by He et al. (2023). In short  $\text{H}_2\text{SO}_4$  is produced via the reaction of  $\text{SO}_2$  with OH  
12 in a calibration source directly in front of the instrument. OH is produced via the photolysis of water from a humidified  $\text{N}_2$   
13 flow and the  $\text{H}_2\text{SO}_4$  concentration is varied by variation of the humidified inflow.

14 The expected  $\text{H}_2\text{SO}_4$  concentration is calculated with an open-source python library provided by Shen and He (2023). The  
15 model simulates the necessary gas phase chemistry based on a set of differential equations and uses two-dimensional  
16 convection-diffusion-reaction equations to take into account the losses of  $\text{H}_2\text{SO}_4$  in the tubing. All that is needed for this  
17 calculation is the dimensions of the exact calibration setup. Details about the model can be found in He et al. (2023).

18 For the analyte signal we used the signal sum of the detected product ions  $\text{HSO}_4^-$ ,  $\text{H}_2\text{SO}_4(\text{NO}_3)^-$  and  $\text{H}_2\text{SO}_4(\text{HNO}_3\text{NO}_3)^-$  and  
19 normalized the signal with the sum of the  $\text{NO}_3^-$  ion and  $(\text{HNO}_3\text{NO}_3)^-$  cluster. The resulting calibration curve can be found in  
20 **Figure S1**. The calibration yielded a calibration factor of  $7.0 \cdot 10^9$  molecules $\cdot\text{cm}^{-3}\cdot\text{ncps}^{-1}$ , which is in the range of calibration  
21 factors reported before for different  $\text{NO}_3^-$ -MION inlets, for comparison see Rissanen et al. (2019)  
22 ( $1.4 \cdot 10^9$  molecules $\cdot\text{cm}^{-3}\cdot\text{ncps}^{-1}$ ) and He et al. (2023) ( $1.3 \cdot 10^{10}$  molecules $\cdot\text{cm}^{-3}\cdot\text{ncps}^{-1}$ ).



23  
24 **Figure S1: Calibration curve  $\text{NO}_3^-$ -MION-CIMS for  $\text{H}_2\text{SO}_4$  calibration set-up**

## 25 S2 Particle loss rate constant determination in SAPHIR STAR

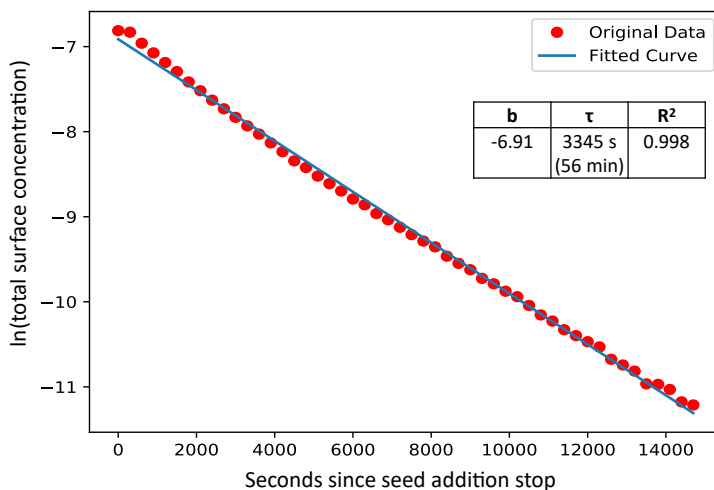
26 The particle loss rate in the SAPHIR STAR chamber was determined by observation of the seed concentration decay in the  
27 chamber after stop of the particle addition. The exponential decay was fitted logarithmic as shown in Eq. (S1) and the lifetime

28  $\tau_{\text{particle}}$  ( $k_{\text{particleLoss}} = \frac{1}{\tau_{\text{particle}}}$ ) was determined. t is the time since start of the decay (time since seed addition stop) and  $\tau$

29 and b are fitted for.

$$\ln(\text{normalized signal}) = -\frac{1}{\tau} * t + b \quad (\text{S1})$$

30 Exemplary the result of the fit for the total surface concentration measured in the SMPS is shown in **Figure S2**. The  
 31 determination via AMS sulfate and ammonium signal as well as the number concentration measurement gave similar results.  
 32 Therefore, the average determined particle lifetime in the chamber of 54 minutes was used. The residence time in the chamber  
 33 was 63 minutes which shows that the seed particles are lost only slightly faster than the flush out rate due to some deposition.



34

35 **Figure S2: Logarithmic fit of particle surface decay timeseries to determine particle lifetime in the chamber**

### 36 **S3 Box model input parameters**

37 The input parameters into the model are defined by the flows into the reactor and consist of the flows themselves, their humidity  
 38 and the contained  $\alpha$ -pinene,  $O_3$  and CO concentration. Additional inputs are the temperature, pressure, and  $J(O^1D)$ . The UVC  
 39 light is characterized by an on/off switch and the gap opening of the shielding. In separate experiments  $J(O^1D)$  was calculated  
 40 from  $O_3$  loss as a function of the gap opening. Other necessary input parameters are the OH background reactivity (loss of OH  
 41 without VOC present) and the wall loss of the  $RO_2$  and  $HO_2$  species in the STAR chamber. It is assumed that the product  
 42 species in the MCM are too volatile to be lost on the walls, but that the radical species are lost upon wall collision. An OH  
 43 background reactivity measurement (kOH instrument, see Lou et al. (2010), Fuchs et al. (2017) for more detailed information)  
 44 was performed in the empty, very clean chamber at the same humidity as in the experiments. This yielded a reactivity of  $3 \text{ s}^{-1}$ .  
 45 The background reactivity was adapted to represent the  $\alpha$ -pinene consumption in the photooxidation phase correctly, resulting  
 46 in a maximum  $k_{OH \text{ Background}} = 5 \text{ s}^{-1}$ . A possible reason for the discrepancy is that the background reactivity determination  
 47 was done in a very clean chamber while during the experiment series small residual contaminations, resisting flushing over >  
 48 6 residence times, may have contributed to the background reactivity.

49 For the estimation of the maximum wall loss the following experiment was performed twice: In a gas phase  $\alpha$ -pinene  
50 photooxidation steady state the light was turned off and the decay of HOM product signals were observed in the NO<sub>3</sub>-MION-  
51 CIMS. This approach was used before by Ehn et al. (2014) and Sarrafzadeh et al. (2016) to determine the maximum loss in  
52 the JPAC chamber.

53 Only products showing a clear single exponential decay were considered and it is assumed that the chosen HOMs are no longer  
54 produced after light off and lost on wall contact. Their timeseries is used to calculate an individual lifetime  $\tau$  by fitting the  
55 decay curve to the function shown in **Eq. (S1)**. From the observation of the decay of C10 products an average lifetime of  
56  $\tau=171$  s is determined.

57 The derived wall loss rate for HOM was also applied to describe the wall loss of RO<sub>2</sub> radicals, and therefore,  $k_{RO_2\ wall}$  is set  
58 as  $1/170$  s<sup>-1</sup>. The lifetime is correlated to the transport through the diffusion layer of the chamber thus should scale with the  
59 inverse of the square root of the molar mass (under the assumption of perfect mixing of the chamber core). It is therefore  
60 expected that the smaller HO<sub>2</sub> radical is lost faster due to its faster transport. Additionally, the removal efficiency for HO<sub>2</sub> and  
61 RO<sub>2</sub> radicals might differ further as RO<sub>2</sub> are not lost necessarily on every collision with the wall. The specific RO<sub>2</sub> removal  
62 efficiency depends on the radical's molecular structure (Miyazaki, 2012).

63 To estimate a value for the HO<sub>2</sub> wall loss, the expected diffusion constant for a HOM-Mon, HOM-Acc and HO<sub>2</sub> are calculated  
64 by the parametrization developed by Fuller et al. (1966) and recently reviewed by Tang et al. (2015). The results can be found  
65 in **Table S1**.

66 **Table S1. Calculated diffusion coefficients of an exemplary HOM-Mon, exemplary HOM-Acc and HO<sub>2</sub>**

Compound	Diffusion constant at 1 bar (cm <sup>2</sup> s <sup>-1</sup> )
C <sub>10</sub> H <sub>15</sub> O <sub>6</sub> (HOM-Mon proxy)	0.053
C <sub>20</sub> H <sub>30</sub> O <sub>10</sub> (HOM-Acc proxy)	0.038
HO <sub>2</sub>	0.202

67  
68 If the wall loss is only dependent on the diffusion to the wall (i.e. 100 % loss on wall contact), the lifetime should inversely  
69 scale with the diffusion speed. To verify this assumption, the ratio of the average lifetimes of HOM-Mon and HOM-Acc were  
70 compared to the ratio of their diffusion constants: The HOM-Acc proxy's diffusion constant is 0.71 of the monomer proxy's  
71 diffusion constant. The observed accretion products decay resulted in average lifetime of  $\tau = 202$  s, leading to  
72  $k_{HOM-Acc\ wall} / k_{HOM-Mon\ wall} = 0.85$ . Within the uncertainties of the diffusion constants calculation and the lifetime  
73 determination, the wall loss seems to depend indeed on the diffusion to the surface layer, thus on the diffusion constant.  
74 Therefore, considering the diffusion constant of HO<sub>2</sub>,  $k_{HO_2\ wall} = 1/50$  s<sup>-1</sup> is chosen.

75 To study the sensitivity of the modelled HO<sub>2</sub>/RO<sub>2</sub> ratio to the assumed wall loss rates, a sensitivity study was performed by  
 76 varying the rate coefficients for wall losses. The RO<sub>2</sub> wall loss was varied within 1σ of the determined HOM product wall loss.  
 77 The HO<sub>2</sub> wall loss was varied in a wider range to cover the case that not all collision with the wall lead to loss of HO<sub>2</sub>.  
 78 Therefore, the lifetime of HO<sub>2</sub> was either set as 50 s or to a maximum lifetime of 170 s as determined by HOM monomer loss.  
 79 The resulting HO<sub>2</sub>/RO<sub>2</sub> ratios of the sensitivity study for the Exp1 experiment are displayed in **Table S2** as an example.

80 **Table S2. Box model HO<sub>2</sub>/RO<sub>2</sub> ratio results at varying RO<sub>2</sub> and HO<sub>2</sub> wall loss at low HO<sub>2</sub>/RO<sub>2</sub> (left) and high HO<sub>2</sub>/RO<sub>2</sub> (right) in**  
 81 **the Exp1 experiment**

$\tau(\text{HO}_2) \backslash \tau(\text{RO}_2)$	low HO <sub>2</sub> /RO <sub>2</sub>		high HO <sub>2</sub> /RO <sub>2</sub>	
	<u>50 s</u>	<u>170 s</u>	<u>50 s</u>	<u>170 s</u>
<u>145 s</u>	6.8E-3	7.5E-3	0.7	1.0
<u>170 s</u>	6.4E-3	7.0E-3	0.6	0.9
<u>195 s</u>	6.1E-3	6.7E-3	0.6	0.9

82  
 83 The sensitivity study shows that independent of the assumed wall loss rate the HO<sub>2</sub>/RO<sub>2</sub> ratio is around 0.007 and near one in  
 84 the low and high HO<sub>2</sub>/RO<sub>2</sub> case, respectively. In any case, the modelling results are only used to qualify the change of chemical  
 85 regime and not to yield absolute values.

#### 86 S4 Model results for HO<sub>2</sub>, RO<sub>2</sub> and pinonaldehyde

87 **Table S3. Overview of modelled steady-state concentrations for HO<sub>2</sub>, the peroxy radical sum and pinonaldehyde. Results are**  
 88 **presented for all experiments for low HO<sub>2</sub>/RO<sub>2</sub> conditions and high HO<sub>2</sub>/RO<sub>2</sub> conditions (background highlighted in grey).**

Conditions	[HO <sub>2</sub> ] <sub>ss</sub>	[RO <sub>2</sub> ] <sub>ss</sub> sum	Pinonaldehyde
<i>Exp1: Low HO<sub>2</sub>/RO<sub>2</sub></i>	3.8E+7 cm <sup>-3</sup>	6.0E+9 cm <sup>-3</sup>	1.3E+10 cm <sup>-3</sup>
<i>Exp1: High HO<sub>2</sub>/RO<sub>2</sub></i>	1.2E+9 cm <sup>-3</sup>	1.9E+9 cm <sup>-3</sup>	4.8E+9 cm <sup>-3</sup>
<i>Exp2.1: Low HO<sub>2</sub>/RO<sub>2</sub></i>	4.6E+7 cm <sup>-3</sup>	6.8E+9 cm <sup>-3</sup>	1.1E+10 cm <sup>-3</sup>
<i>Exp2.1: High HO<sub>2</sub>/RO<sub>2</sub></i>	1.5E+9 cm <sup>-3</sup>	2.0E+9 cm <sup>-3</sup>	3.7E+9 cm <sup>-3</sup>
<i>Exp2.2: Low HO<sub>2</sub>/RO<sub>2</sub></i>	4.7E+7 cm <sup>-3</sup>	6.9E+9 cm <sup>-3</sup>	1.1E+10 cm <sup>-3</sup>
<i>Exp2.2: High HO<sub>2</sub>/RO<sub>2</sub></i>	1.5E+9 cm <sup>-3</sup>	1.9E+9 cm <sup>-3</sup>	3.6E+9 cm <sup>-3</sup>
<i>Exp3: Low HO<sub>2</sub>/RO<sub>2</sub></i>	4.4E+7 cm <sup>-3</sup>	6.3E+9 cm <sup>-3</sup>	9.8E+9 cm <sup>-3</sup>
<i>Exp3: High HO<sub>2</sub>/RO<sub>2</sub></i>	1.7E+9 cm <sup>-3</sup>	1.7E+9 cm <sup>-3</sup>	3.1E+9 cm <sup>-3</sup>

89 The box model results expect average HO<sub>2</sub>/RO<sub>2</sub> ratios of 6.9E-3 (~1/150) for low HO<sub>2</sub>/RO<sub>2</sub> conditions and 0.8 for high  
 90 HO<sub>2</sub>/RO<sub>2</sub> conditions. The modelled pinonaldehyde concentration is reduced to 34 % at high HO<sub>2</sub>/RO<sub>2</sub>. These calculations  
 91 only serve as indication of the expected trends as we cannot verify their results.

92 S5 Peaklist of oxidation products identified in NO<sub>3</sub>-MION-CIMS

93 Table S4. Peaklist NO<sub>3</sub>-MION-CIMS. All compounds were detected as clusters with (NO<sub>3</sub>). The table is sorted into fragments,  
 94 monomers, and accretion products. Some compounds were just assignable in certain experiments, this is indicated by the superscript,  
 95 no superscript indicated that the compound was assigned in all experiments.

Fragments		Monomers	Accretion products				
C <sub>5</sub> H <sub>6</sub> O <sub>4</sub> <sup>E1</sup>	C <sub>8</sub> H <sub>10</sub> O <sub>6</sub>	C <sub>10</sub> H <sub>14</sub> O <sub>5</sub>	C <sub>14</sub> H <sub>20</sub> O <sub>9</sub>	C <sub>17</sub> H <sub>24</sub> O <sub>7</sub>	C <sub>19</sub> H <sub>26</sub> O <sub>8</sub> <sup>E1,E2</sup>	C <sub>20</sub> H <sub>28</sub> O <sub>9</sub>	
C <sub>5</sub> H <sub>6</sub> O <sub>5</sub>	C <sub>8</sub> H <sub>10</sub> O <sub>7</sub>	C <sub>10</sub> H <sub>14</sub> O <sub>6</sub>	C <sub>14</sub> H <sub>22</sub> O <sub>10</sub>	C <sub>17</sub> H <sub>24</sub> O <sub>9</sub>	C <sub>19</sub> H <sub>28</sub> O <sub>7</sub>	C <sub>20</sub> H <sub>28</sub> O <sub>11</sub>	
C <sub>5</sub> H <sub>6</sub> O <sub>6</sub>	C <sub>8</sub> H <sub>10</sub> O <sub>10</sub> <sup>E1</sup>	C <sub>10</sub> H <sub>14</sub> O <sub>7</sub>	C <sub>14</sub> H <sub>22</sub> O <sub>11</sub> <sup>E1,E2</sup>	C <sub>17</sub> H <sub>24</sub> O <sub>10</sub> <sup>E1,E2</sup>	C <sub>19</sub> H <sub>28</sub> O <sub>8</sub>	C <sub>20</sub> H <sub>30</sub> O <sub>6</sub>	
C <sub>5</sub> H <sub>6</sub> O <sub>7</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>5</sub> <sup>E1,E2</sup>	C <sub>10</sub> H <sub>14</sub> O <sub>8</sub>	C <sub>14</sub> H <sub>26</sub> O <sub>11</sub>	C <sub>17</sub> H <sub>24</sub> O <sub>11</sub>	C <sub>19</sub> H <sub>28</sub> O <sub>9</sub>	C <sub>20</sub> H <sub>30</sub> O <sub>7</sub>	
C <sub>5</sub> H <sub>6</sub> O <sub>8</sub> <sup>E2</sup>	C <sub>8</sub> H <sub>12</sub> O <sub>6</sub>	C <sub>10</sub> H <sub>14</sub> O <sub>9</sub>		C <sub>17</sub> H <sub>24</sub> O <sub>13</sub> <sup>E1,E2</sup>	C <sub>19</sub> H <sub>28</sub> O <sub>10</sub>	C <sub>20</sub> H <sub>30</sub> O <sub>8</sub>	
C <sub>5</sub> H <sub>7</sub> O <sub>8</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>7</sub>	C <sub>10</sub> H <sub>14</sub> O <sub>10</sub>	C <sub>15</sub> H <sub>20</sub> O <sub>14</sub> <sup>E1</sup>	C <sub>17</sub> H <sub>26</sub> O <sub>8</sub>	C <sub>19</sub> H <sub>28</sub> O <sub>11</sub>	C <sub>20</sub> H <sub>30</sub> O <sub>9</sub>	
C <sub>5</sub> H <sub>8</sub> O <sub>7</sub>	C <sub>8</sub> H <sub>12</sub> O <sub>8</sub>	C <sub>10</sub> H <sub>14</sub> O <sub>11</sub>	C <sub>15</sub> H <sub>22</sub> O <sub>9</sub>	C <sub>17</sub> H <sub>26</sub> O <sub>9</sub>	C <sub>19</sub> H <sub>28</sub> O <sub>12</sub> <sup>E1,E2</sup>	C <sub>20</sub> H <sub>30</sub> O <sub>10</sub>	
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C <sub>6</sub> H <sub>10</sub> O <sub>7</sub>	C <sub>8</sub> H <sub>14</sub> O <sub>6</sub>	C <sub>10</sub> H <sub>15</sub> O <sub>8</sub>	C <sub>15</sub> H <sub>22</sub> O <sub>14</sub> <sup>E1</sup>	C <sub>17</sub> H <sub>26</sub> O <sub>14</sub> <sup>E1,E2</sup>	C <sub>19</sub> H <sub>30</sub> O <sub>6</sub>	C <sub>20</sub> H <sub>30</sub> O <sub>15</sub>	
	C <sub>8</sub> H <sub>14</sub> O <sub>7</sub>	C <sub>10</sub> H <sub>15</sub> O <sub>9</sub>	C <sub>15</sub> H <sub>24</sub> O <sub>13</sub> <sup>E1,E2</sup>	C <sub>17</sub> H <sub>28</sub> O <sub>8</sub>	C <sub>19</sub> H <sub>30</sub> O <sub>7</sub>	C <sub>20</sub> H <sub>30</sub> O <sub>16</sub>	
C <sub>7</sub> H <sub>8</sub> O <sub>5</sub> <sup>E3</sup>	C <sub>8</sub> H <sub>14</sub> O <sub>8</sub>	C <sub>10</sub> H <sub>15</sub> O <sub>10</sub>	C <sub>15</sub> H <sub>26</sub> O <sub>10</sub> <sup>E1,E2</sup>	C <sub>17</sub> H <sub>28</sub> O <sub>9</sub>	C <sub>19</sub> H <sub>30</sub> O <sub>8</sub>	C <sub>20</sub> H <sub>30</sub> O <sub>18</sub>	
C <sub>7</sub> H <sub>8</sub> O <sub>6</sub> <sup>E3</sup>	C <sub>8</sub> H <sub>14</sub> O <sub>9</sub>	C <sub>10</sub> H <sub>15</sub> O <sub>11</sub>		C <sub>17</sub> H <sub>28</sub> O <sub>10</sub>	C <sub>19</sub> H <sub>30</sub> O <sub>9</sub>	C <sub>20</sub> H <sub>32</sub> O <sub>6</sub>	
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C <sub>7</sub> H <sub>10</sub> O <sub>7</sub>	C <sub>9</sub> H <sub>12</sub> O <sub>8</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>6</sub>	C <sub>16</sub> H <sub>24</sub> O <sub>12</sub> <sup>E1,E2</sup>	C <sub>18</sub> H <sub>26</sub> O <sub>10</sub>	C <sub>19</sub> H <sub>30</sub> O <sub>14</sub> <sup>E1,E2</sup>	C <sub>20</sub> H <sub>32</sub> O <sub>11</sub>	
C <sub>7</sub> H <sub>10</sub> O <sub>8</sub>	C <sub>9</sub> H <sub>12</sub> O <sub>9</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>7</sub>	C <sub>16</sub> H <sub>26</sub> O <sub>8</sub>	C <sub>18</sub> H <sub>26</sub> O <sub>11</sub>	C <sub>19</sub> H <sub>30</sub> O <sub>15</sub> <sup>E1,E2</sup>	C <sub>20</sub> H <sub>32</sub> O <sub>12</sub>	
C <sub>7</sub> H <sub>10</sub> O <sub>9</sub> <sup>E1,E2</sup>	C <sub>9</sub> H <sub>12</sub> O <sub>12</sub> <sup>E2</sup>	C <sub>10</sub> H <sub>16</sub> O <sub>8</sub>	C <sub>16</sub> H <sub>26</sub> O <sub>9</sub>	C <sub>18</sub> H <sub>26</sub> O <sub>15</sub> <sup>E1</sup>	C <sub>19</sub> H <sub>30</sub> O <sub>16</sub> <sup>E1</sup>	C <sub>20</sub> H <sub>32</sub> O <sub>13</sub>	
C <sub>7</sub> H <sub>10</sub> O <sub>10</sub>	C <sub>9</sub> H <sub>13</sub> O <sub>9</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>9</sub>	C <sub>16</sub> H <sub>26</sub> O <sub>10</sub>	C <sub>18</sub> H <sub>28</sub> O <sub>6</sub>	C <sub>19</sub> H <sub>32</sub> O <sub>7</sub>	C <sub>20</sub> H <sub>32</sub> O <sub>14</sub>	
C <sub>7</sub> H <sub>14</sub> O <sub>5</sub> <sup>E1,E2</sup>	C <sub>9</sub> H <sub>13</sub> O <sub>10</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>10</sub>	C <sub>16</sub> H <sub>26</sub> O <sub>11</sub>	C <sub>18</sub> H <sub>28</sub> O <sub>8</sub>	C <sub>19</sub> H <sub>32</sub> O <sub>8</sub>	C <sub>20</sub> H <sub>32</sub> O <sub>15</sub>	
C <sub>7</sub> H <sub>14</sub> O <sub>6</sub>	C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>	C <sub>10</sub> H <sub>16</sub> O <sub>11</sub>	C <sub>16</sub> H <sub>26</sub> O <sub>12</sub>	C <sub>18</sub> H <sub>28</sub> O <sub>9</sub> <sup>E1</sup>	C <sub>19</sub> H <sub>32</sub> O <sub>9</sub>	C <sub>20</sub> H <sub>34</sub> O <sub>6</sub>	
	C <sub>9</sub> H <sub>14</sub> O <sub>5</sub>		C <sub>16</sub> H <sub>26</sub> O <sub>13</sub> <sup>E2</sup>	C <sub>18</sub> H <sub>28</sub> O <sub>10</sub>	C <sub>19</sub> H <sub>32</sub> O <sub>10</sub>	C <sub>20</sub> H <sub>34</sub> O <sub>7</sub>	
	C <sub>9</sub> H <sub>14</sub> O <sub>6</sub>	C <sub>10</sub> H <sub>17</sub> O <sub>6</sub>	C <sub>16</sub> H <sub>28</sub> O <sub>18</sub> <sup>E1,E2</sup>	C <sub>18</sub> H <sub>28</sub> O <sub>11</sub>	C <sub>19</sub> H <sub>32</sub> O <sub>11</sub>	C <sub>20</sub> H <sub>34</sub> O <sub>8</sub>	
	C <sub>9</sub> H <sub>14</sub> O <sub>7</sub>	C <sub>10</sub> H <sub>17</sub> O <sub>7</sub>		C <sub>18</sub> H <sub>28</sub> O <sub>12</sub> <sup>E1,E2</sup>	C <sub>19</sub> H <sub>32</sub> O <sub>12</sub>	C <sub>20</sub> H <sub>34</sub> O <sub>9</sub>	
	C <sub>9</sub> H <sub>14</sub> O <sub>8</sub>	C <sub>10</sub> H <sub>17</sub> O <sub>8</sub>		C <sub>18</sub> H <sub>28</sub> O <sub>13</sub>	C <sub>19</sub> H <sub>32</sub> O <sub>13</sub> <sup>E1</sup>	C <sub>20</sub> H <sub>34</sub> O <sub>10</sub>	
	C <sub>9</sub> H <sub>14</sub> O <sub>9</sub>	C <sub>10</sub> H <sub>17</sub> O <sub>9</sub>		C <sub>18</sub> H <sub>28</sub> O <sub>14</sub> <sup>E1,E3</sup>	C <sub>19</sub> H <sub>32</sub> O <sub>14</sub> <sup>E1,E2</sup>	C <sub>20</sub> H <sub>34</sub> O <sub>11</sub>	
	C <sub>9</sub> H <sub>14</sub> O <sub>10</sub>	C <sub>10</sub> H <sub>17</sub> O <sub>10</sub> <sup>E1,E3</sup>		C <sub>18</sub> H <sub>28</sub> O <sub>15</sub> <sup>E1</sup>		C <sub>20</sub> H <sub>34</sub> O <sub>12</sub>	
	C <sub>9</sub> H <sub>16</sub> O <sub>5</sub>	C <sub>10</sub> H <sub>17</sub> O <sub>11</sub> <sup>E3</sup>		C <sub>18</sub> H <sub>28</sub> O <sub>16</sub> <sup>E1,E3</sup>		C <sub>20</sub> H <sub>34</sub> O <sub>13</sub>	
	C <sub>9</sub> H <sub>16</sub> O <sub>6</sub>			C <sub>18</sub> H <sub>30</sub> O <sub>7</sub>			
	C <sub>9</sub> H <sub>16</sub> O <sub>7</sub>	C <sub>10</sub> H <sub>18</sub> O <sub>4</sub>		C <sub>18</sub> H <sub>30</sub> O <sub>8</sub>			
	C <sub>9</sub> H <sub>16</sub> O <sub>8</sub>	C <sub>10</sub> H <sub>18</sub> O <sub>5</sub>		C <sub>18</sub> H <sub>30</sub> O <sub>9</sub>			
		C <sub>10</sub> H <sub>18</sub> O <sub>6</sub>		C <sub>18</sub> H <sub>30</sub> O <sub>10</sub>			
		C <sub>10</sub> H <sub>18</sub> O <sub>7</sub>		C <sub>18</sub> H <sub>30</sub> O <sub>11</sub>			
		C <sub>10</sub> H <sub>18</sub> O <sub>8</sub>		C <sub>18</sub> H <sub>30</sub> O <sub>12</sub>			
		C <sub>10</sub> H <sub>18</sub> O <sub>9</sub>		C <sub>18</sub> H <sub>30</sub> O <sub>13</sub>			
				C <sub>18</sub> H <sub>30</sub> O <sub>14</sub> <sup>E1</sup>			

96 **S6 Exemplary reported HO<sub>2</sub>/RO<sub>2</sub> ratios from field studies**97 **Table S5. Measured HO<sub>2</sub> and RO<sub>2</sub> concentrations from field studies under different atmospheric conditions.**

Conditions	HO <sub>2</sub> (10 <sup>8</sup> cm <sup>-3</sup> )	RO <sub>2</sub> (10 <sup>8</sup> cm <sup>-3</sup> )	HO <sub>2</sub> /RO <sub>2</sub>	Source
<u>Autumn, Pearl Riva Delta, China</u> (polluted) <i>Morning (median)</i> <i>Afternoon (median)</i>	0.8 2.5	0.3 1.7	2.7 1.5	(Tan et al., 2019)
<u>Winter, Beijing, China</u> (urban) <i>Background (24 h average)</i> <i>Clean (24 h average)</i> <i>Polluted (24 h average)</i>	1.04 ± 0.62 0.93 ± 0.72 0.52 ± 0.23	0.70 ± 0.34 0.76 ± 0.46 0.71 ± 0.41	1.5 1.2 0.7	(Tan et al., 2018)
<u>Jülich, Germany</u> (rural) <i>Spring &amp; Summer noon (median)</i>	3.0	3.0	1.0	(Cho et al., 2023)
<u>Summer, Michigan, USA</u> (rural forest) <i>Average diurnal maximum</i>	3.5	4.0	1.1	(Bottorff et al., 2023)
<u>September, Colorado, USA</u> (remote) <i>Single measurements:</i> <i>High NO<sub>x</sub> (1.9 ppbv)</i> <i>Low NO<sub>x</sub> (0.5 ppbv)</i>	(Uncertainty factor of 2) 0.3 1	4.7 ± 2.0 4 ± 2	(Uncertainty factor of 2) 0.1 0.3	(Stevens et al., 1997)
Schauinsland/Pabsthum, Germany (rural)	-	-	<i>Reported ratios around 1 for a range of NO concentrations (0.1 – 1.5 ppbv)</i>	(Mihelcic et al., 2003)

98

99 **S7 Estimation of change in peroxy radical steady state concentration between low and high HO<sub>2</sub>/RO<sub>2</sub>**

100 Starting from the balance equation **Eq. (S2)**, we derived an equation for the steady state concentration (indicated by subscript

101 SS) of an  $[RO_2]_i$  (**Eq. (S3)**). The equations assume a primary production term  $Pri_i$  for  $[RO_2]_i$ , as well as only three significant

102 loss pathways: The reaction with the pool of available  $[RO_2]$  with a bulk reaction rate constant  $k_{RO_2RO_2}$ , the reaction with  $[HO_2]$

103 with a reaction rate of  $k_{RO_2HO_2}=2.46 \cdot 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$  at 20 °C as defined in the MCM (Jenkin et al., 1997; Saunders et al., 2003)

104 and the wall loss. A wall loss rate coefficient of 1/170 s was used, as determined by our measurements for HOM products (see

105 supplement section **S3**). The rate coefficient  $k_{RO_2RO_2}$  was varied in a range  $1.0\text{-}5.0 \cdot 10^{-12} \text{ cm}^3 \cdot \text{s}^{-1}$ , typical values expected for

106 substituted organic peroxy radicals (Jenkin et al., 2019), to determine what bulk rate coefficient would be reconcilable with

107 our observations. To compare directly to the measured ratio of HOM-RO<sub>2</sub> signal, we calculated the RO<sub>2</sub> concentration ratio at  
 108 high to low HO<sub>2</sub>/RO<sub>2</sub> applying **Eq. (S4)**. In **Eq. (S4)** the primary production term  $Pri_i$  could be eliminated as the primary  
 109 production was same at high and low HO<sub>2</sub>/RO<sub>2</sub> in our experiments.

$$\frac{d[RO_2]_i}{dt} = Pri_i - k_{RO_2RO_2}[RO_2][RO_2]_i - k_{HO_2}[HO_2][RO_2]_i - k_{wall}[RO_2]_i \quad (\text{S2})$$

$$[RO_2]_{i,SS} = \frac{Pri_i}{k_{RO_2RO_2}[RO_2] + k_{HO_2}[HO_2] + k_{wall}} \quad (\text{S3})$$

$$\frac{[RO_2]_{i,SS,highHO_2}}{[RO_2]_{i,SS,lowHO_2}} = \frac{k_{RO_2RO_2}[RO_2]_{SS,lowHO_2} + k_{HO_2}[HO_2]_{SS,lowHO_2} + k_{wall}}{k_{RO_2RO_2}[RO_2]_{SS,highHO_2} + k_{HO_2}[HO_2]_{SS,highHO_2} + k_{wall}} \quad (\text{S4})$$

## 110 **S8 Calculation of condensation rate constant $k_{cond}$**

111 The condensation rate constant  $k_{cond}$  of each compound was calculated as shown in **Eq. (S5)**. Here  $\alpha$  is the accommodation  
 112 coefficient and is set to 1.  $\bar{v}$  is the mean molecular speed calculated from the molar mass of the compound and  $S_{Ptot}$  is the total  
 113 particle surface measured in the chamber.  $f_{FS}$  is the Fuchs-Sutugin factor which is calculated as shown in **Eq. (S6)**, where  $knn$   
 114 is the Knudsen Number calculated as shown in **Eq. (S7)**.  $\bar{s}$  represents the mean free path of the molecule and  $p_{dia}$  the particle  
 115 diameter. For  $p_{dia}$  we used the median diameter of the particle surface distribution measured (McFiggans et al., 2019).

$$k_{cond} = \alpha * f_{FS} * \frac{\bar{v}}{4} * S_{Ptot} \quad (\text{S5})$$

$$f_{FS} = \frac{1 + knn}{1 + (0.75 * \frac{\alpha}{knn}) + knn + (0.283 * \alpha)} \quad (\text{S6})$$

$$knn = \frac{2 * \bar{s}}{p_{dia}} \quad (\text{S7})$$

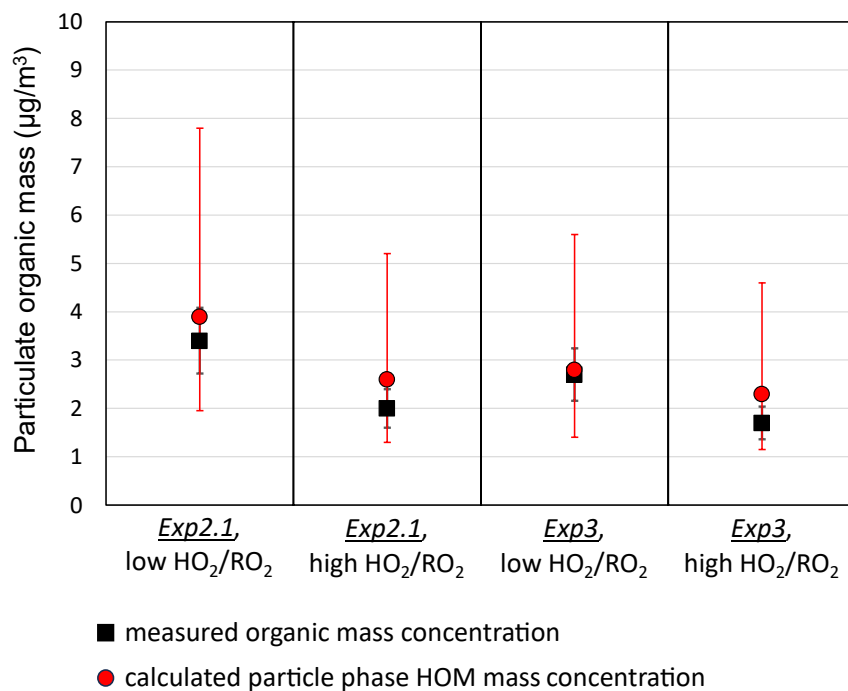


116 **S9 Error estimation via error propagation**

117 Error propagation was utilized to estimate the error of derived parameters. For a parameter  $q$ , the error is defined by the errors  
118 of the variables  $x, \dots, z$  necessary to calculate  $q$ . The general equation to calculate the absolute uncertainty  $\delta q$  can be found in  
119 **Eq. (S8)**. This equation is only valid if the uncertainties in  $x, \dots, z$  are independent and random. (Taylor, 1997)

$$\delta q = \sqrt{\left(\frac{\partial q}{\partial x} \delta x\right)^2 + \dots + \left(\frac{\partial q}{\partial z} \delta z\right)^2} \quad (\text{S8})$$

120 For all measured parameters the measured standard deviation in steady state was used as the absolute uncertainty. For  
121 parameters that cannot be measured directly their uncertainties were calculated with error propagation as shown in **Eq. (S8)**.  
122 For the diffusion coefficient we used uncertainties reported in the literature: Tang et al. (2015) reviewed diffusion coefficient  
123 calculation and came to the result that the difference between measurement and estimation via the method of Fuller et al.  
124 (1966) are mostly below 10 %. Therefore, we assumed a 10 % uncertainty for the diffusion coefficient of each formula  
125 composition.



127

128 Figure S3: Comparison of particulate, organic mass concentration (measured by AMS) and approximation from NO<sub>3</sub>-MION-  
 129 CIMS measurements. Error of AMS measurement is estimated as 20%. For calculated particle phase HOM mass  
 130 concentration we assumed an uncertainty of factor 2 in the calibration factor (He et al., 2023).

131 **References**

- 132 Bottorff, B., Lew, M. M., Woo, Y., Rickly, P., Rollings, M. D., Deming, B., Anderson, D. C., Wood, E., Alwe, H. D., Millet,  
133 D. B., Weinheimer, A., Tyndall, G. S., Ortega, J., Dusanter, S., Leonardis, T., Flynn, J., Erickson, M., Alvarez, S., Rivera-  
134 Rios, J. C., Shutter, J. D., Keutsch, F., Helmig, D., Wang, W., Allen, H. M., Slade, J. H., Shepson, P. B., Bertman, S., and  
135 Stevens, P.: OH, HO<sub>2</sub>, and RO<sub>2</sub> radical chemistry in a rural forest environment: measurements, model comparisons, and  
136 evidence of a missing radical sink, *Atmos. Chem. Phys.*, 23, 10287-10311, <https://doi.org/10.5194/acp-23-10287-2023>, 2023.
- 137 Cho, C., Fuchs, H., Hofzumahaus, A., Holland, F., Bloss, W. J., Bohn, B., Dorn, H. P., Glowania, M., Hohaus, T., Liu, L.,  
138 Monks, P. S., Niether, D., Rohrer, F., Sommariva, R., Tan, Z., Tillmann, R., Kiendler-Scharr, A., Wahner, A., and Novelli,  
139 A.: Experimental chemical budgets of OH, HO<sub>2</sub>, and RO<sub>2</sub> radicals in rural air in western Germany during the JULIAC  
140 campaign 2019, *Atmos. Chem. Phys.*, 23, 2003-2033, <https://doi.org/10.5194/acp-23-2003-2023>, 2023.
- 141 Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B.,  
142 Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J.,  
143 Nieminen, T., Kurtén, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petaja,  
144 T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility  
145 secondary organic aerosol, *Nature*, 506, 476-479, <https://doi.org/10.1038/nature13032>, 2014.
- 146 Fuchs, H., Tan, Z. F., Lu, K. D., Bohn, B., Broch, S., Brown, S. S., Dong, H. B., Gomm, S., Häsel, R., He, L. Y.,  
147 Hofzumahaus, A., Holland, F., Li, X., Liu, Y., Lu, S. H., Min, K. E., Rohrer, F., Shao, M., Wang, B. L., Wang, M., Wu, Y. S.,  
148 Zeng, L. M., Zhang, Y. S., Wahner, A., and Zhang, Y. H.: OH reactivity at a rural site (Wangdu) in the North China Plain:  
149 contributions from OH reactants and experimental OH budget, *Atmos. Chem. Phys.*, 17, 645-661, <https://doi.org/10.5194/acp-17-645-2017>, 2017.
- 151 Fuller, E. N., Schettler, P. D., and Giddings, J. C.: New method for prediction of binary gas-phase diffusion coefficients,  
152 *Industrial & Engineering Chemistry*, 58, 18-27, <https://doi.org/10.1021/ie50677a007>, 1966.
- 153 He, X.-C., Shen, J., Iyer, S., Juuti, P., Zhang, J., Koirala, M., Kytökari, M. M., Worsnop, D. R., Rissanen, M., Kulmala, M.,  
154 Maier, N. M., Mikkilä, J., Sipilä, M., and Kangasluoma, J.: Characterisation of gaseous iodine species detection using the  
155 multi-scheme chemical ionisation inlet 2 with bromide and nitrate chemical ionisation methods, *Atmos. Meas. Tech.*, 16, 4461-  
156 4487, <https://doi.org/10.5194/amt-16-4461-2023>, 2023.
- 157 Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for  
158 mechanism development, *Atmos. Environ.*, 31, 81-104, [https://doi.org/10.1016/S1352-2310\(96\)00105-7](https://doi.org/10.1016/S1352-2310(96)00105-7), 1997.
- 159 Jenkin, M. E., Valorso, R., Aumont, B., and Rickard, A. R.: Estimation of rate coefficients and branching ratios for reactions  
160 of organic peroxy radicals for use in automated mechanism construction, *Atmos. Chem. Phys.*, 19, 7691-7717,  
161 <https://doi.org/10.5194/acp-19-7691-2019>, 2019.
- 162 Kürten, A., Rondo, L., Ehrhart, S., and Curtius, J.: Calibration of a chemical ionization mass spectrometer for the measurement  
163 of gaseous sulfuric acid, *J. Phys. Chem. A*, 116, 6375-6386, <https://doi.org/10.1021/jp212123n>, 2012.
- 164 Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Häsel, R., Kita, K., Kondo, Y., Li,  
165 X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., and Hofzumahaus, A.: Atmospheric OH reactivities in the Pearl  
166 River Delta - China in summer 2006: measurement and model results, *Atmos. Chem. Phys.*, 10, 11243-11260,  
167 <https://doi.org/10.5194/acp-10-11243-2010>, 2010.
- 168 McFiggans, G., Mentel, T. F., Wildt, J., Pullinen, I., Kang, S., Kleist, E., Schmitt, S., Springer, M., Tillmann, R., Wu, C., Zhao,  
169 D., Hallquist, M., Faxon, C., Le Breton, M., Hallquist, A. M., Simpson, D., Bergstrom, R., Jenkin, M. E., Ehn, M., Thornton,

- 170 J. A., Alfarra, M. R., Bannan, T. J., Percival, C. J., Priestley, M., Topping, D., and Kiendler-Scharr, A.: Secondary organic  
171 aerosol reduced by mixture of atmospheric vapours, *Nature*, 565, 587-593, <https://doi.org/10.1038/s41586-018-0871-y>, 2019.
- 172 Mihelcic, D., Holland, F., Hofzumahaus, A., Hoppe, L., Konrad, S., M $\ddot{u}$ sgen, P., P $\ddot{a}$ tz, H. W., Sch $\ddot{a}$ fer, H. J., Schmitz, T., Volz-  
173 Thomas, A., B $\ddot{a}$ chmann, K., Schlomski, S., Platt, U., Geyer, A., Alicke, B., and Moortgat, G. K.: Peroxy radicals during  
174 BERLIOZ at Pabstthum: Measurements, radical budgets and ozone production, *J. Geophys. Res. Atmos.*, 108,  
175 <https://doi.org/10.1029/2001JD001014>, 2003.
- 176 Miyazaki, K.: Study of the nature and roles of peroxy radicals in the atmosphere towards the understanding of oxidant  
177 formation using laser-flash photolysis and LIF detection technique, Tokyo Metropolitan University; University of Lille, 2012.
- 178 Rissanen, M. P., Mikkil $\ddot{a}$ , J., Iyer, S., and Hakala, J.: Multi-scheme chemical ionization inlet (MION) for fast switching of  
179 reagent ion chemistry in atmospheric pressure chemical ionization mass spectrometry (CIMS) applications, *Atmos. Meas.*  
180 *Tech.*, 12, 6635-6646, <https://doi.org/10.5194/amt-12-6635-2019>, 2019.
- 181 Sarrafzadeh, M., Wildt, J., Pullinen, I., Springer, M., Kleist, E., Tillmann, R., Schmitt, S. H., Wu, C., Mentel, T. F., and Zhao,  
182 D.: Impact of NO $_x$  and OH on secondary organic aerosol formation from  $\beta$ -pinene photooxidation, *Atmospheric chemistry*  
183 *and physics*, 16, 11237-11248, 2016.
- 184 Saunders, S. M., Jenkin, M. E., Derwent, R., and Pilling, M.: Protocol for the development of the Master Chemical Mechanism,  
185 MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3, 161-180,  
186 <https://doi.org/10.5194/acp-3-161-2003>, 2003.
- 187 Shen, J. and He, X.-C.: MARFORCE-Flowtube model, <https://github.com/momo-catcat/MARFORCE-flowtube> [code],  
188 <https://doi.org/10.5281/zenodo.8318790>, 2023.
- 189 Stevens, P., Mather, J., Brune, W. H., Eisele, F., Tanner, D., Jefferson, A., Cantrell, C., Shetter, R., Sewall, S., Fried, A.,  
190 Henry, B., Williams, E., Baumann, K., Goldan, P., and Kuster, W.: HO $_2$ /OH and RO $_2$ /HO $_2$  ratios during the Tropospheric  
191 OH Photochemistry Experiment: Measurement and theory, *J. Geophys. Res. Atmos.*, 102, 6379-6391,  
192 <https://doi.org/10.1029/96JD01704>, 1997.
- 193 Tan, Z., Lu, K., Hofzumahaus, A., Fuchs, H., Bohn, B., Holland, F., Liu, Y., Rohrer, F., Shao, M., Sun, K., Wu, Y., Zeng, L.,  
194 Zhang, Y., Zou, Q., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Experimental budgets of OH, HO $_2$ , and RO $_2$  radicals  
195 and implications for ozone formation in the Pearl River Delta in China 2014, *Atmos. Chem. Phys.*, 19, 7129-7150,  
196 <https://doi.org/10.5194/acp-19-7129-2019>, 2019.
- 197 Tan, Z., Rohrer, F., Lu, K., Ma, X., Bohn, B., Broch, S., Dong, H., Fuchs, H., Gkatzelis, G. I., Hofzumahaus, A., Holland, F.,  
198 Li, X., Liu, Y., Liu, Y., Novelli, A., Shao, M., Wang, H., Wu, Y., Zeng, L., Hu, M., Kiendler-Scharr, A., Wahner, A., and  
199 Zhang, Y.: Wintertime photochemistry in Beijing: observations of RO $_x$  radical concentrations in the North China Plain during  
200 the BEST-ONE campaign, *Atmos. Chem. Phys.*, 18, 12391-12411, <https://doi.org/10.5194/acp-18-12391-2018>, 2018.
- 201 Tang, M., Shiraiwa, M., P $\ddot{o}$ schl, U., Cox, R., and Kalberer, M.: Compilation and evaluation of gas phase diffusion coefficients  
202 of reactive trace gases in the atmosphere: Volume 2. Diffusivities of organic compounds, pressure-normalised mean free paths,  
203 and average Knudsen numbers for gas uptake calculations, *Atmos. Chem. Phys.*, 15, 5585-5598,  
204 <https://doi.org/10.5194/acp-15-5585-2015>, 2015.
- 205 Taylor, J.: Introduction to error analysis, the study of uncertainties in physical measurements, 1997.
- 206