Manuscript prepared for Atmos. Chem. Phys.
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Date: 29 April 2011

Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA)

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1 Supporting Information

1.1 laboratory SOA and OPOA precursors

Figure S1 shows molecular structures for twelve of the fourteen precursors studied in the present work; diesel fuel and 10W-30 engine lubricating oil are not shown. As discussed in Section 2.3, SOA particles were generated via gas-phase oxidation of volatile organic compounds (VOCs) and intermediate-volatility organic compounds (IVOCs) in the PAM. The VOC precursors used in this study were *n*-decane (n-C_{10}), isoprene, α-pinene, β-pinene, toluene, m-xylene, and mesitylene. The IVOC precursors used in this study were *n*-heptadecane (n-C_{17}), diesel fuel, longifolene, and naphthalene. OPOA was generated by heterogenous oxidation of bis(2-ethylhexyl) sebacate (BES) and 10W-30 engine lubricating oil particles. Another set of experiments was conducted with an internally mixed primary aerosol composed of glyoxal and ammonium sulfate.

1.2 thermally denuded PAM-generated SOA

In a subset of experiments, an Aerodyne thermal denuder (Huffman et al., 2008) was placed upstream of the AMS and SMPS to investigate the chemical composition of PAM-generated SOA as a function of organic aerosol concentration. The heated section of the thermal denuder was set to several constant temperatures (T = 60- 250^{o}C) and allowed to equilibrate before measurements. Combined flows through the thermal denuder ranged between 2 - 3 lpm, corresponding to residence times of 3-5 sec and 3-4 sec in the heater and denuder sections, respectively. Figure S2 shows f_{44} versus f_{43} for thermally denuded SOA generated from naphthalene and α-pinene oxidation in the PAM. As is evident, thermally denuding the aerosol increases f_{44} and decreases f_{43}. At a specific OH exposure, f_{44} of α-pinene SOA increased by 12% - 26% as a function of thermal denuding, accompanied by a 15% - 33% decrease in f_{43}. Likewise, the f_{44} of naphthalene SOA increased by 6% - 232%, accompanied by a 12% - 17% decrease in f_{43}. Similar trends were observed by lowering the SOA precursor concentration that was input to the PAM. These results are consistent with OOA at *m/z*=43 and *m/z* = 44 representing semivolatile and low-volatilty organics, respectively.

1.3 PAM-generated SOA containing f_{43} curvature

Figure S3 shows f_{44} as a function of f_{43} for SOA generated from nine of the fourteen precursors in the PAM. These SOA systems were characterized by increases and subsequent decreases in f_{43} with oxidation, suggesting the formation and decay of early-generation oxidation products containing high f_{43} (specifically, $C_2H_3O^+$ ions).

1.4 O/C-f_{44} and H/C-f_{43} of PAM-generated SOA

Figures S4a and S4b shows O/C ratio as a function of f_{44} and H/C ratio as a function of f_{43} for PAM-generated SOA and OPOA. The dashed line Fig. S4a (O/C = $3.82\times f_{44}$ + 0.0794) is the best fit to multiple laboratory and field datasets (Aiken et al., 2008). The black dashed line in Fig. S4b (H/C = 1 + $5.16\times f_{43}$ $8.85\times {f_{43}}^2$) is a quadratic fit to smog chamber and field data (Ng et al., 2011b); grey dashed lines represent 10% confidence intervals to the quadratic fit as presented by Ng et al.

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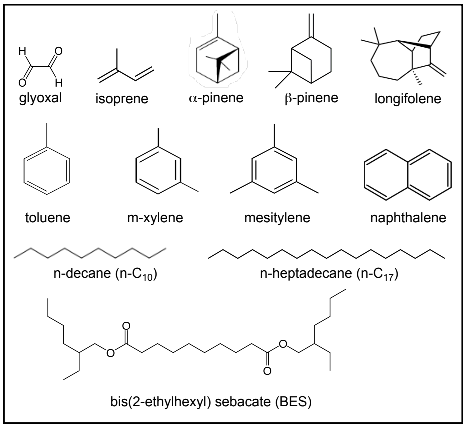

Fig. S1. Molecular structures of gas- and condensed-phase oxidized organic aerosol precursors used in this study.

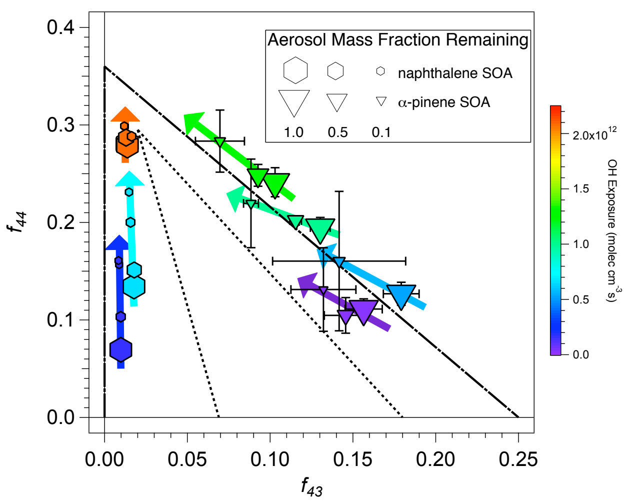

Fig. S2. f_{44} shown as a function of f_{43} for thermally denuded naphthalene and α-pinene SOA. Symbols are colored by OH exposure in the PAM and sized by aerosol mass fraction remaining (relative to non-denuded conditions). Error bars represent $\pm 1\sigma$ in measurements. Dashed lines indicate range of ambient f_{44} and f_{43} measurements, while dashed-and-dotted lines indicate range of laboratory PAM measurements.

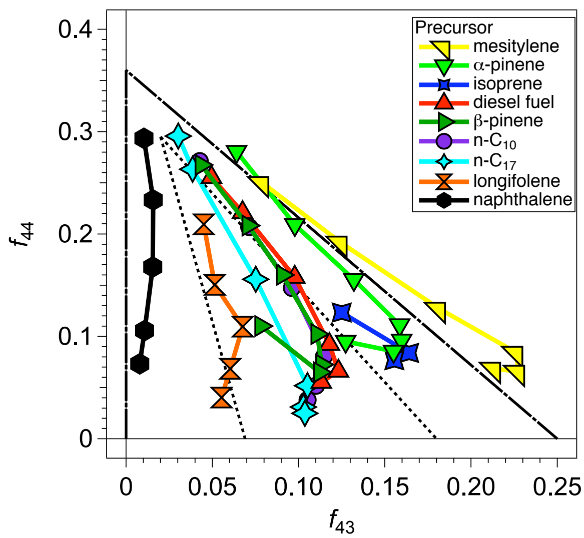

Fig. S3. f_{44} shown as a function of f_{43} for PAM-generated SOA characterized by f_{44}–f_{43}-curvature (replotted from Fig. 2). Dashed lines indicate range of ambient f_{44} and f_{43} measurements, while dashed-and-dotted lines indicate range of laboratory PAM measurements.

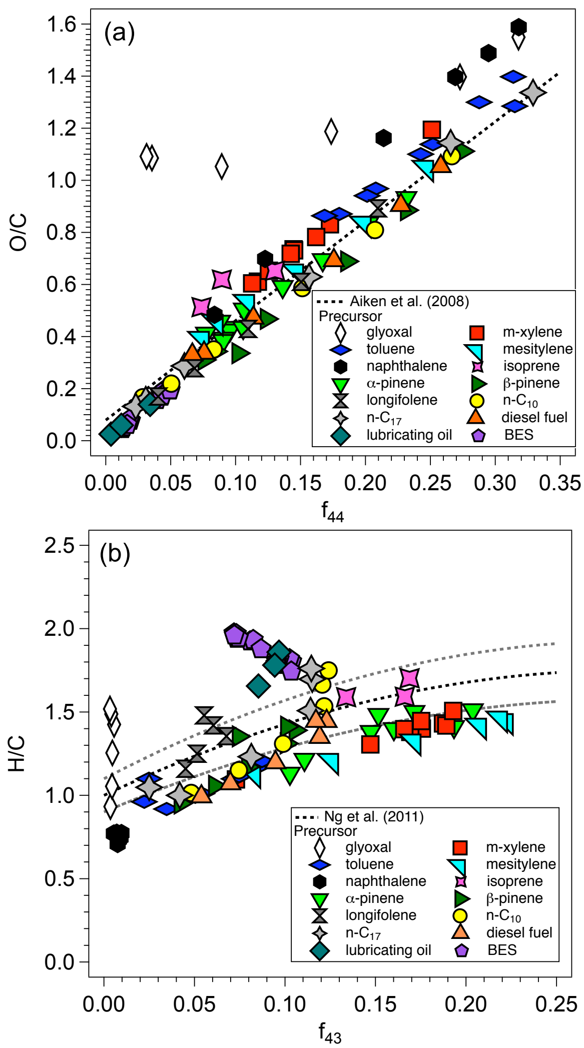

Fig. S4. (a) Oxygen-to-carbon (O/C) ratio as a function of f_{44} and (b) hydrogen-to-carbon (H/C) ratio as a function of f_{43} for PAM-generated SOA and OPOA. Dashed lines represent O/C-f_{44} and H/C-f_{43} parameterizations from Aiken et al. (2008) and Ng et al. (2011b) respectively. Glyoxal OPOA (diamonds) deviates from Aiken et al. and Ng et al. parameterizations for reasons described in the text.