Supplement of

Aerosol mass yields of selected biogenic volatile organic compounds – a theoretical study with nearly explicit gas-phase chemistry

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1 **Supplement material**

2 Table 1s(a). List of compounds contributing to > 95% of SOA mass yield for α-pinene ozonolysis at 258K. The names of compounds are given in MCM format. The PRAM compounds are highlighted in red.

| Molecular Weight (g/mol) | Species name            | Contribution (%) |
|--------------------------|-------------------------|------------------|
| 430                      | C20H30O10               | 0.16             |
| 198                      | C10H14O4                | 0.17             |
| 462                      | C20H30O12               | 0.18             |
| 214                      | C10H14O5                | 0.18             |
| 174.19                   | C810OOH                 | 0.19             |
| 178.14                   | C621OOH                 | 0.19             |
| 277                      | C10H15O8N1              | 0.19             |
| 130.1                    | H1C23C4CHO              | 0.2              |
| 341                      | C10H15O12N1             | 0.21             |
| 203.19                   | C810NO3                 | 0.22             |
| 446                      | C20H30O11               | 0.22             |
| 293                      | C10H15O9N1              | 0.24             |
| 309                      | C10H15O10N1             | 0.24             |
| 312                      | C10H16O11               | 0.24             |
| 206.19                   | C813OOH                 | 0.25             |
| 190.19                   | C812OOH                 | 0.26             |
| 170.21                   | C89CO2H                 | 0.28             |
| 174.19                   | C811OOH                 | 0.29             |
| 188.22                   | C920OOH                 | 0.29             |
| 220.22                   | C922OOH                 | 0.3              |
| 204.22                   | C921OOH                 | 0.3              |
| 310                      | C10H14O11               | 0.32             |
| 325                      | C10H15O11N1             | 0.33             |
| 235.19                   | C813NO3                 | 0.36             |
| 294                      | C10H14O10               | 0.52             |
| 230                      | C10H14O6                | 0.55             |
| 203.19                   | C811NO3                 | 0.56             |
| 296                      | C10H16O10               | 0.58             |
| 262                      | C10H14O8                | 0.65             |
| 280                      | C10H16O9                | 0.84             |
| 246                      | C10H14O7                | 0.88             |
| 278                      | C10H14O9                | 0.93             |
| 264                      | C10H16O8                | 1.11             |
| 248                      | C10H16O7                | 1.12             |
| 232                      | C10H16O6                | 1.13             |
| Molecular Weight (g/mol) | Species names       | Contribution (%) |
|-------------------------|---------------------|------------------|
| 496                     | C19H28O15           | 0.45             |
| 174.15                  | C717OOH             | 0.53             |
| 344                     | C10H16O13           | 0.57             |
| 446                     | C20H30O11           | 0.59             |
| 448                     | C19H28O12           | 0.62             |
| 248                     | C10H16O7            | 0.67             |
| 200.23                  | HOPINONIC           | 0.7              |
| 462                     | C20H30O12           | 0.7              |
| 480                     | C19H28O14           | 0.76             |
| 186.21                  | PINIC               | 0.77             |
| 188.22                  | C920OOH             | 0.79             |
| 510                     | C20H30O15           | 0.79             |
| 325                     | C10H15O11N1         | 0.8              |
| 464                     | C19H28O13           | 0.82             |
| 373                     | C10H15O14N1         | 0.9              |
| 178.14                  | C621OOH             | 1.03             |
| 478                     | C20H30O13           | 1.1              |
| 246                     | C10H14O7            | 1.17             |

Table 1s(b). List of compounds contributing to > 95% of SOA mass yield for α-pinene ozonolysis at 293K. The names of compounds are given in MCM format.
| Molecular Weight (g/mol) | Species names       | Contribution (%) |
|-------------------------|---------------------|------------------|
| 526                     | C20H30O16           | 0.54             |
| 512                     | C19H28O16           | 0.55             |
| 450                     | C18H26O13           | 0.56             |
| 482                     | C18H26O15           | 0.6              |
| 280                     | C10H16O9            | 0.6              |
| 294                     | C10H14O10           | 0.7              |
| 466                     | C18H26O14           | 0.79             |
| Number | Molecular Formula | Weight | Value |
|--------|-------------------|--------|-------|
| 296    | C10H16O10         | 0.9    |       |
| 278    | C10H14O9          | 1      |       |
| 464    | C19H28O13         | 1.2    |       |
| 204.22 | C98OOH            | 1.42   |       |
| 344    | C10H16O13         | 1.51   |       |
| 496    | C19H28O15         | 1.65   |       |
| 480    | C19H28O14         | 1.77   |       |
| 178.14 | C621OOH           | 1.93   |       |
| 373    | C10H15O14N1       | 1.95   |       |
| 510    | C20H30O15         | 2.57   |       |
| 204.22 | C921OOH           | 3.03   |       |
| 494    | C20H30O14         | 3.15   |       |
| 220.22 | C922OOH           | 3.26   |       |
| 164.11 | C516OOH           | 3.85   |       |
| 357    | C10H15O13N1       | 4.63   |       |
| 312    | C10H16O11         | 5.62   |       |
| 326    | C10H14O12         | 6.04   |       |
| 328    | C10H16O12         | 6.56   |       |
| 235.19 | C813NO3           | 6.83   |       |
| 190.19 | C812OOH           | 6.95   |       |
| 206.19 | C813OOH           | 7.46   |       |
| 310    | C10H14O11         | 18.28  |       |
Figure S1. SOA mass yields for α-pinene oxidation using O₃ for different CS values. For the OFR runs the yields level off above a CS value of 0.067 s⁻¹, while chamber simulation show negligible variation with CS. Hence 0.067 s⁻¹ is selected as CS for the OFR simulations while chamber simulations are run with 0.00067 s⁻¹.
Figure S2. Mass spectra of SOA formed from α-pinene ozonolysis in the particle phase. The upper panel indicates spectra from chamber simulations while the lower panel represents the spectra from OFR simulations.
**Figure S3(a).** MCM and PRAM compounds contributing to > 95% of SOA mass at 258 K and 50 ppb O$_3$ and α-pinene concentrations. It can be noted that a large fraction of the PRAM species that contribute to the SOA mass at 258 K are not classified as HOM (i.e. contain at least 6 oxygen atoms), and many of them will not be detected in the gas-phase using the present state-of-the-art Chemical Ionization-Atmospheric Pressure Interface TOF (CI-API-TOF) technique.
Figure S3(b). MCM and PRAM compounds contributing to > 95% of SOA mass at 313.15 K and 50ppb O$_3$ and α-pinenone concentrations.

The importance of using the MCM+PRAM scheme is illustrated in Fig. S4 which shows the relative contribution by PRAM and MCM compounds for the oxidation of α-pinene, β-pinene and limonene by OH (upper panel) and O$_3$ (lower panel) for their respective maximum SOA mass yields for both chamber and flow tube setup simulations. The present PRAM mechanism does not include the peroxy radical autooxidation products from β-pinene ozonolysis, products from oxidation of isoprene and β-caryophyllene and the products from NO$_3$ oxidation of BVOCs. Therefore, they are excluded from Fig. S4.

The impact of PRAM compounds contribution to limonene ozonolysis, irrespective of chamber or flow tube setup is considered. It is evident from Fig. S4 (lower panel), which shows that upon using the standalone MCM mechanism underpredicts the SOA mass yields with PRAM compounds.
contributing ~ 80% and 60% respectively. For α-pinene ozonolysis, the standalone MCM scheme under-predicts the modelled mass yields by approximately 25 % and 22.5 % respectively.

Figure S4. Relative contribution of HOM and MCM compounds for selected maximum mass yields of α- pinene, β- pinene and limonene oxidation by OH (upper panel) and O₃ (lower panel) at 293.15 K.

Summary of experimental data used for comparison

Kristensen et al., (2017) investigated α-pinene ozonolysis SOA mass yields at temperatures of 258 and 293 K. Additionally SOA mass yields from OH oxidation of α-pinene were also investigated. Yields for α-pinene at higher temperatures of 313 K were investigated by Pathak et al., (2007), wherein they performed experiments using ammonium sulfate seed particles. Shilling et al., (2008) performed experiments for lower concentrations of α-pinene ozonolysis combinations and hence used to compare yields for loading's < 10 µg m⁻³. Griffin et al., (1999) used smog chambers
to investigate the aerosol forming potential of various BVOCs such as β-pinene by ozonolysis and β-caryophyllene by OH oxidation. The SOA mass yields deriev from the OH oxidation of isoprene, β-caryophyllene and β-pinene were experimented by Lee et al., (2006b).

The SOA mass yields derived from the ozonolysis of α-pinene and limonene using an OFR were compared with the experimental yield from Kang and Root, (2007). The experiments also provided estimates on SOA mass yields underestimation when performed with/without acidic seed particles in the OFR. Yields simulated from the OH oxidation of α-pinene were compared against yields measured by (Bruns et al., 2015) as they had used similar initial BVOC and oxidant concentrations. The simulated yields were also compared with experimental yields from Friedman and Farmer, (2018) due to similar initial oxidant concentrations used.