Supplementary Material for

Particle Mass Yield from β-Caryophyllene Ozonolysis

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A. Wall-loss correction in a continuously mixed flow reactor (CMFR)

The mass balance of organic aerosol in a CMFR is described by the following equation:

$$\frac{dM_{\text{org, CMFR}}}{dt} = \frac{M_{\text{org, inflow}}}{\tau_{\text{CMFR}}} - \frac{M_{\text{org, CMFR}}}{\tau_{\text{CMFR}}} + F_{\text{org}} - \beta M_{\text{org, CMFR}} \quad \text{(A1)}$$

where $M_{\text{org,CMFR}}$, $M_{\text{org,inflow}}$, τ_{CMFR}, F_{org}, and β represent the particle organic mass concentration in the CMFR (μg m^{-3}), the particle organic mass concentration in the inflow (μg m^{-3}), the mean residence time of the CMFR (s), the production rate of particle-phase organic material (μg m^{-3} s^{-1}), and the assumed first-order particle wall-loss coefficient (s^{-1}), respectively. In our experiments, $M_{\text{org,inflow}} = 0$. At steady state, $\frac{dM_{\text{org, CMFR}}}{dt} = 0$ and $M_{\text{org, CMFR}} = M_{\text{org, ss}}$. Equation A1 then becomes:

$$F_{\text{org}} = M_{\text{org, ss}} \left(\frac{1}{\tau_{\text{CMFR}}} + \beta \right) \quad \text{(A2)}$$

At $\beta = 0$ (i.e., no particle wall loss),

$$F_{\text{org}}^{\beta=0} = M_{\text{org, ss}}^{\beta=0} \frac{1}{\tau_{\text{CMFR}}} \quad \text{(A3)}$$

As discussed in Section 2.1, F_{org} is constant under different wall-loss conditions at steady state. The solution for Equations A2 and A3 is as follows:

$$M_{\text{org, ss}}^{\beta=0} = \left(1 + \beta\tau_{\text{CMFR}}\right) M_{\text{org, ss}} \quad \text{(A4)}$$

$M_{\text{org, ss}}^{\beta=0}$ is the organic mass concentration corrected by wall losses.

Gas-wall partitioning represents the net process of the re-evaporation of secondary organic material deposited on the walls and the absorption or reactive uptake of molecules from the gas phase, as well as direct deposition of particles to the walls.

This re-partitioning affects the gas-phase concentration of condensable species and hence the gas-phase chemistry as well as the gas-particle partitioning. Matsunaga and Ziemann (2010) showed that the gas-wall partitioning of various organic compounds was nearly independent of bag conditions and reversible, achieving equilibrium with time constants typically under one hour. For the 12-hour transient period used in our CMFR experiments, the surface layers of the Teflon bag material can be anticipated to become saturated, including the pore spaces near the surface. The non-reactive processes on the wall are expected to be in dynamic equilibrium with the CMFR at steady state, and depositing aerosol particles and the organic film on the walls can be supposed to have nearly identical compositions. Any reactive wall losses should then mimic any heterogeneous uptake on the suspended particles inside the bag.

B. β-Caryophyllene dark ozonolysis in a continuously mixed flow reactor (CMFR)

Based on the reaction rate constants of k_1 and k_2, a simplified gas-phase reaction scheme for the β-caryophyllene ozonolysis can be described as:

$$\mathrm{VOC} + \mathrm{O_3} \xrightarrow{k_1} \mathrm{G_1} + \mathrm{O_3} \xrightarrow{k_2} \mathrm{G_2} \tag{B5}$$

where VOC, G_1, and G_2 represent the precursor volatile organic compound, the first-generation products, and the second-generation products, respectively. Under an assumption of negligible wall losses of gas-phase species, the three differential equations that govern the species concentrations inside the CMFR are as follows:

$$\frac{d[\mathrm{VOC}]}{dt} = \frac{[\mathrm{VOC}]_0}{\tau} - \frac{[\mathrm{VOC}]}{\tau} - k_1[\mathrm{O_3}][\mathrm{VOC}] \tag{B6}$$

$$\frac{d[\mathrm{G_1}]}{dt} = -\frac{[\mathrm{G_1}]}{\tau} + k_1[\mathrm{O_3}][\mathrm{VOC}] - k_2[\mathrm{O_3}][\mathrm{G_1}] \tag{B7}$$

$$\frac{d[G_2]}{dt} = -\frac{[G_2]}{\tau} + k_2[O_3][G_1] \quad \text{(B8)}$$

where τ is the residence time of the CMFR, $[VOC]_0$ is the concentration of β-caryophyllene in the CMFR inflow, $[O_3]$ is the ozone concentration, and [VOC], $[G_1]$, and $[G_2]$ are the species concentrations in the CMFR outflow.

At steady state, $\frac{d[VOC]}{dt} = \frac{d[G_1]}{dt} = \frac{d[G_2]}{dt} = 0$. The algebraic solution for Equations B2 to B4 are as follows:

$$[VOC]_{ss} = \frac{[VOC]_0}{\tau k_1[O_3]_{ss} + 1} \quad \text{(B9)}$$

$$[G_1]_{ss} = \frac{\tau k_1[O_3]_{ss}[VOC]_0}{(\tau k_1[O_3]_{ss} + 1)(\tau k_2[O_3]_{ss} + 1)} \quad \text{(B10)}$$

$$[G_2]_{ss} = \frac{\tau^2 k_1 k_2[O_3]_{ss}^{\ 2}[VOC]_0}{(\tau k_1[O_3]_{ss} + 1)(\tau k_2[O_3]_{ss} + 1)} \quad \text{(B11)}$$

The ozone concentration was maintained at steady state in the CMFR for each experiment. The reaction rate constants are 1.16×10^{-14} molecule^{-1} cm^3 s^{-1} for the ozonolysis of the endo-cyclic double bond (k_1) of β-caryophyllene (Shu and Atkinson, 1995) and 1.1×10^{-16} molecule^{-1} cm^3 s^{-1} for the ozonolysis of the exo-cyclic double bond (k_2) of the first generation products (Winterhalter et al., 2009). The mean residence time of the chamber is 13000 s.

C. Parameters used in air quality models

Regional and global chemical transport models have employed parameterizations derived from the data reported by Griffin et al. (1999) to estimate the contribution of sesquiterpenes to the ambient organic particle mass concentrations (Chung and Seinfeld,

2002; Sakulyanontvittaya et al., 2008; Carlton et al., 2010; Zhang and Ying, 2011). Table S2 listed the parameters used in Goddard Institute for Space Studies General Circulation Model II-prime (GISS GCM II-prime) and Community Multiscale Air Quality Model (CMAQ). The mass-based stoichiometric yield α and the product saturation concentration C^* were derived for one-product model (Odum et al., 1996; Kroll and Seinfeld, 2008) as described as follows:

$$Y(M_{\text{org}}) = \alpha\left(1+\frac{C^*}{M_{\text{org}}}\right)^{-1} \quad \text{(C1)}$$

where Y is the particle mass yield and M_{org} is the organic mass concentration. The gas-to-particle partitioning of semivolatile compounds depends on temperature. C^* is therefore defined by the Clausius-Clapeyron equation as follows:

$$C^*(T) = C^*(T_0)\frac{T_0}{T}\exp\left[\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right)\right] \quad \text{(C2)}$$

where ΔH_{vap} is the vaporization enthalpy, R is the ideal gas constant, and T_0 is the reference temperature (i.e., 308 K for β-caryophyllene oxidation in Griffin et al. (1999)). Recent experimental data suggest that the ΔH_{vap} values used in earlier versions of CMAQ (ΔH_{vap} = 156 or 163 kJ mol^{-1} in version 4.3 to 4.6) were overestimates (Offenberg et al., 2006). The new ΔH_{vap} value of 40 kJ mol^{-1} was used in CMAQ version 4.7 (Carlton et al., 2010; Zhang and Ying, 2011).

The original analysis of Griffin et al. (1999) assumed a density of 1000 kg m^{-3} for secondary organic material (SOM), which was adapted by Chung and Seinfeld (2002) and Sakulyanontvittaya et al. (2008) in their models. The original CMAQ v4.7 (Zhang and Ying, 2011) scaled the values of α by 30% to account for recent laboratory

measurements of density of 1300 kg m^{-3} for β-caryophyllene-derived SOM (Bahreini et al., 2005). More accurately, Carlton et al. (2010) derived a new set of α and C^* from the original data from Griffin et al. (1999) in which both Y and M_{org} were corrected by the SOM density of 1300 kg m^{-3} and the data from Hoffmann et al. (1997) were excluded.

The parameters for β-caryophyllene (Table S2) were used for all sesquiterpenes when estimating sesquiterpene-derived particle mass concentrations in Sakulyanontvittaya et al. (2008). In CMAQ v4.7 (original and revised) and GISS GCM II-prime, the parameters for both β-caryophyllene and α-humulene oxidation were lumped together to represent the overall sesquiterpene oxidation.

Excess Ozone (ppbv)	α_0	α_1	α_2
50	0.15 ± 0.02	0.16 ± 0.07	0.32 ± 0.13
100	0.13 ± 0.03	0.22 ± 0.10	0.38 ± 0.15
200	0.17 ± 0.05	0.11 ± 0.17	1.03 ± 0.30

Table S1. Summary of the optimized mass-based stoichiometric yields α_i of product class i for β-caryophyllene ozonolysis. The volatility of product class i is prescribed in decadal units of 10^{-i}, where 10^{-i} is denoted as C_i^*.

Reference	Model	α	C^* at 298 K (μg m^{-3})	C^* at 308 K (μg m^{-3})	ΔH_{vap} (kJ mol^{-1})
Chung et al. (2002)	GISS GCM II-prime	1.000	14.329	24.039	42
Sakulyanontvittaya et al. (2008)	CMAQ v4.5	1.000	2.935	24.039	163
Zhang et al. (2011)	CMAQ original v4.7	1.300	14.710	24.039	40
Carlton et al. (2010) (cf. Table S-1)	CMAQ revised v4.7	1.537	29.893	48.852	40

Table S2. Summary of the mass-based stoichiometric yield α, the product saturation concentration C^*, and the vaporization enthalpy ΔH_{vap} used in four different regional and global models for β-caryophyllene oxidation. Parameters were derived for one-product model (Eq. C1) based on the yield data (or partially data) reported by Griffin et al. (1999) for β-caryophyllene photooxidation at 308 K.

List of Figures

products. The conversions from first- to second-generation products are presented by arrows. The red label calls attention to a product that appears to have been incorrectly assigned in previous work (Li et al., 2011).

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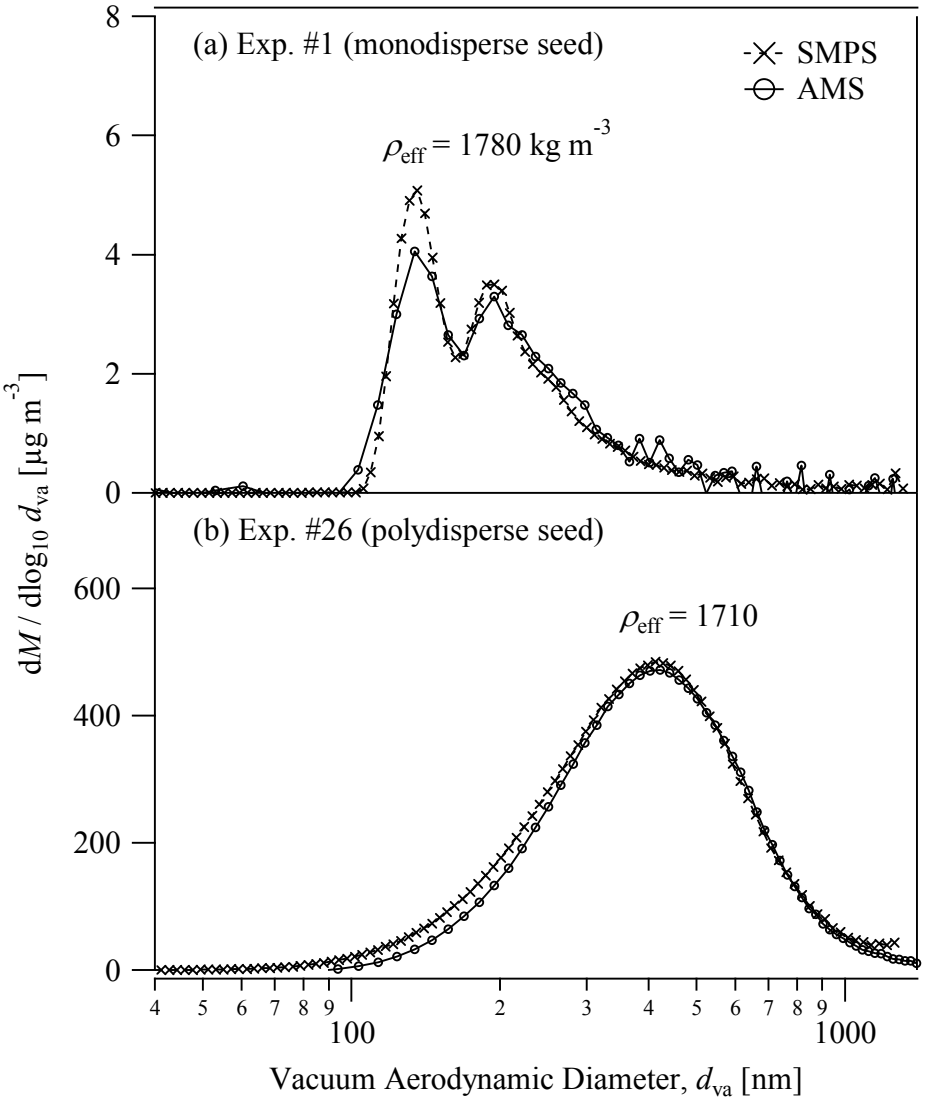
(a) Exp. #1 (monodisperse seed)
SMPS
AMS
ρ_{eff} = 1780 kg m^{-3}
(b) Exp. #26 (polydisperse seed)
ρ_{eff} = 1710
dM / dlog$_{10}$ d_{va} [µg m^{-3}]
Vacuum Aerodynamic Diameter, d_{va} [nm]

Figure S1

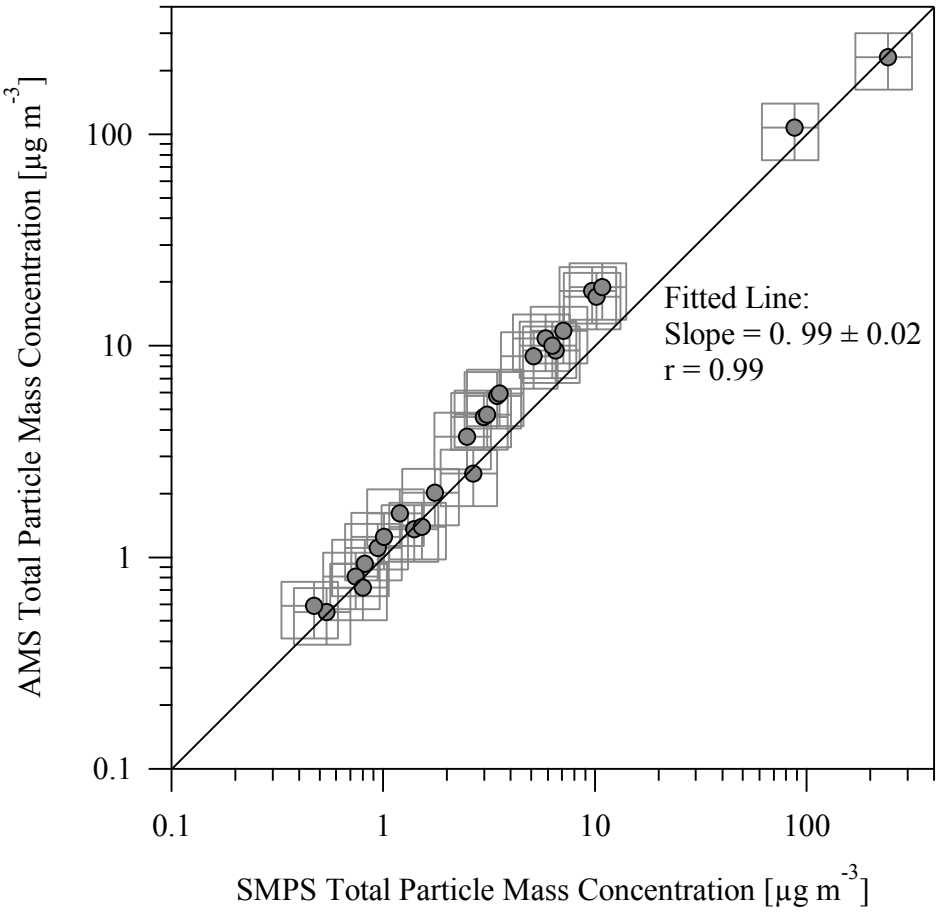
AMS Total Particle Mass Concentration [µg m-3]
SMPS Total Particle Mass Concentration [µg m-3]
Fitted Line:
Slope = 0. 99 ± 0.02
r = 0.99
0.1
1
10
100

Figure S2

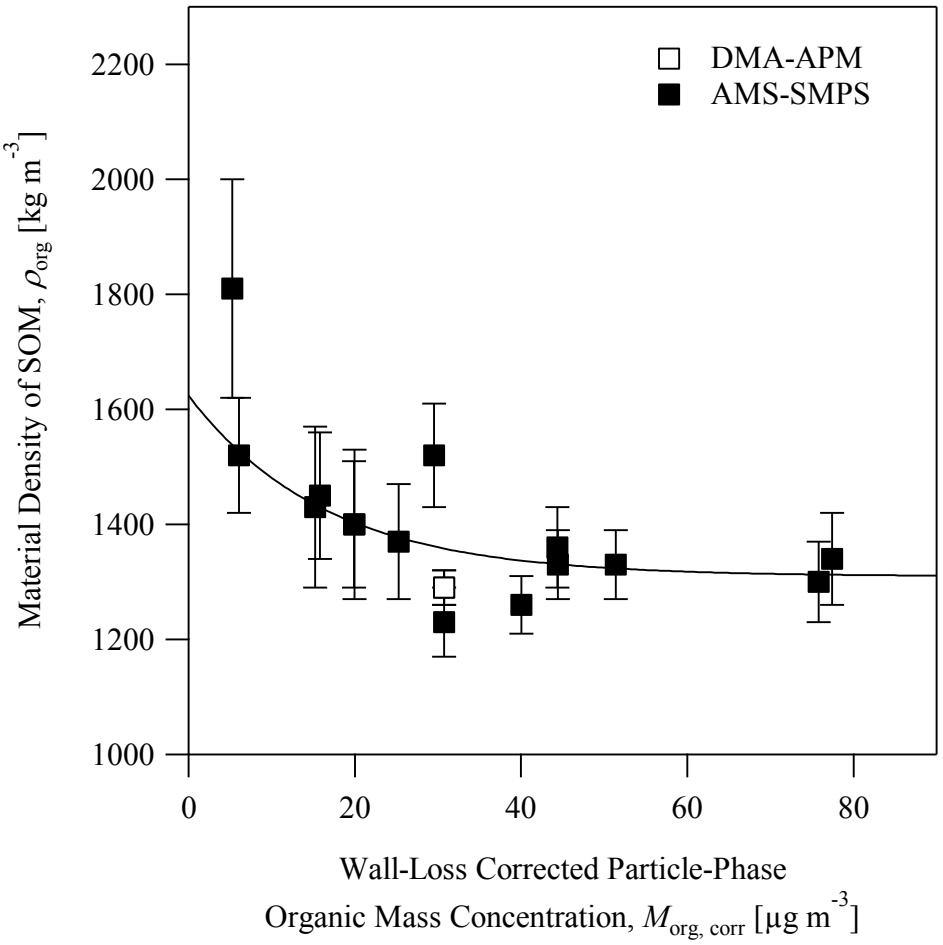
DMA-APM
AMS-SMPS
Material Density of SOM, ρ_{org} [kg m^{-3}]
2200
2000
1800
1600
1400
1200
1000
0
20
40
60
80
Wall-Loss Corrected Particle-Phase
Organic Mass Concentration, $M_{org, corr}$ [µg m^{-3}]

Figure S3

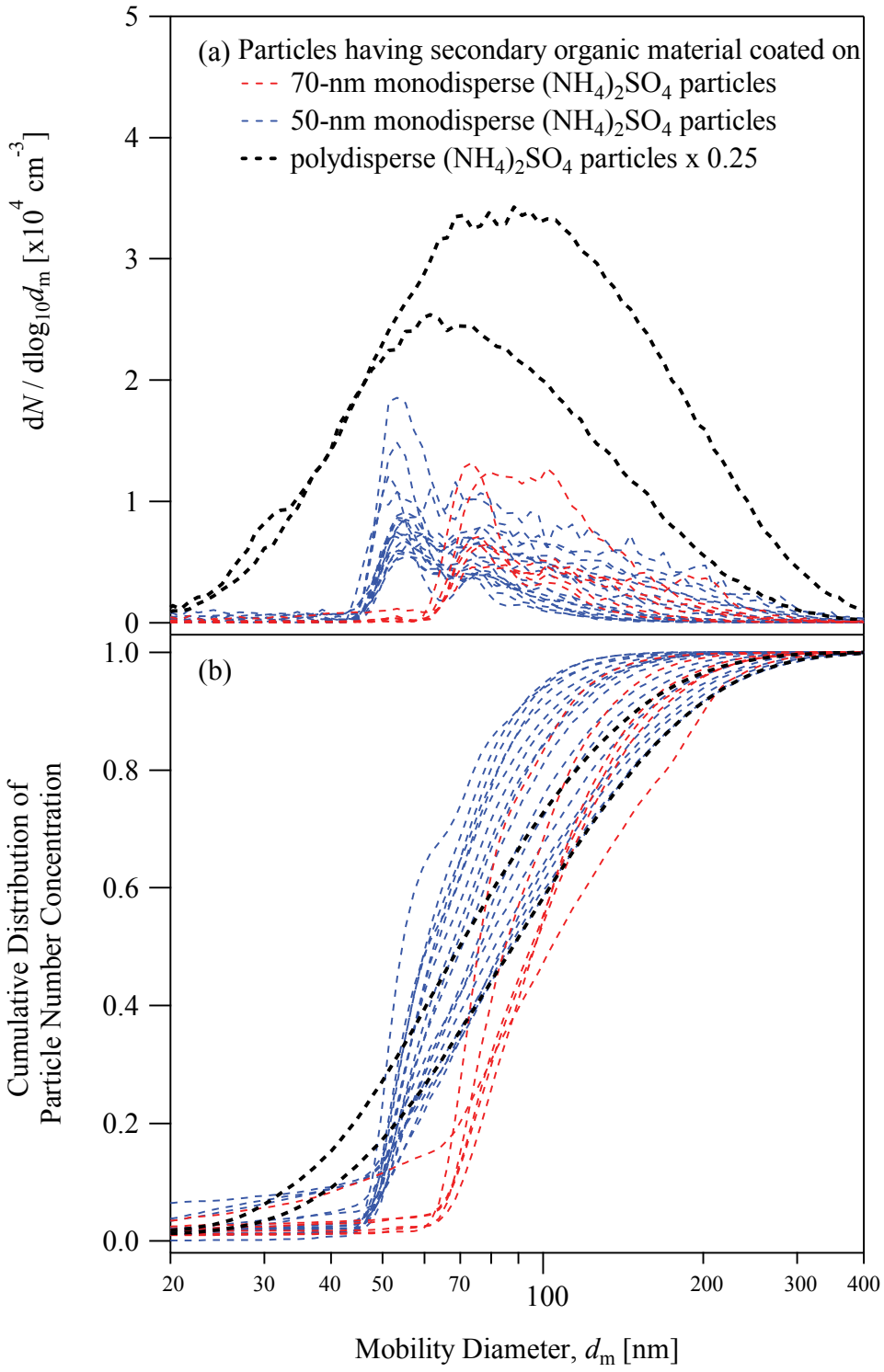
(a) Particles having secondary organic material coated on
70-nm monodisperse $(NH_4)_2SO_4$ particles
50-nm monodisperse $(NH_4)_2SO_4$ particles
polydisperse $(NH_4)_2SO_4$ particles x 0.25
$dN / d\log_{10}d_m$ [x10^4 cm^{-3}]
(b)
Cumulative Distribution of Particle Number Concentration
Mobility Diameter, d_m [nm]

Figure S4

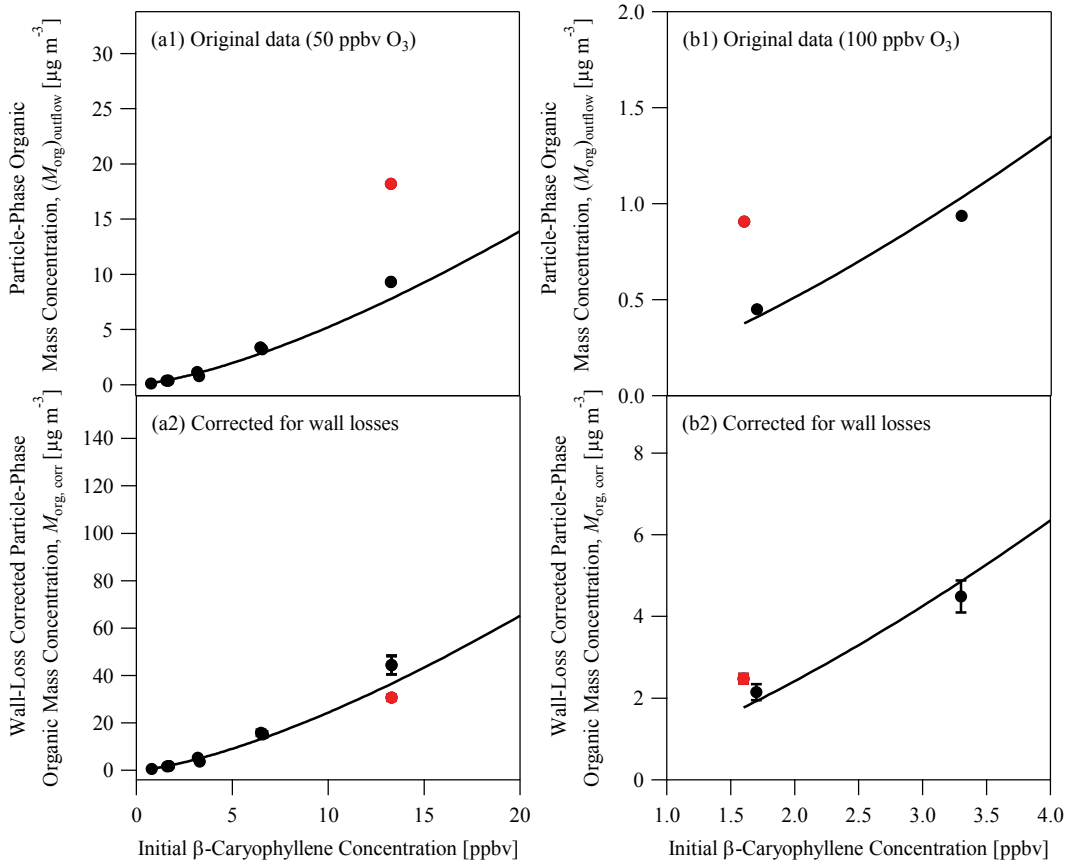
(a1) Original data (50 ppbv O_3)
(a2) Corrected for wall losses
(b1) Original data (100 ppbv O_3)
(b2) Corrected for wall losses
Particle-Phase Organic Mass Concentration, $(M_{org})_{outflow}$ [µg m^{-3}]
Wall-Loss Corrected Particle-Phase Organic Mass Concentration, $M_{org, corr}$ [µg m^{-3}]
Initial β-Caryophyllene Concentration [ppbv]
Initial β-Caryophyllene Concentration [ppbv]

Figure S5

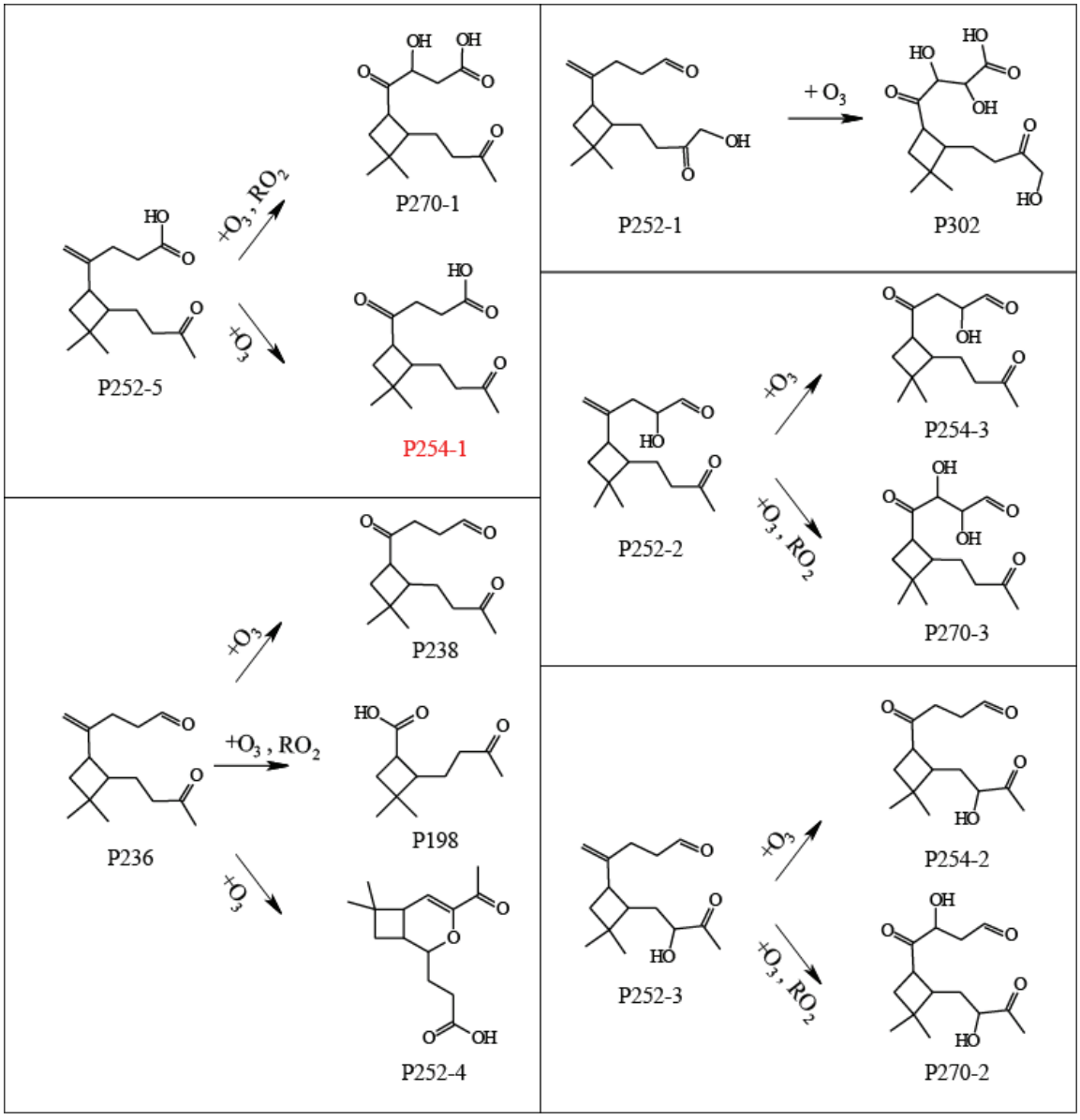
P270-1
P252-5
+O3 , RO2
+O3
P254-1
P252-1
+ O3
P302
P254-3
P252-2
+O3
+O3 , RO2
P270-3
P238
+O3
P236
+O3 , RO2
P198
+O3
P252-4
P254-2
P252-3
+O3
+O3 , RO2
P270-2

Figure S6