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Supporting Information

Superoxide Formation from Aqueous Reactions of Biogenic Secondary Organic Aerosols

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| Supporting Information Content | |
|--------------------------------|----|
| Number of pages | 10 |
| Number of tables | 3 |
| Number of figures | 4 |

9 SOA chemistry

10 There are numerous reactions involving SOA components with other reactive functionalities,¹ but
11 it is very challenging to make an exhaustive list with all possible reactions. The main focus of kinetic
12 modeling is on reactions leading to the ROS formation, with the rest of reactions either lumped or omitted
13 in the kinetic model. The termination reaction of α -hydroxyperoxyl radicals by HO_2^\bullet (R7 in Table S2) and
14 $^\bullet\text{OH}$ oxidation of other SOA components represents the lumped reactions with other reactive functionalities,
15 such as aldehydes and ketones. Even at the diffusion-limited rate of $10^{-11} \text{ cm}^3 \text{ s}^{-1}$,² the sensitivity analysis
16 indicates that these reactions have negligible impacts on the formation of radicals and BMPO adducts. For
17 the potential reactions of aldehyde and ROOH, Marteau et al.³ demonstrated that they only act as a minor
18 pathway for the initiation of a $\text{R}(\text{CO})^\bullet$ radical and subsequent autoxidation, while the major pathways are
19 through UV irradiation, transition metal catalysis (not present in our system) and O_2 oxidation (more
20 probable). Furthermore, due to the relatively slow reaction rates of ROOH with ketones/aldehydes⁴ ($k \ll$
21 $1.0 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$), the aldehyde-ROOH reaction is unlikely to be competitive with the unimolecular
22 decomposition of ROOH (R1 in Table S2, $k_1 \sim 10^{-5} \text{ s}^{-1}$). Given that no $^\bullet\text{OH}$ or $\text{O}_2^\bullet\text{-}/\text{HO}_2^\bullet$ would be generated
23 through this reaction³, we did not treat it in the kinetic model. A recent study by Peng and Jimenez⁵
24 discussed the potential formation of organic trioxide (ROOOH) from $\text{RO}_2^\bullet + ^\bullet\text{OH}$ in the PAM chamber,
25 however, it is unlikely that ROOOH would contribute substantially to ROS formation in the aqueous phase
26 as observed in this study. The ROOOH + $^\bullet\text{OH}$ reaction by the H abstraction from the -OOOH is expected
27 to be very fast at a near diffusion-controlled rate ($\sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) to form ROOO $^\bullet$, which rapidly decomposes
28 to RO^\bullet , leading to carbonyl production. Thus, the condensation of ROOOH into the particle phase may not
29 be significant as it should either be decomposed or reacted away prior to or shortly after partitioning. In
30 addition, we compared the ROS formation from SOA samples collected freshly versus the ones stored in a
31 freezer (-20°C) for one month, which showed no statistically significant difference indicating that the
32 compounds responsible for ROS formation in the SOA particles should be relatively stable.

33

34 **H₂O₂ fluorometric assay**

35 The H₂O₂ reactions with •OH and HO₂• (R8, R12 in Table S2) are unlikely to cause noticeable
36 interference in ROS quantification. Specifically, H₂O₂ reacts with both •OH and HO₂• relatively slowly
37 (5.5×10^{-14} and 5.0×10^{-21} cm³ s⁻¹, respectively). Sensitivity analysis indicates that these reactions are
38 negligible pathways for the loss of •OH and HO₂• compared to BMPO trapping. On the other hand, the
39 H₂O₂ probe (i.e., red peroxidase substrate) is in excess when performing H₂O₂ analysis and reacts with H₂O₂
40 relatively fast compared to the H₂O₂-•OH and H₂O₂-HO₂• reactions. This probe is very sensitive and specific
41 to H₂O₂ analysis as it does not yield fluorescence other than from its reaction with H₂O₂. Therefore, it is
42 unlikely that other oxidants interfere with the H₂O₂ analysis. On a related issue, we note that the control
43 experiment showed no EPR signal from BMPO + H₂O₂, indicating no inference of H₂O₂ in the EPR
44 measurement.

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46 **Table S1.** H₂O₂ yields of aqueous reactions of SOA_{O₃} and SOA_{OH}.

| Precursor | H ₂ O ₂ yield of SOA _{O₃} , % | H ₂ O ₂ yield of SOA _{OH} , % |
|-------------|---|--|
| isoprene | 4.2 ± 0.7 | 4.3 ± 0.4 |
| β-pinene | 1.8 ± 0.3 | 0.2 ± 0.05 |
| α-terpineol | 3.2 ± 0.7 | 0.4 ± 0.1 |
| d-limonene | 4.0 ± 0.5 | 0.3 ± 0.07 |

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 48 **Table S2.** Chemical reactions and parameters included in the kinetic model to simulate ROS formation
 49 from aqueous reactions of SOA. In the third column, the first row denotes the uncertainty range, while the
 50 second row denotes values for best fits for SOA_{O₃} and SOA_{OH} (dashed lines in Fig. 3), respectively. The
 51 units of k_1 , k_3 , k_{17} and k_{20} are s⁻¹, while the others are cm³ s⁻¹.

| Reaction number | Reaction | Rate coefficient, best fit and uncertainty range | Refence or comment |
|-----------------|--|--|--------------------------|
| SOA chemistry | | | |
| R1 | ROOH → RO + OH | $k_1 = (0.9 - 6.5) \times 10^{-5}$ $1.1 \times 10^{-5}, 5.2 \times 10^{-5}$ | Determined from MCGA |
| R2 | $R_1R_2CHOH + OH \xrightarrow{O_2} c_1 R_1R_2C(O_2)OH$ | $k_2 = (0.4 - 2.0) \times 10^{-11}$ $0.9 \times 10^{-11}, 2.0 \times 10^{-11}$ $c_1 = 0.16 - 0.30$ 0.28, 0.30 | Determined from MCGA |
| R3 | $R_1R_2C(O_2)OH \rightarrow R_1C(O)R_2 + HO_2$ | $k_3 = 17 - 595$ 456, 492 | Determined from MCGA |
| R4 | OH + ROOH → RO ₂ + H ₂ O | $k_4 = k_8$ | Assumed to be same as R8 |
| R5 | $R_1R_2C(O_2)OH + OH \rightarrow \text{products}$ | 10 ⁻¹¹ (insensitive) | |
| R6 | SOA + OH → SOA' | $k_6 = (0.7 - 9.9) \times 10^{-12}$ $1.5 \times 10^{-12}, 9.8 \times 10^{-12}$ | Determined from MCGA |
| R7 | $R_1R_2C(O_2)OH + HO_2 \rightarrow \text{products}$ | 10 ⁻¹³ (insensitive) | |
| ROS chemistry | | | |
| R8 | $O_2^- + OH \rightarrow O_2 + OH^-$ | $k_7 = 1.3 \times 10^{-11}$ | 6 |
| R9 | $H_2O_2 + OH \rightarrow H_2O + HO_2$ | $k_8 = 5.5 \times 10^{-14}$ | 7 |

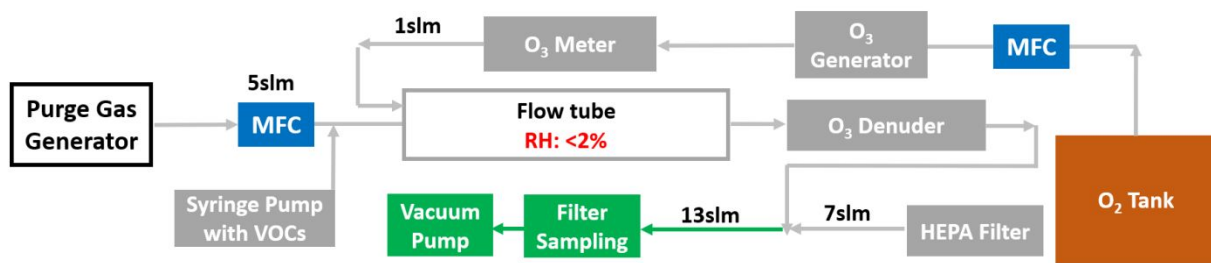
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|----------------|--|--|-------------------------|
| R10 | $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$ | $k_9 = 8.6 \times 10^{-12}$ | 8 |
| R11 | $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$ | $k_{10} = 1.2 \times 10^{-11}$ | 8 |
| R12 | $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ | $k_{11} = 1.4 \times 10^{-15}$ | 9 |
| R13 | $\text{H}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{OH}$ | $k_{12} = 5.0 \times 10^{-21}$ | 10 |
| R14 | $\text{HO}_2 + \text{O}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{OH}^- + \text{O}_2$ | $k_{13} = 1.7 \times 10^{-13}$ | 9 |
| R15 | $\text{H}^+ + \text{O}_2^- \rightarrow \text{HO}_2$ | $k_{14} = 2.9 \times 10^{-11}$ | 11 |
| R16 | $\text{HO}_2 \rightarrow \text{H}^+ + \text{O}_2^-$ | $k_{15} = 2.3 \times 10^5$ | 11 |
| BMPO chemistry | | | |
| R17 | $\text{BMPO} + \text{OH} \rightarrow \text{BMPO} - \text{OH}$ | $k_{16} = (0.1 - 1.3) \times 10^{-12}$ $0.5 \times 10^{-12}, 0.2 \times 10^{-12}$ | Determined from MCGA |
| R18 | $\text{BMPO} - \text{OH} \rightarrow \text{products}$ | $k_{17} = (4.8 - 8.0) \times 10^{-4}$ $7.5 \times 10^{-4}, 7.6 \times 10^{-4}$ | Determined from MCGA |
| R19 | $\text{BMPO} + \text{O}_2^- + \text{H}^+ \rightarrow \text{BMPO} - \text{OOH}$ | $k_{18} = (0.1 - 7.0) \times 10^{-14}$ $4.0 \times 10^{-14}, 3.0 \times 10^{-14}$ | Determined from MCGA |
| R20 | $\text{BMPO} + \text{HO}_2 \rightarrow \text{BMPO} - \text{OOH}$ | $k_{19} = (0.1 - 7.0) \times 10^{-14}$ $2.5 \times 10^{-14}, 6.8 \times 10^{-14}$ | Determined from MCGA |
| R21 | $\text{BMPO} - \text{OOH} \rightarrow \text{products}$ | $k_{20} = (0.8 - 2.0) \times 10^{-3}$ $1.3 \times 10^{-3}, 0.8 \times 10^{-3}$ | Determined from MCGA |

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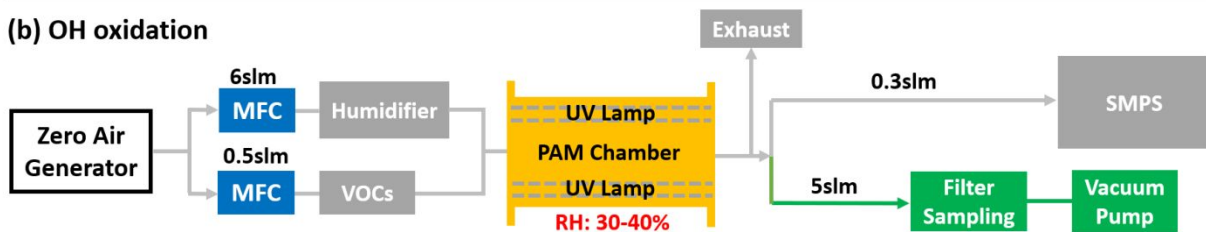
53 **Table S3.** Molar fractions (in percent) of ROOH and R₁R₂CHOH in isoprene, β-pinene, α-terpineol and
54 d-limonene SOA_{O₃} and SOA_{OH}. The values indicate best fit values with uncertainty ranges in brackets.

| Functionality in SOA and reaction yield | SOA _{O₃} | SOA _{OH} |
|---|------------------------------|-------------------|
| %ROOH – isoprene | 10 (6 – 25) | 3 (3 – 5) |
| %ROOH – β-pinene | 12 (7 – 35) | 2 (1 – 3) |
| %ROOH – α-terpineol | 9 (6 – 14) | 1 (1 – 3) |
| %ROOH – d-limonene | 5 (2 – 12) | 3 (2 – 4) |
| %R ₁ R ₂ CHOH – isoprene | 72 (45 – 74) | 78 (40 – 78) |
| %R ₁ R ₂ CHOH – β-pinene | 40 (20 – 61) | 72 (46 – 78) |
| %R ₁ R ₂ CHOH – α-terpineol | 0.2 (0.1 – 1) | 74 (34 – 74) |
| %R ₁ R ₂ CHOH – d-limonene | 78 (57 – 79) | 69 (43 – 73) |

(a) Ozonolysis



(b) OH oxidation

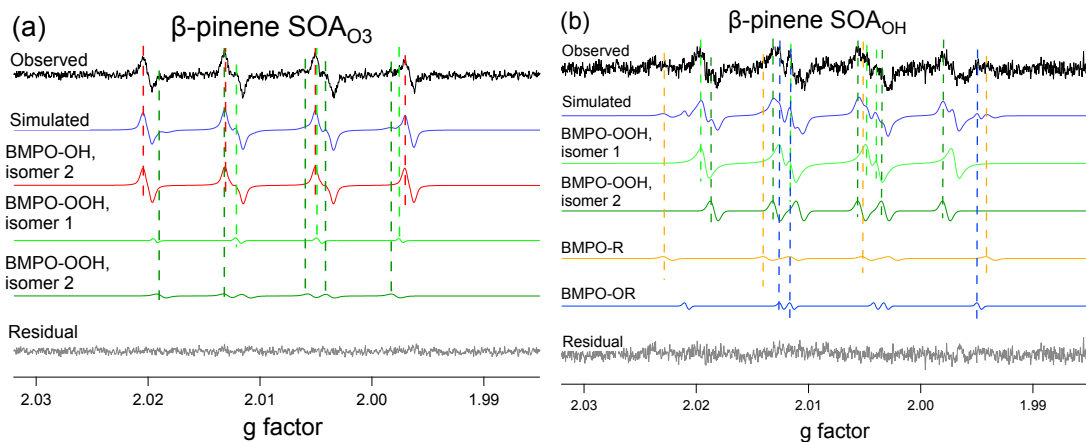


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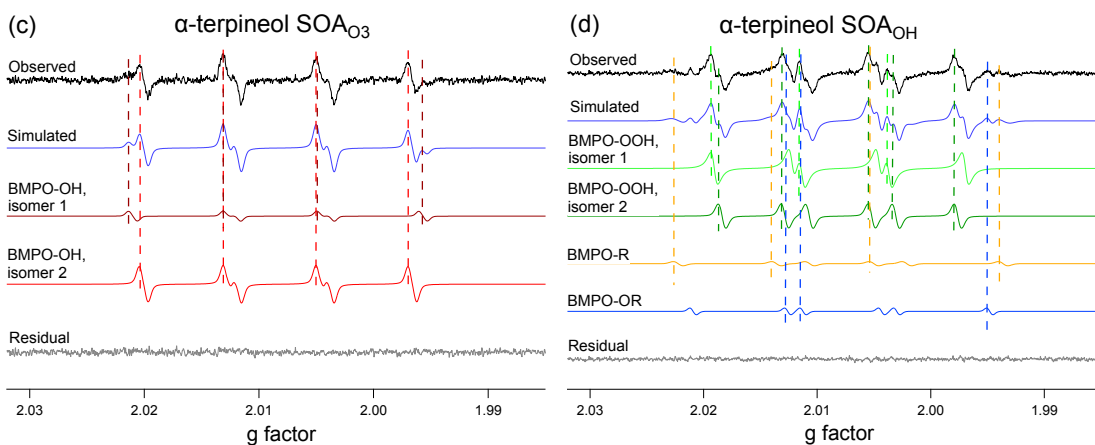
57 **Figure S1.** Schematics of (a) dark ozonolysis in the flow tube and (b) •OH photooxidation in the PAM
58 reactor for generating SOA particles. MFC represents mass flow controller.

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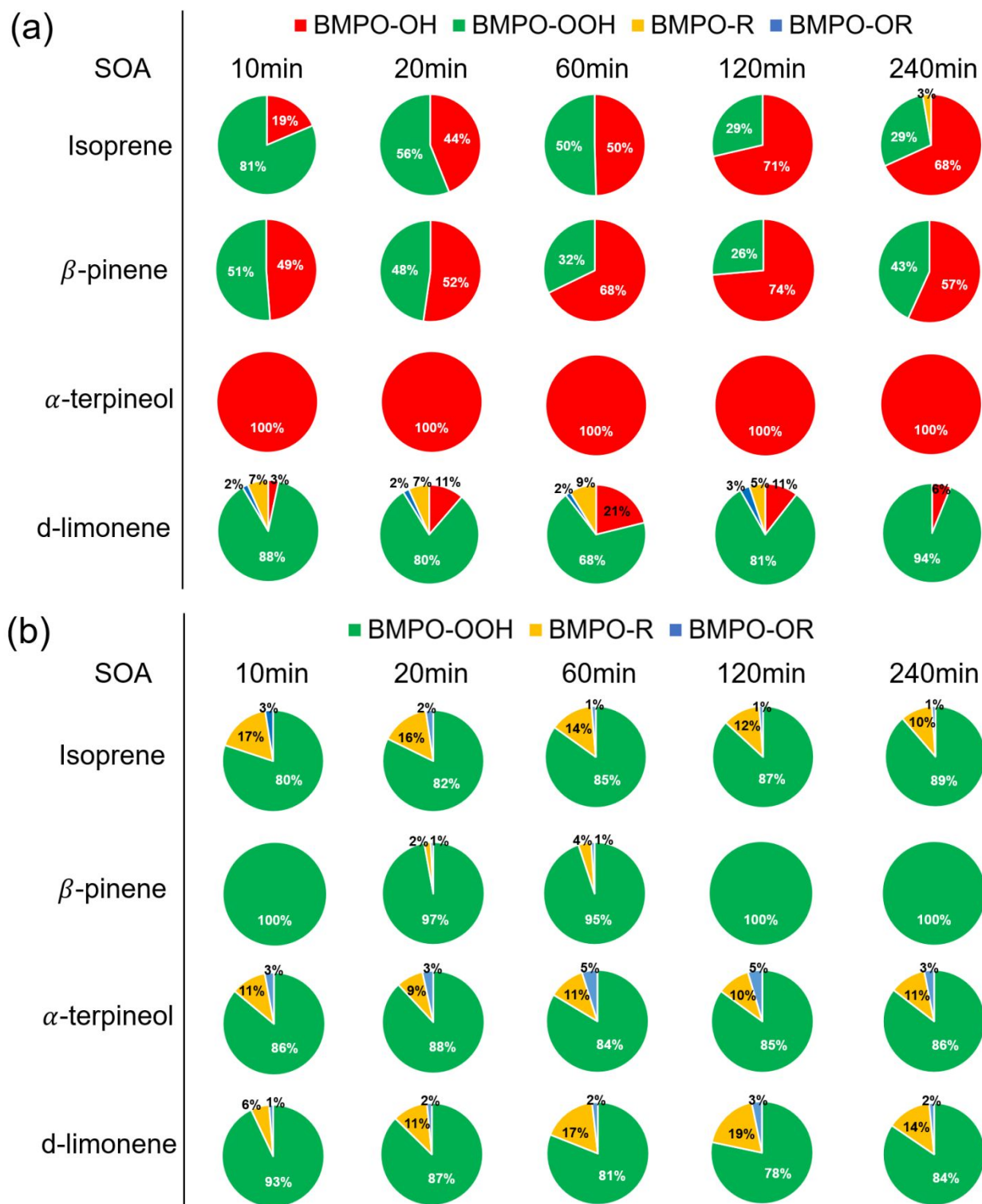
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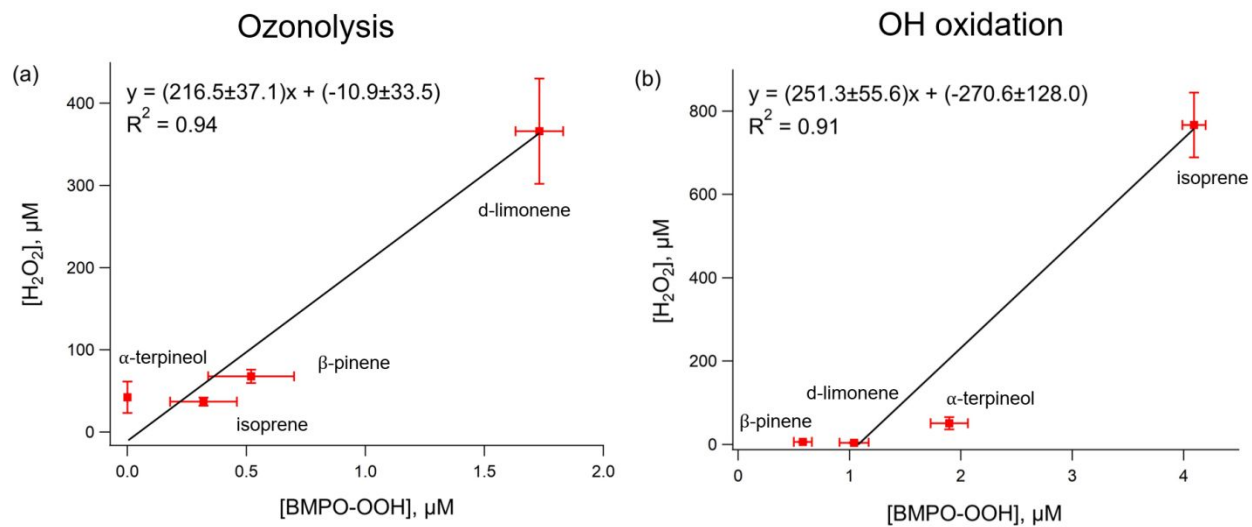
64 **Figure S2.** EPR spectra of sample solutions mixed with the spin-trapping agent BMPO: (a) β -pinene SOA_{O_3} ,
 65 (b) β -pinene SOA_{OH} , (c) α -terpineol SOA_{O_3} , (d) α -terpineol SOA_{OH} , (e) d-limonene SOA_{O_3} , (f) d-limonene
 66 SOA_{OH} . The observed spectra (black) are simulated (purple) and deconvoluted into BMPO-OH isomer 1
 67 (brown), BMPO-OH isomer 2 (red), BMPO-OOH isomer 1 (light green), BMPO-OOH isomer 2 (dark
 68 green), BMPO-R (yellow), BMPO-OR (blue), and residual (grey).



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71 **Figure S3.** Temporal evolution of relative yields of BMPO- radical adduct from aqueous reactions of SOA
 72 generated by (a) ozonolysis versus (b) \cdot OH photooxidation of isoprene, β -pinene, α -terpineol and d-
 73 limonene.



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75 **Figure S4.** Correlation of BMPO-OOH and H₂O₂ concentrations in aqueous reactions of (a) SOA_{O₃} and

76 (b) SOA_{OH}.

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