Supplement of
A comparison of secondary organic aerosol (SOA) yields and composition from ozonolysis of monoterpenes at varying concentrations of $\mathrm{NO}_{2}$
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## Kinetics Modeling

To account for uncertainties in measured BVOC and $\mathrm{NO}_{2}$ concentrations during experiments, each experiment was modeled to provide an independent estimate of the full time series of each species as well as to simulate the $1^{\text {st }}$ generation oxidation chemistry.

A simple kinetics box model was written to iteratively solve the differential rate laws for each species expected to be present in the chamber and to mimic the steady state flow conditions (constant addition and dilution) of the chamber, assuming instantaneous mixing. We start each model run allowing either $\mathrm{O}_{3}$ or $\mathrm{O}_{3}+\mathrm{NO}_{2}$ to reach steady state in the chamber. The laboratory $\mathrm{O}_{3}$ source is highly stable and thus matched well by the same initial parameters (flask concentration, flow rate) for every experiment. During this oxidant stabilization period, $\mathrm{NO}_{2}$ is the only chemical sink for $\mathrm{O}_{3}$, so we are able to tune the $\mathrm{NO}_{2}$ source concentration until the modeled and observed $\mathrm{O}_{3}$ time series match. This period is shown in Figure S. 1 in the shaded region. Once oxidant stabilization is achieved, BVOC is added. BVOC addition causes $\mathrm{O}_{3}$ to decay faster, now from both direct reaction with BVOC and additional $\mathrm{NO}_{3}$ formation from $\mathrm{O}_{3}+\mathrm{NO}_{2}$. Since $\left[\mathrm{NO}_{2}\right]$ is well characterized by the time BVOC is added, the BVOC source concentration is the only parameter that needs to be adjusted to match this final $\mathrm{O}_{3}$ decay (unshaded region in Figure S.1).


Figure S.1. Sample model run of $\beta$-pinene with the lowest $\mathrm{NO}_{2}$ concentration showing agreement between modeled and measured $\mathrm{O}_{3}$ and modeled $\mathrm{NO}_{2}+\mathrm{N}_{2} \mathrm{O}_{5}$ to measured $\mathrm{NO}_{2}$ (a, shaded region); agreement between measured and modeled $\mathrm{O}_{3}$ following the addition of $\beta$-pinene (a, unshaded region), and the instantaneous concentrations of bulk oxidation products from each oxidant (b).

The full list of rate constants used is described in Table S.1. Explicit kinetics data exists for all of the initial stages of chemistry (inter-oxidant reactions and BVOC oxidation). While these rate constants, for e.g. $\mathrm{BVOC}+\mathrm{NO}_{3}$, are based on a small number of measurements and thus have significant uncertainty associated with them, the least certain rate constants used here are those describing the fate of the $\mathrm{RO}_{2}$ radical formed following BVOC oxidation.

Table S.1. Rate constants used in kinetics model.

| Reaction | k (298 K) (cm $\mathrm{molec}^{-1} \mathrm{~s}^{-1}$ unless otherwise indicated) | Ref. |
| :---: | :---: | :---: |
| $\mathrm{NO}_{2}+\mathrm{O}_{3}+\mathrm{M} \rightarrow \mathrm{NO}_{3}+\mathrm{O}_{2}+\mathrm{M}$ | $3.5 \times 10^{-17}$ | Atkinson et al. (2004) |
| $\mathrm{NO}_{2}+\mathrm{NO}_{3} \rightarrow \mathrm{~N}_{2} \mathrm{O}_{5}$ | $1.18 \times 10^{-12}$ | Sander et al. (2011) |
| $\mathrm{N}_{2} \mathrm{O}_{5} \rightarrow \mathrm{NO}_{2}+\mathrm{NO}_{3}$ | $0.041 \mathrm{~s}^{-1}$ | Sander et al. (2011) |
| $\mathrm{OH}+\mathrm{NO}_{2}+\mathrm{M} \rightarrow \mathrm{HNO}_{3}+\mathrm{M}$ | $1.1 \times 10^{-11}$ | DeMore et al. (1994) |
| $\mathrm{OH}+\mathrm{HNO}_{3} \rightarrow \mathrm{NO}_{3}+\mathrm{H}_{2} \mathrm{O}$ | $2.7 \times 10^{-39}$ | DeMore et al. (1994) |
| $\mathrm{NO}+\mathrm{NO}_{3} \rightarrow 2 \mathrm{NO}_{2}$ | $2.6 \times 10^{-11}$ | DeMore et al. (1994) |
| $\mathrm{NO}+\mathrm{O}_{3} \rightarrow \mathrm{NO}_{2}+\mathrm{O}_{2}$ | $1.8 \times 10^{-14}$ | DeMore et al. (1994) |
| $\mathrm{NO}_{3}+\mathrm{BVOC} \rightarrow$ products (assumed $\mathrm{RO}_{2}$ ) <br> BVOC $=\alpha$-pinene <br> $\beta$-pinene <br> $\Delta$-carene <br> limonene | $\begin{gathered} 6.2 \times 10^{-12} \\ 2.51 \times 10^{-12} \\ 9.1 \times 10^{-12} \\ 1.22 \times 10^{-11} \end{gathered}$ | Atkinson and Arey (2003) |
| $\begin{aligned} & \hline \mathrm{O}_{3}+\mathrm{BVOC} \rightarrow \text { products (assumed } \\ & \left.\mathrm{RO}_{2}\right) \\ & \mathrm{BVOC}=\alpha \text {-pinene } \\ & \beta \text {-pinene } \\ & \Delta \text {-carene } \\ & \\ & \text { limonene } \\ & \hline \end{aligned}$ | $\begin{aligned} & 8.4 \times 10^{-17} \\ & 1.5 \times 10^{-17} \\ & 3.7 \times 10^{-17} \\ & 2.1 \times 10^{-16} \end{aligned}$ | Atkinson and Arey (2003) |
| $\mathrm{OH}+\mathrm{BVOC} \rightarrow$ products (assumed $\mathrm{RO}_{2}$ ) <br> BVOC $=\alpha$-pinene <br> $\beta$-pinene <br> $\Delta$-carene <br> limonene | $\begin{gathered} 5.23 \times 10^{-11} \\ 7.43 \times 10^{-11} \\ 8.8 \times 10^{-11} \\ 1.64 \times 10^{-10} \end{gathered}$ | Atkinson and Arey (2003) |
| $\begin{gathered} \mathrm{O}_{3}+\mathrm{BVOC} \rightarrow \mathrm{OH} \\ \mathrm{BVOC}=\alpha \text {-pinene } \\ \beta \text {-pinene } \\ \hline \end{gathered}$ | $\begin{aligned} & 0.85 \times\left(8.4 \times 10^{-17}\right) \\ & 0.35 \times\left(1.5 \times 10^{-17}\right) \end{aligned}$ | Atkinson and Arey (2003) ( $\mathrm{O}_{3}$ rate constants); |


| $\Delta$-carene <br> limonene | $1.06 \times\left(3.7 \times 10^{-17}\right)$ <br> $0.86 \times\left(2.1 \times 10^{-16}\right)$ | Atkinson et al. <br> $(1992)(\mathrm{OH}$ <br> yields) |
| :--- | :---: | :--- |
| $\mathrm{RO}_{2}+\mathrm{RO}_{2} \rightarrow$ products | $1 \times 10^{-15}-1 \times 10^{-12}$ | Ziemann and <br> Atkinson (2012); <br> Ehn et al. (2014); <br> Orlando and <br> Tyndall (2012); <br> Lightfoot et al. <br> $(1992)$ |
| $\mathrm{RO}_{2}+\mathrm{NO}_{3} \rightarrow$ products | $2 \times 10^{-12}$ | Vaughan et al. <br> $(2006) ;$ Orlando <br> and Tyndall <br> $(2012)$ |
| $\mathrm{RO}_{2}+\mathrm{NO}_{2} \rightarrow \mathrm{ROONO}_{2}$ | $4.8 \times 10^{-11}$ | Sander et al. <br> $(2011)$ |
| $\mathrm{ROONO}_{2} \rightarrow \mathrm{RO}_{2}+\mathrm{NO}_{2}$ | $22 \mathrm{~s}^{-1}$ | Sander et al. <br> $(2011)$ |

The three most likely reaction partners to $\mathrm{RO}_{2}$ radicals in these experiments are $\mathrm{RO}_{2}$, $\mathrm{NO}_{3}$, and $\mathrm{NO}_{2} . \mathrm{HO}_{2}$ chemistry is not incorporated into the model, as we expect mainly tertiary $\mathrm{RO}_{2}$ to form and thus negligible $\mathrm{HO}_{2}$ production. We note that this lack of $\mathrm{HO}_{2}$ is a significant deviation from the real atmosphere where nighttime $\mathrm{HO}_{2}$ concentrations can be comparable to $\mathrm{RO}_{2}$ concentrations (Wolfe et al., 2014; Andres-Hernandez et al., 2013). In these experiments, we understand the relative rate constants of $\mathrm{RO}_{2}+\mathrm{RO}_{2}$ and $\mathrm{RO}_{2}+\mathrm{NO}_{3}$ to be the most substantial driver of how much BVOC reacts in the $\mathrm{NO}_{2}-$ influenced experiments because they determine how much $\mathrm{NO}_{3}$ remains available to react with BVOC. $\mathrm{RO}_{2}+\mathrm{NO}_{2}$ will affect both the $\mathrm{RO}_{2}$ reservoir as well as $\mathrm{NO}_{3}$ formation potential, but since the products $\left(\mathrm{ROONO}_{2}\right)$ are understood to be fairly unstable (Sander et al., 2011), they decompose appreciably back into $\mathrm{RO}_{2}$ and $\mathrm{NO}_{2}$ and thus are not as directly influential on [BVOC]. The $\mathrm{RO}_{2}+\mathrm{NO}_{3}$ rate constant has been measured to be approximately $2 \times 10^{-12} \mathrm{~cm}^{3} \mathrm{molec}^{-1} \mathrm{~s}^{-1}$ for multiple $\mathrm{RO}_{2}$. It has not been measured for the $\mathrm{RO}_{2}$ radicals expected to be in this system, but the rate constant does not seem to show a strong dependence on size or branching of the $\mathrm{RO}_{2}$ and thus the molecules for which it has been measured are likely a good proxy for the chemistry here (Vaughan et al., 2006). The $\mathrm{RO}_{2}+\mathrm{RO}_{2}$ rate constants that have been measured, however, are much more variable. Examination of trends in the literature shows that increasing the size (\# C atoms) of the $\mathrm{RO}_{2}$ radical can increase its self-reaction rate constant by multiple orders of magnitude; increasing branching of the $\mathrm{RO}_{2}$ (from primary to tertiary) decreases the rate constant by multiple orders of magnitude; functional group substitution at the $\beta$-carbon can increase the rate constant by up to two orders of magnitude (Ziemann and Atkinson, 2012; Orlando and Tyndall, 2012; Lightfoot et al., 1992).

In each monoterpene system, we expect to be making mainly tertiary, $\mathrm{NO}_{3}{ }^{-}$ functionalized $\mathrm{C}_{10} \mathrm{RO}_{2}$ 's. Having a $\beta$-nitrato tertiary $\mathrm{RO}_{2}$ gives us our low estimate of the $\mathrm{RO}_{2}+\mathrm{RO}_{2}$ rate constant $\left(\mathrm{k}=1 \times 10^{-15} \mathrm{~cm}^{3} \mathrm{molec}^{-1} \mathrm{~s}^{-1}\right)$ (Ziemann and Atkinson,

2012; Atkinson, 1997). These $\mathrm{C}_{10}$ 's are at least 4 carbons bigger than any with measured rate constants, though, and thus it is entirely possible that the real rate constant is a few orders of magnitude higher. For this study we choose $\mathrm{k}=1 \times 10^{-12} \mathrm{~cm}^{3} \mathrm{molec}^{-1} \mathrm{~s}^{-1}$ as a reasonable upper limit (Ehn et al., 2014). This difference of 3 orders of magnitude dominates the uncertainty for this modeling approach. Using each of these two $\mathrm{RO}_{2}+$ $\mathrm{RO}_{2}$ rate constants, we can then determine the BVOC source concentration that matches the observed $\mathrm{O}_{3}$ decay, thus giving us a best estimate range of [BVOC].

Once the precursor concentrations are decided upon, the percentage of BVOC reacted by each oxidant is calculated within the model (Figure S.2). Since no OH scavenger was used during experiments, we assume that stabilized Criegee intermediates from ozonolysis produced OH at the yields reported by (Atkinson et al., 1992; shown in Table S.1).


Figure S.2. Sample model run of $\beta$-pinene with the lowest $\mathrm{NO}_{2}$ concentration showing the cumulative oxidation products from each oxidant.

## BVOC measurement and characterization of uncertainties

As described in the main body of the text, the BVOC delivery system was designed to maintain a constant vapor pressure of the BVOC in the source flask, which could then be flowed continuously into the chamber. This constant vapor pressure was achieved by injecting a small ( $<0.2 \mathrm{~mL}$ ) liquid sample of the monoterpene into a flask submerged into a chiller bath held at the appropriate temperature to give a concentration of 100 ppm in the headspace of the flask (Figure S.3). This methodology relies on several assumptions. We assume that the vapor pressure-driven concentration (and temperature) inside the flask reaches equilibrium within the residence time of the flask. $(14 \mathrm{~mL} / \mathrm{min}$ air flow through a 100 mL flask $\approx 7 \mathrm{~min})$. We also assume that the surface area of the liquid sample remains constant over time. However, in nearly every experiment, the measured VOC flask concentration decreased over time, in some cases by $>50 \%$, suggesting that one or more of the above assumptions are not true.


Figure S.3. Temperature dependence of vapor pressure of $\alpha$-pinene, $\beta$-pinene, and limonene (Haynes et al., 2012). $\Delta$-3-carene is assumed to reach the target vapor pressure at $-25^{\circ} \mathrm{C}$, between $\alpha$-pinene and $\beta$-pinene.

To obtain an independent estimate of what the actual gas-phase chamber concentrations were during each experiment, data was fit using the gas-phase kinetics model described above, where $\mathrm{NO}_{2}$ and BVOC are both tunable to fit the observed $\mathrm{O}_{3}$ decay. The largest source of uncertainty in the model affecting the predicted BVOC concentration is the $\mathrm{RO}_{2}+\mathrm{RO}_{2}$ rate constant, which is unknown for the $\mathrm{RO}_{2}$ species formed from this chemistry and thus must be approximated from much smaller proxy molecules. We chose a range shown in Table S.1, spanning three orders of magnitude in $\mathrm{k}_{\mathrm{RO} 2+\mathrm{RO} 2}$, which predicts a range of BVOC concentrations that varies by no more than a factor of two. GC measurements directly from the source flask are averaged for each experiment and plotted against the range of modeled BVOC concentrations for that experiment (Figure S.4). In this study we use the modeled values as the bounds of the BVOC concentration during each experiment in order to have a complete BVOC time series. We acknowledge that these values may be overestimates of [BVOC] according to Figure S.4, and thus the yields shown in Table 3 would be lower limits to the true yields.


Figure S.4. Average GC-FID measurements of BVOC source concentrations plotted against the BVOC source concentration range predicted by kinetics modeling for each experiment. Solid lines indicate the range in modeled values calculated using the upper and lower limits of $\mathrm{k}_{\mathrm{RO} 2+\mathrm{RO} 2}$. $\mathrm{O}_{3}$-only experiments do not have a range because they did not have competing $\mathrm{RO}_{2}+\mathrm{RO}_{2}$ and $\mathrm{RO}_{2}+\mathrm{NO}_{3}$ chemistry and thus the predicted BVOC was independent of $\mathrm{k}_{\mathrm{RO} 2+\mathrm{RO} 2}$. Dashed line indicates where model and measurements would show perfect agreement.

One possible explanation for the systematic bias of limonene below the $1: 1$ line (modeled $>$ measured) in Figure S. 4 is the possibility of the oxidation of the $2^{\text {nd }}$ double bond (Zhang et al., 2006) since the model generates [BVOC] assuming a single BVOC + oxidant reaction.

## Wall loss characterization

Aerosol wall losses in this chamber were characterized according to the method employed by several previous studies (McMurry et al., 1985; Fry et al., 2014). An approximately 0.02 M solution of $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ was atomized, dried through a diffusion dryer, and measured directly into the SEMS to obtain a known input aerosol distribution. The concentration of the seed solution was optimized to span the full size range (20-800 nm ) of aerosol that was observed during experiments. The seed aerosol at the same flow rate was then introduced into the chamber and measured with the SEMS at the outlet of the chamber (Figure S.5a). First order size-dependent wall loss coefficients, $\beta\left(D_{p}\right)$, were calculated according to Eq. 1, using average size distributions going into ( $\mathrm{N}_{\text {in }}$ ) and coming out of the chamber $\left(\mathrm{N}_{\text {out }}\right)$, the chamber flow rate $(\mathrm{Q})$, chamber volume $(\mathrm{V})$, and assuming the chamber to behave as a continuously stirred tank reactor.

$$
\begin{equation*}
\beta\left(D_{p}\right)=\left(\frac{Q}{V}\right)\left[\left(\frac{N_{\text {in }}\left(D_{p}\right)}{N_{\text {out }}\left(D_{p}\right)}\right)-1\right] \tag{1}
\end{equation*}
$$



Figure S.5. (a) Input and output number size distributions of the seed aerosol entering and leaving the chamber; (b) Size-dependent wall loss rates; Uncorrected and corrected time series of total aerosol number concentrations (c) and mass (d) from a representative experiment ( $\alpha$-pinene $+\mathrm{O}_{3}$ ).

Raw size distributions from experiments were corrected cumulatively for wall losses (McMurry et al., 1985; Fry et al., 2014). At each time step, loss rates were multiplied by the raw size distribution to determine how many particles in each size bin were lost to the walls. These losses were then added back to the corrected dataset. This process assumes that any particle lost to the walls remains there and does not grow past the size it was when it was lost. This method provides reasonable corrections for total mass and total number of particles produced, but adding back static sized particles obscures observed growth dynamics. Figure S. 6 shows a representative uncorrected and corrected growth event, illustrating how the particles added back remain at the size they were when they were lost to the walls.


Figure S.6. Uncorrected (top) and wall loss corrected (bottom) aerosol growth events from a representative experiment ( $\alpha$-pinene $+\mathrm{O}_{3}$ ).

## Identification of products from HPLC-ESI-MS

Chromatographic separation coupled to high resolution mass spectrometry allows for relatively straightforward identification of products. A list of compounds was generated for each experiment from both positive and negative ion modes, using Agilent MassHunter software and employing a minimum relative intensity threshold of $1.5 \%$ of the highest intensity peak. Compound lists were then manually adjusted to ensure accurate ion adduct assignments, removal of redundant adducts at identical retention times, and formula assignments with consistent relative mass error. Although the product threshold was governed by relative intensity instead of an absolute cutoff, each of the software-identified products was manually searched for, at the same retention time, in the other experiments studying the same monoterpene. If any of those products were not identified by the software, but present at $>3000$ counts, they were added back to the product list for that experiment. This was done to minimize reporting $\mathrm{NO}_{3}$ products that "are not formed" by $\mathrm{O}_{3}$ oxidation, and vice versa, if they are formed but were missed by the software. Table S. 2 shows the complete list of products included in Table 6 and Figure 7. Table S. 3 lists the most intense peaks and includes proposed structures according to specific products other studies have identified in similar systems as well as speculative structures simply showing that some of the high molecular weight products observed could be reasonably formed via oligomerization reactions of known monomers from these systems.

Table S.2. SOA compound formulae identified by HPLC-ESI-MS. Tables organized into $\mathrm{O}_{3}$ and $\mathrm{NO}_{3}$ regimes for each monoterpene, where any compound present in both oxidant regimes is only listed in the $\mathrm{O}_{3}$ regime. Unless otherwise stated (see notes), compounds were observed only in the positive ion mode. Masses and formulae refer to the precursor (non-adduct) compound, which is reported as the nominal mass for any adducts mis-assigned by the software.

| $\alpha$-pinene $+\mathrm{O}_{3}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Mass | Formula | Relative Mass <br> Difference (MFG) | RT | Notes |
| 184.1115 | C10 H16 O3 | -8.32 | 7.1 | b |
| 106.079 | C8 H10 | -6.91 | 7.184 |  |
| 168.117 | C10 H16 O2 | -11.65 | 7.212 |  |
| 182.1328 | C11 H18 O2 | -11.42 | 7.213 |  |
| 168 | C10 H16 O2 | -13.15 | 8.685 |  |
| 168 | C10 H16 O2 | -7.64 | 9.109 |  |
| 152.1214 | C10 H16 O | -8.47 | 9.377 |  |
| 376.193 | C21 H28 O6 | -11.76 | 10.238 |  |
| 243.1852 | C13 H25 N O3 | -7.36 | 11.029 | b |
| 421 | C21 H27 N O8 | -10.33 | 11.67 | b |
| 289.2647 | C16 H35 N O3 | -10.5 | 11.877 |  |
| 216.1756 | C12 H24 O3 | -14.1 | 11.971 |  |
| 128.121 | C8 H16 O | -6.74 | 11.971 |  |
| 287.2863 | C17 H37 N O2 | -13.31 | 11.982 |  |
| 229.2437 | C14 H31 N O | -13.81 | 12.022 |  |
| 216.1755 | C12 H24 O3 | -13.78 | 12.027 |  |
| 287.285 | C17 H37 N O2 | -9.01 | 12.242 |  |
| 240.0714 | C10 H12 N2 O5 |  | 12.694 | c |
| 276.1769 | C17 H24 O3 | -15.91 | 12.697 |  |
| 220.1128 | C13 H16 O3 | -13.08 | 12.697 |  |
| 466 | C33 H22 O3 | 5.57 | 12.716 | c |
| 342.152 | C20 H22 O5 | -15.27 | 13.145 | a |
| 148.0178 | C8 H4 O3 | -11.81 | 13.293 | d |
| 278.1553 | C16 H22 O4 | -12.67 | 13.294 | d |
| 204.0815 | C12 H12 O3 | -13.98 | 13.294 | d |
| 278.1554 | C16 H22 O4 | -12.79 | 13.454 | d |
| 148.0179 | C8 H4 O3 | -12.3 | 13.455 | d |
| 228.2052 | C14 H28 O2 | 16.29 | 13.528 | c |

a) Peak only appears in $\mathrm{O}_{3}$ experiment.
b) Peak present in both positive and negative ion mode.
c) Peak present in negative ion mode only.
d) Known phthalate impurity.

| $\alpha$-pinene + NO (excluding products listed in $\alpha$-pinene $+\mathrm{O}_{3}$ ) |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| Mass | Formula | Relative Mass <br> Difference (MFG) | RT | Notes |
| 186.0863 | C9 H14 O4 | 15.8 | 5.802 | c |
| 138.106 | C9 H14 O | -10.84 | 7.1 |  |
| 114.0692 | C6 H10 O2 | -9.8 | 7.1 |  |
| 213 | C10 H15 N O4 | -11.54 | 9.763 |  |
| 201 | C9 H15 N O4 | -14.11 | 9.951 |  |
| 152.1207 | C10 H16 O | -3.79 | 11.236 |  |
| 215 | C10 H17 N O4 | -10.25 | 11.236 |  |
| 231 | C10 H17 N O5 | -12.33 | 11.315 |  |
| 366 | C20 H30 O6 | -12.89 | 11.684 |  |
| 310 | C18 H30 O4 | -11.55 | 11.867 |  |
| 260 | C10 H16 N2 O6 | -10.05 | 12.135 |  |
| 383.1987 | C19 H29 N O7 | -11.09 | 13.433 | b |
| 256.2363 | C16 H32 O2 | 15.18 | 17.179 | c, |
| 215.0551 | C12 H9 N O3 | 14.75 | 11.425 | c |
| 229.2426 | C14 H31 N O | -9.08 | 11.857 |  |
| 276.176 | C17 H24 O3 | -12.47 | 12.434 |  |

a) Peak only appears in $\mathrm{O}_{3}$ experiment.
b) Peak present in both positive and negative ion mode.
c) Peak present in negative ion mode only.
d) Known phthalate impurity.

| $\boldsymbol{\beta - p i n e n e + \mathbf { O } _ { 3 }}$ |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| Mass | Formula | Relative Mass <br> Difference (MFG) | RT | Notes |
| 186.091 | C9 H14 O4 | -9.51 | 5.902 |  |
| 154.1001 | C9 H14 O2 | -4.94 | 5.923 |  |
| 169.1112 | C9 H12 O2 | -5.26 | 6.125 |  |
| 94.0789 | C7 H10 | -7.3 | 6.952 |  |
| 108.0942 | C8 H12 | -2.54 | 6.953 |  |
| 154.0998 | C9 H14 O2 | -2.87 | 6.954 |  |
| 184.111 | C10 H16 O3 | -5.5 | 7.1 | b |
| 182.1315 | C11 H18 O2 | -4.44 | 7.21 |  |
| 168.1159 | C10 H16 O2 | -5.42 | 7.211 |  |
| 154.0999 | C9 H14 O2 | -3.27 | 7.579 |  |
| 170 | C10 H18 O2 | -5.75 | 8.861 |  |
| 138.1048 | C9 H14 O | -2.59 | 9.058 |  |
| 82.0427 | C5 H6 O | -10.45 | 9.06 |  |
| 358 | C17 H26 O8 | -8.98 | 9.231 | a, b |
| 138.1053 | C9 H14 O | -5.79 | 9.286 |  |
| 170 | C10 H18 O2 | -6.1 | 9.348 |  |
| 376.1919 | C21 H28 O6 | -8.85 | 10.24 |  |


| 370.2015 | C19 H30 O7 | -6.22 | 10.782 | a, $b$ |
| :--- | :--- | :--- | :--- | :--- |
| 243.1849 | C13 H25 N O3 | -6.05 | 11.03 | b |
| 421 | C21 H27 N O8 | -8.43 | 11.673 | b |
| 287.2845 | C17 H37 N O2 | -7.21 | 11.985 |  |
| 287.284 | C17 H37 N O2 | -5.3 | 12.245 |  |
| 240.0706 |  | 14.02 | 12.695 | a, c |
| 278.1537 | C16 H22 O4 | -6.77 | 13.293 | d |
| 148.0165 | C8 H4 O3 | -3.24 | 13.293 | d |
| 278.1536 | C16 H22 O4 | -6.56 | 13.452 | d |
| 148.0164 | C8 H4 O3 | -2.41 | 13.452 | d |
| 204.0803 | C12 H12 O3 | -8.04 | 13.453 | d |
| 256.2354 | C16 H32 O2 | 18.66 | 17.254 | c |

a) Peak only appears in $\mathrm{O}_{3}$ experiment.
b) Peak present in both positive and negative ion mode.
c) Peak present in negative ion mode only.
d) Known phthalate impurity.

| $\beta$-pinene + NO3 (excluding products listed in $\beta$-pinene $+\mathrm{O}_{3}$ ) |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| Mass | Formula | Relative Mass <br> Difference (MFG) | RT | Notes |
| 170 | C10 H18 O2 | -2.67 | 7.173 |  |
| 227.0811 | C10 H13 N O5 | -7.5 | 8.255 |  |
| 245.0857 | C10 H15 N O6 | 17.12 | 8.901 | c |
| 229 | C10 H15 N O5 | -4.38 | 9.245 |  |
| 186 | C10 H18 O3 | -1.84 | 9.614 |  |
| 264.133 | C10 H20 N2 O6 | -3.33 | 9.644 |  |
| 230.1281 | C10 H18 N2 O4 | -6.15 | 9.767 |  |
| 277.1107 | C11 H19 N O7 | 19.83 | 9.789 | c |
| 184.1059 | C10 H16 O3 |  | 10.358 | c |
| 227.1904 | C13 H25 N O2 | -8.17 | 11.107 |  |
| 229.0909 | C10 H15 N O5 | 17.94 | 11.226 | c |
| 230.1278 | C10 H18 N2 O4 | -4.77 | 11.233 |  |
| 215 | C10 H17 N O4 | -2.94 | 11.241 |  |
| 197.1066 | C10 H15 N O3 | -7.08 | 11.382 |  |
| 215 | C10 H17 N O4 | -2.5 | 11.382 |  |
| 134.1094 | C10 H14 | 0.92 | 11.382 |  |
| 156.1117 |  |  | 11.386 | c |
| 96.0581 | C6 H8 O | -5.97 | 11.386 |  |
| 152.1197 | C10 H16 O | 2.44 | 11.386 |  |
| 217.1685 | C11 H23 N O3 | -3.26 | 11.415 |  |
| 215.054 | C12 H9 N O3 | 19.61 | 11.7334 | c |
| 215 | C10 H17 N O4 | -3.42 |  |  |
| 277.1109 | C11 H19 N O7 | 18.8 |  |  |
| 231 | C10 H17 N O5 | -2.01 |  |  |
|  |  |  | 1.734 |  |
|  |  |  |  |  |


| 260.1382 | C11 H20 N2 O5 | -3.77 | 11.944 |  |
| :--- | :--- | :--- | :--- | :--- |
| 260 | C10 H16 N2 O6 | -3.69 | 12.139 |  |
| 260 | C10 H16 N2 O6 | -3.16 | 12.722 |  |
| 397.2037 | C20 H31 N O7 | 15.95 | 13.802 | c |
| 383.1882 | C19 H29 N O7 | 16.06 | 13.845 | c |
| 430.2329 | C20 H34 N2 O8 | -3.11 | 14.298 |  |
| 413.1976 | C20 H31 N O8 | 17.88 | 14.316 | c |
| 413 | C21 H35 N O7 | -3.6 | 14.858 |  |
| 385 | C19 H31 N O7 | -4.71 | 15.6 |  |
| 429 | C21 H35 N O8 | -3.15 | 15.608 |  |
| 431.209 | C20 H33 N O9 | 15.11 | 15.629 | c |
| 415 | C20 H33 N O8 | -5.37 | 15.895 |  |
| 442 | C20 H30 N2 O9 | -4.83 | 15.977 |  |
| 428.2174 | C20 H32 N2 O8 | -3.65 | 16.684 | b |
| 444 | C20 H32 N2 O9 | -5.54 | 16.807 |  |
| 460 | C20 H32 N2 O10 | -2.88 | 17.298 |  |

a) Peak only appears in $\mathrm{O}_{3}$ experiment.
b) Peak present in both positive and negative ion mode.
c) Peak present in negative ion mode only.
d) Known phthalate impurity.

| $\Delta$-carene + O3 |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| Mass | Formula | Relative Mass <br> Difference (MFG) | RT | Notes |
| 154.098 | C9 H14 O2 | 8.63 | 6.676 | a |
| 186.0886 | C9 H14 O4 | 3.12 | 7.494 | $\mathrm{a}, \mathrm{c}$ |
| 184.1086 | C10 H16 O3 | 7.32 | 7.706 | b |
| 114.0675 | C6 H10 O2 | 5.22 | 7.73 |  |
| 184.1094 | C10 H16 O3 | 3.15 | 8.155 | c |
| 222.1209 | C11 H20 O3 | 10.28 | 8.211 |  |
| 184.1086 | C10 H16 O3 | 7.33 | 8.28 |  |
| 138.1032 | C9 H14 O | 8.99 | 8.311 |  |
| 200 | C11 H20 O3 | 7.55 | 8.434 |  |
| 92.0631 | C7 H8 | -4.95 | 8.44 |  |
| 122.1089 | C9 H14 | 5.05 | 8.442 |  |
| 106.0777 | C8 H10 | 5.1 | 8.445 |  |
| 168.1137 | C10 H16 O2 | 7.62 | 9.029 |  |
| 201.1353 | C10 H16 O3 | 5.94 | 9.049 |  |
| 138.1032 | C9 H14 O | 9.16 | 9.263 |  |
| 168 | C10 H16 O2 | 9.3 | 10.032 |  |
| 168 | C10 H16 O2 | 7.51 | 11.021 |  |
| 168.1139 | C10 H16 O2 | 6.93 |  |  |
| 170 | C10 H18 O2 | 6.74 | 4.33 |  |
| 222.0882 | C12 H14 O4 |  |  |  |
|  |  | 9.523 |  |  |


| 243.1813 | C13 H25 N O3 | 8.63 | 11.482 | b |
| :--- | :--- | :--- | :--- | :--- |
| 294.1457 | C16 H22 O5 | 3.55 | 11.833 | a |
| 287.2808 | C17 H37 N O2 | 5.53 | 12.356 |  |
| 287.2807 | C17 H37 N O2 | 6.09 | 12.609 |  |
| 220.1082 | C13 H16 O3 | 7.97 | 13.055 |  |
| 160.0875 | C9 H14 O |  | 13.055 |  |
| 276.1708 | C17 H24 O3 | 6.4 | 13.056 |  |
| 148.0147 | C8 H4 O3 | 9.37 | 13.681 | d |
| 278.1501 | C16 H22 O4 | 6.25 | 13.682 | d |
| 222.0881 | C12 H12 O3 |  | 13.683 | a, d |
| 148.0141 | C8 H4 O3 | 12.97 | 13.856 | d |
| 278.1504 | C16 H22 O4 | 5.1 | 13.865 | d |

a) Peak only appears in $\mathrm{O}_{3}$ experiment.
b) Peak present in both positive and negative ion mode.
c) Peak present in negative ion mode only.
d) Known phthalate impurity.

| $\Delta$-carene + NO (excluding products listed in $\Delta$-carene $+\mathrm{O}_{3}$ ) |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| Mass | Formula | Relative Mass <br> Difference <br> (MFG) | RT | Notes |
| 186.0878 | C9 H14 O4 | 7.6 | 6.51 | c |
| 172.1084 | C9 H16 O3 | 9.06 | 6.946 |  |
| 152.1186 | C10 H16 O | 9.66 | 7.13 |  |
| 199.1193 | C10 H17 N O3 | 7.64 | 7.33 |  |
| 110.0725 | C7 H10 O | 5.7 | 7.498 |  |
| 168.1137 | C10 H16 O2 | 8.21 | 7.499 |  |
| 140.0825 | C8 H12 O2 | 9.09 | 7.514 |  |
| 211.155 | C12 H21 N O2 | 10.39 | 7.541 |  |
| 70.0419 | C4 H6 O | -0.86 | 7.731 |  |
| 138.1034 | C9 H14 O | 7.44 | 7.731 |  |
| 211.1548 | C12 H21 N O2 | 11.61 | 8.475 |  |
| 227.0772 | C10 H13 N O5 | 9.7 | 8.873 |  |
| 108.0566 | C7 H8 O | 8.81 | 9.298 |  |
| 200 | C10 H16 O4 | 8.31 | 9.406 |  |
| 199 | C9 H13 N O4 | 9.7 | 10.178 |  |
| 380.1585 | C18 H24 N2 O7 | -0.52 | 10.626 |  |
| 229.1663 | C12 H23 N O3 | 6.37 | 10.737 |  |
| 168 | C10 H16 O2 | 11.79 | 10.886 |  |
| 168 | C10 H16 O2 | 11.36 | 11.097 |  |
| 358.176 | C21 H26 O5 | 4.25 | 11.797 |  |
| 215 | C10 H17 N O4 | 10.75 | 11.853 |  |
| 134.1072 | C10 H14 | 17.16 | 11.855 |  |
| 200 | C11 H20 O3 | 14.23 |  |  |
|  |  |  |  |  |


| 472.1599 | C21 H28 O12 | 3.94 | 11.874 |  |
| :--- | :--- | :--- | :--- | :--- |
| 215 | C10 H17 N O4 | 9.89 | 11.966 |  |
| 168.1134 | C10 H16 O2 | 9.98 | 12.058 |  |
| 152.1187 | C10 H16 O | 9.42 | 12.059 |  |
| 215 | C10 H17 N O4 | 9.99 | 12.061 |  |
| 182.1285 | C11 H20 O3 | 11.75 | 12.079 |  |
| 243 | C11 H17 N O5 | 11.82 | 12.363 |  |
| 400.187 | C23 H28 O6 | 3.9 | 12.48 |  |
| 564.1592 | C25 H28 N2 O13 | -0.17 | 12.722 |  |
| 190.0977 | C10 H16 O2 |  | 12.8 |  |
| 340.1651 | C21 H24 O4 | 6.91 | 12.803 |  |
| 478.2132 | C20 H34 N2 O11 | 6.42 | 13.748 |  |
| 312.1332 | C19 H20 O4 | 9.43 | 13.791 |  |
| 418.2283 | C19 H34 N2 O8 | 7.68 | 13.837 |  |
| 204.0769 | C12 H12 O3 | 8.34 | 13.893 | d |
| 476 | C20 H32 N2 O11 | 4.91 | 14.72 |  |
| 413 | C20 H31 N O8 | 5.94 | 14.772 |  |
| 413 | C20 H31 N O8 | 5.48 | 14.932 |  |
| 476 | C20 H32 N2 O11 | 4.11 | 15.309 |  |
| 476 | C20 H32 N2 O11 | 4.2 | 15.501 |  |

a) Peak only appears in $\mathrm{O}_{3}$ experiment.
b) Peak present in both positive and negative ion mode.
c) Peak present in negative ion mode only.
d) Known phthalate impurity.

| limonene + O 3 |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| Mass | Formula | Relative Mass <br> Difference (MFG) | RT | Notes |
| 154.0972 | C9 H14 O2 | 14.38 | 5.616 |  |
| 186.0868 | C9 H14 O4 | 13.14 | 7.438 |  |
| 80.0619 | C6 H8 | 8.6 | 7.438 |  |
| 126.0669 | C7 H10 O2 | 9.43 | 7.441 |  |
| 186.0871 | C9 H14 O4 | 11.07 | 7.701 | b |
| 184.1072 | C10 H16 O3 | 14.71 | 7.754 |  |
| 184.1075 | C10 H16 O3 | 13.27 | 8.373 | b |
| 200 | C11 H20 O3 | 12.66 | 8.667 |  |
| 92.0625 | C7 H8 | 1.56 | 8.674 |  |
| 132.0921 | C10 H12 | 13.52 | 8.682 |  |
| 122.1083 | C9 H14 | 10.11 | 8.684 |  |
| 168.1129 | C10 H16 O2 | 12.91 | 8.685 |  |
| 106.077 | C8 H10 | 11.72 | 8.685 |  |
| 188 | C9 H16 O4 | 12.51 | 9.177 |  |
| 222.0864 | C12 H14 O4 | 12.68 | 11.064 |  |
| 157.1446 | C9 H19 N O | 13.25 | 11.205 |  |


| 243.1803 | C13 H25 N O3 | 12.85 | 11.518 | b |
| :--- | :--- | :--- | :--- | :--- |
| 287.2792 | C17 H37 N O2 | 11.17 | 12.392 |  |
| 128.1183 | C8 H16 O | 14.21 | 12.399 |  |
| 216 | C12 H24 O3 | 11.07 | 12.406 |  |
| 287.2789 | C17 H37 N O2 | 12.16 | 12.649 |  |
| 314 | C18 H34 O4 | 14.78 | 13.084 |  |
| 276.1702 | C17 H24 O3 | 8.54 | 13.091 |  |
| 220.1072 | C13 H16 O3 | 12.36 | 13.099 |  |
| 330.1774 | C18 H28 O4 | 9.89 | 13.105 |  |
| 300.1657 | C14 H24 N2 O5 | 9.51 | 13.226 |  |
| 358 | C20 H38 O5 | 11.94 | 13.312 |  |
| 278.1487 | C16 H22 O4 | 11.26 | 13.732 | d |
| 148.0138 | C8 H4 O3 | 15.22 | 13.732 | d |
| 222.087 | C12 H14 O4 | 9.87 | 13.732 | a |
| 312.1314 | C19 H20 O4 | 15.22 | 13.819 |  |
| 278.1491 | C16 H22 O4 | 9.8 | 13.918 | d |
| 286.2102 | C16 H30 O4 | 14.65 | 14.828 |  |
| 402.2203 | C20 H34 O8 | 12.51 | 15.376 |  |

a) Peak only appears in $\mathrm{O}_{3}$ experiment.
b) Peak present in both positive and negative ion mode.
c) Peak present in negative ion mode only.
d) Known phthalate impurity.

| limonene + NO (excluding products listed in limonene $+\mathrm{O}_{3}$ ) |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| Mass | Formula | Relative Mass <br> Difference <br> (MFG) | RT | Notes |
| 245.0868 | C10 H15 N O6 | 12.7 | 5.916 |  |
| 154.097 | C9 H14 O2 | 15.36 | 6.171 |  |
| 217.092 | C9 H15 N O5 | 13.76 | 6.584 | b |
| 279 | C10 H17 N O8 | 13.3 | 6.658 | b |
| 215 | C9 H13 N O5 | 13.8 | 7.522 |  |
| 217.0921 | C9 H15 N O5 | 12.87 | 8.491 |  |
| 227.076 | C10 H13 N O5 | 15.01 | 8.892 |  |
| 168.1124 | C10 H16 O2 | 15.8 | 9.381 |  |
| 245 | C10 H15 N1 O6 | 12.95 | 9.934 |  |
| 278.0727 | C9 H14 N2 O8 | 8.17 | 10.094 | c |
| 294.1041 | C10 H18 N2 O8 | 7.42 | 10.148 | c |
| 310.0985 | C10 H18 N2 O9 | 8.93 | 10.292 | c |
| 338.0937 | C11 H18 N2 O10 | 7.19 | 10.331 | c |
| 524.182 | C20 H32 N2 O14 | 6.4 | 10.568 | c |
| 380.1558 | C18 H24 N2 O7 | 6.74 | 10.664 |  |
| 176.045 | C10 H8 O3 | 13.57 | 11.066 |  |
| 292.1277 | C16 H20 O5 | 11.45 | 11.694 |  |


| 358.1737 | C21 H26 O5 | 11.98 | 11.834 |  |
| :---: | :---: | :---: | :---: | :---: |
| 472.1564 | C27 H24 N2 O6 | 14.98 | 11.913 |  |
| 280.0698 | C17 H12 O4 | 13.32 | 12.035 |  |
| 492 | C20 H32 N2 O12 | 8.62 | 12.127 |  |
| 555 | C20 H33 N3 O15 | 10.67 | 12.187 | b |
| 432 | C18 H28 N2 O10 | 8.23 | 12.245 |  |
| 290.1823 | C16 H28 O3 | 12.04 | 12.387 |  |
| 236.1743 | C15 H24 O2 | 14.2 | 12.389 |  |
| 492 | C20 H32 N2 O12 | 8.22 | 12.428 |  |
| 432 | C18 H28 N2 O10 | 9.88 | 12.495 |  |
| 492.1912 | C20 H32 N2 O12 | 8.77 | 12.528 |  |
| 218.1639 | C15 H24 O2 | 14.48 | 12.536 |  |
| 190.0965 | C12 H14 O2 | 15.27 | 12.839 |  |
| 432 | C18 H28 N2 O10 | 9.19 | 12.84 |  |
| 340.1631 | C21 H24 O4 | 13.12 | 12.84 |  |
| 446 | C19 H30 N2 O10 | 9.82 | 12.917 |  |
| 432 | C18 H28 N2 O10 | 10.16 | 13.009 |  |
| 509 | C19 H31 N3 O13 | 7.32 | 13.131 |  |
| 446 | C19 H30 N2 O10 | 9.82 | 13.192 |  |
| 509 | C19 H31 N3 O13 | 7.66 | 13.34 |  |
| 446 | C19 H30 N2 O10 | 9.84 | 13.342 |  |
| 523 | C20 H33 N3 O13 | 9.27 | 13.366 |  |
| 258.1795 | C14 H26 O4 | 13.94 | 13.515 |  |
| 476 | C20 H32 N2 O11 | 8.29 | 13.518 |  |
| 523 | C20 H33 N3 O13 | 8.02 | 13.564 |  |
| 482.1834 | C20 H32 N2 O10 | 8.71 | 13.712 |  |
| 446 | C19 H30 N2 O10 | 8.84 | 13.788 |  |
| 446 | C19 H30 N2 O10 | 9.18 | 13.915 |  |
| 204.076 | C12 H12 O3 | 12.92 | 13.927 | d |
| 523 | C20 H33 N3 O13 | 8.38 | 14.278 |  |
| 460 | C20 H32 N2 O10 | 9.33 | 14.304 |  |
| 523 | C20 H33 N3 O13 | 8.98 | 14.434 |  |
| 358.2446 | C18 H34 N2 O5 | 5.98 | 14.871 |  |
| 304.2374 | C20 H32 O2 |  | 14.871 |  |

a) Peak only appears in $\mathrm{O}_{3}$ experiment.
b) Peak present in both positive and negative ion mode.
c) Peak present in negative ion mode only.
d) Known phthalate impurity.

Table S.3. Masses and elemental composition for (a) all peaks with intensity greater than $10 \%$ of the strongest peak observed in any of the ESI-MS spectra for each BVOC, (b) additional molecular formulae that have been identified by other studies, and (c) selected high-mass peaks. Possible molecular structures are listed for most molecular formulae. As in Table S.2, masses and formulae refer to the precursor (non-adduct) compound, which is reported as the nominal mass for any adducts misassigned by the software.

| Measured m/z |  | Relative abundance | Oxidants observed with | Molecular formula | Possible structures | References (if previously observed) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\alpha$-pinene |  |  |  |  |  |  |
| (a) 215 | 1 |  | $\mathrm{NO}_{3}$ | C10 H17 NO4 | 2-hydroxypinane-3-nitrate | $\mathrm{NO}_{3}$ : Wangberg et al. (1997), Perraud et al. (2010), Ayres et al, in prep (2015) |
| 184.1115 | 0.51 |  | $\mathrm{NO}_{3}$ | C10 H16 O3 | pinonic acid <br> 10-hydroxy-pinonaldehyde <br> $\&$ isomers | $\mathrm{O}_{3}$ : Yu et al. (1999), Glasius et al. (2000), Doezema et al. (2012) $\mathrm{NO}_{3}$ : Perraud et al. (2010) |
| 213 | 0.15 |  | $\mathrm{NO}_{3}$ | C10 H15 N O4 | 3-oxopinane-2-nitrate | $\mathrm{NO}_{3}$ : Wangberg 1997, Perraud 2010 |


| 260 | 0.15 | $\mathrm{NO}_{3}$ | C10 H16 N2 O6 | 2,3-dinitrato-pinane |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| (b) 168.1166 | 0.08, 0.04 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C10 H16 O2 | pinonaldehyde | $\mathrm{O}_{3}$ : Glasius 2000, Yu <br> 1999, <br> Doezema et <br> al. (2012) <br> $\mathrm{NO}_{3}$ : <br> Wangberg et al. <br> (1997), <br> Hallquist et <br> al. (1999), <br> Perraud et <br> al. (2010) |
| 231 | 0.07 | $\mathrm{NO}_{3}$ | C10 H17 N O5 | 2-hydroperoxypinane-3-nitrate | $\begin{aligned} & \mathrm{NO}_{3}: \text { Ayres } \\ & \text { et al, in } \\ & \text { prep (2015) } \end{aligned}$ |
| 152.1214 | 0.05, 0.02 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C10 H16 O | pinane epoxide | $\mathrm{NO}_{3}$ : <br> Wangberg et al. <br> (1997) |
| (c) 383.1987 | 0.08 | $\mathrm{NO}_{3}$ | C19 H29 N O7 |  | speculative, loosely following Heaton et al. (2007) |


| 366 | 0.05 | $\mathrm{NO}_{3}$ | C20 H30 O6 |  | speculative |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\beta$-pinene |  |  |  |  |  |
| (a) 138.1048 | 0.47, 0.49 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C9 H14 O |  | $\mathrm{O}_{3}$ : Glasius et al. <br> (2000), Yu et al. <br> (1999) <br> $\mathrm{NO}_{3}$ : <br> Hallquist et <br> al. (1999) |
| 215 | 0.43 | $\mathrm{NO}_{3}$ | C10 H17 N O4 |  | $\mathrm{NO}_{3}$ : Fry et al. (2009), Ayres in prep (2015) |
| 154.0999 | 0.29. 0.30 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C9 H14 O2 | hydroxypinaketone | $\begin{aligned} & \mathrm{O}_{3} \text { : Glasius } \\ & \text { et al. } \\ & (2000), \mathrm{Yu} \\ & \text { et al. } \\ & (1999) \end{aligned}$ |
| 429 | 0.28 | $\mathrm{NO}_{3}$ | C21 H35 N O8 |  |  |
| 231 | 0.27 | $\mathrm{NO}_{3}$ | C10 H17 N O5 |  | $\mathrm{NO}_{3}$ : Fry et al. (2009), Ayres in prep (2015) |


| 227.0803 | 0.23 | $\mathrm{NO}_{3}$ | C10 H13 N O5 |  | speculative |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 152.0842 | 0.18 | $\mathrm{NO}_{3}$ | C9 H12 O2 |  | $\begin{aligned} & \mathrm{O}_{3}: \text { Yu et } \\ & \text { al. (1999) } \end{aligned}$ |
| 230.1276 | 0.14 | $\mathrm{NO}_{3}$ | C10 H18 N2 O4 |  |  |
| 260 | 0.13 | $\mathrm{NO}_{3}$ | C10 H16 N2 O6 |  |  |
| 385 | 0.13 | $\mathrm{NO}_{3}$ | C19 H31 N O7 |  | speculative, loosely following Heaton et al. (2007) |
| 429 | 0.11 | $\mathrm{NO}_{3}$ | C21 H35 N O8 |  |  |
| 184.1102 | 0.11. 0.03 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C10 H16 O3 | pinonic acid | $\begin{aligned} & \mathrm{O}_{3} \text { : Glasius } \\ & \text { et al. } \\ & (2000) \end{aligned}$ |


| 444 | 0.10 | $\mathrm{NO}_{3}$ | C20 H32 N2 O9 |  | speculative |
| :---: | :---: | :---: | :---: | :---: | :---: |
| (b) 186.0905 | 0.03, 0.02 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C9 H14 O4 | pinic acid <br> hydroxy norpinonic acid | $\begin{aligned} & \mathrm{O}_{3} \text { : Glasius } \\ & \text { et al. } \\ & (2000), \mathrm{Yu} \\ & \text { et al. } \\ & (1999) \end{aligned}$ |
| 245.0857 | Neg ion mode | $\mathrm{NO}_{3}$ | C10 H15 N O6 |  | $\begin{aligned} & \hline \mathrm{NO}_{3}: \mathrm{Ng} \text { et } \\ & \text { al, ACPD } \\ & (2015) \end{aligned}$ |
| (c) 428.2174 | 0.05 | $\mathrm{NO}_{3}$ | C20 H32 N2 O8 |  | speculative |


| 442 | 0.04 | $\mathrm{NO}_{3}$ | C20 H30 N2 O9 |  | speculative |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 415 | 0.03 | $\mathrm{NO}_{3}$ | C20 H33 N O8 |  | speculative |
| $\Delta$-carene |  |  |  |  |  |
| (a) 168.1137 | 0.17, 0.60 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C10 H16 O2 |  | $\mathrm{O}_{3}$ : Glasius et al. <br> (2000) <br> $\mathrm{NO}_{3}$ : <br> Hallquist et <br> al. (1999) |
| 340.1651 | 0.57 | $\mathrm{NO}_{3}$ | C21 H24 O4 |  |  |
| 184.1076 | 0.33, 0.12 | NO3, O3 | C10 H16 O3 | 3-caronic acid <br> 10-hydroxy-3-caronaldehyde | $\begin{aligned} & \mathrm{O}_{3} \text { : Glasius } \\ & \text { et al. } \\ & (2000) \end{aligned}$ |
| 200 | 0.26 | $\mathrm{O}_{3}$ | C11 H20 O3 |  |  |


| 215 | 0.25 | $\mathrm{NO}_{3}$ | C10 H17 N O4 | hydroxynitrate | $\mathrm{NO}_{3}$ : <br> Colville and Griffin (2004), Ayres in prep (2015) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 227.0772 | 0.13 | $\mathrm{NO}_{3}$ | C10 H13 N O5 |  | very speculative ! |
| 276.1708 | 0.12 | $\mathrm{NO}_{3}$ | C17 H24 O3 |  |  |
| 243.1813 | 0.11 | $\mathrm{NO}_{3}$ | C13 H25 N O3 |  |  |
| 186.0886 | Neg ion mode |  | C9 H14 O4 |  | $\mathrm{O}_{3}$ : Glasius et al. <br> (2000), Yu et al. <br> (1999) |
| (c) 476 | 0.05 | $\mathrm{NO}_{3}$ | C20 H32 N2 O11 |  | speculative |
| 380.1585 | 0.04 | $\mathrm{NO}_{3}$ | C18 H24 N2 O7 |  | Very speculative! |
| 413 | 0.04 | $\mathrm{NO}_{3}$ | C20 H31 N O8 |  |  |


| 478.2132 | 0.03 | $\mathrm{NO}_{3}$ | C20 H34 N2 O11 |  | speculative - this formula is consistent with some ringopening in the dimer |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 418.2283 | 0.03 | $\mathrm{NO}_{3}$ | C19 H34 N2 O8 |  | speculative - also consistent with ringopened products |
| limonene |  |  |  |  |  |
| (a) 340.1631 | 0.37 | $\mathrm{NO}_{3}$ | C21 H24 O4 | Extremely low H:C ratio, has to be very conjugated |  |
| 168.1125 | 0.30, 0.27 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C10 H16 O2 |  | $\mathrm{O}_{3}$ : Glasius et al. <br> (2000), <br> Walser et <br> al. (2008) <br> $\mathrm{NO}_{3}$ : <br> Spittler et <br> al. (2006), <br> Hallquist et <br> al. (1999), <br> Fry et al. <br> (2011) |


| 186.0868 | 0.12, 0.28 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C9 H14 O4 |  | $\mathrm{O}_{3}$ : Glasius et al. (2000), Walser et al. (2008) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 182.128 | 0.15, 0.14 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C11 H18 O2 |  |  |
| 268 | 0.12 | $\mathrm{NO}_{3}$ | C16 H28 O3 |  |  |


| (b) 184.1075 | 0.02, 0.03 | $\mathrm{NO}_{3}, \mathrm{O}_{3}$ | C10 H16 O3 | limononic acid: <br> 7-hydroxy-limonaldehyde: | $\mathrm{O}_{3}$ : Glasius et al. (2000), Walser et al. (2008) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 294.1041 | 0.01 | $\mathrm{NO}_{3}$ | C10 H18 N2 O8 |  | $\mathrm{NO}_{3}: \text { Fry et }$ al. (2011) |
| (c) 460 | 0.01 | $\mathrm{NO}_{3}$ | C20 H32 N2 O10 |  | speculative, just intended to show possible dimer structures |
| 476 | 0.01 | $\mathrm{NO}_{3}$ | C20 H32 N2 O11 |  | " |

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