

1 **SUPPLEMENTARY INFORMATION FOR:**

2
3 **Chemically-Resolved Aerosol Volatility Measurements from Two Megacity Field**
4 **Studies**

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19 **Appendix A**

20 List of terms and acronyms:

21 **OA:** Total organic aerosol comprised of multiple components (POA, SOA, etc.)

22 **POA:** Primary organic aerosol emitted into the atmosphere directly into the particle
23 phase

24 **SOA:** Secondary organic aerosol created by chemical reactions leading to a decrease in
25 species volatility and increased partitioning to the particle phase

26 **HOA:** Hydrocarbon-like organic aerosol estimated from factor analysis of AMS spectra.
27 Composed of reduced species, and typically dominated by combustion emissions. HOA
28 is typically used as a surrogate of POA due to the similarity of its spectra with those from
29 primary sources, and the strong correlation of its time series with those of primary tracers
30 (CO, NO_x, EC, etc.) (Zhang et al., 2005a; Zhang et al., 2005b; Lanz et al., 2007; Aiken et
31 al., 2008; Ulbrich et al., 2008).

32 **OOA:** Oxygenated organic aerosol estimated from factor analysis of AMS spectra. HOA
33 is typically used as a surrogate of SOA due to the similarity of its spectra with those from
34 chamber SOA, and the correlation of its time series with those of secondary tracers
35 (ozone, Ox, ammonium nitrate, ammonium chloride, ammonium sulfate, etc.) (Zhang et
36 al., 2005a; Zhang et al., 2005b; Lanz et al., 2007; Aiken et al., 2008; Ulbrich et al., 2008).

37 **OOA-1:** More aged and oxygenated, less volatile fraction of OOA, estimated from factor
38 analysis of AMS spectra in several studies (Lanz et al., 2007; Aiken et al., 2008; Nemitz
39 et al., 2008; Ulbrich et al., 2008).

40 **OOA-2:** Less aged and oxygenated, more volatile fraction of OOA, estimated from factor
41 analysis of AMS spectra in several studies.

42 **BBOA:** Biomass burning organic aerosol. In Mexico City BBOA originated mostly from
43 wildfire and agricultural burning, but wood-fired stoves can also be important in the
44 winter at some locations (Lanz et al., 2007).

45 **LOA:** Local organic aerosol. So named because it is characterized by short (<10 min)
46 spikes of aerosol concentration that indicates a local source. Separated by PMF in both
47 SOAR-1 and MILAGRO campaigns.

48 **VOC:** Volatile organic compound, existing in the atmosphere primarily as gas.

49 **IVOC:** Intermediate-volatility organic compound, with volatility just above that of
50 undiluted POA (Robinson et al., 2007).

51 **SVOC:** Semi-volatile organic compound, which may be of primary origin (evaporated
52 POA material (Robinson et al., 2007)) of secondary origin.

53 **Figure Captions**

54

55 **Figure S1:** Average size distributions at each TD temperature for SMPS and AMS
56 instruments in SOAR-1 and MILAGRO. Panels (a-b) show normalized SMPS mobility
57 size distributions as $dV_d/d\log d_m$ in nm^3/cm^3 . Panels (c-d) show AMS vacuum
58 aerodynamic distributions in $\mu\text{g}/\text{m}^3$.

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60 **Figure S2:** Thermograms for additional ions for SOAR-1 and MILAGRO. Panel (a)
61 shows nitrogen-containing ions: CH_4N^+ , $\text{C}_3\text{H}_8\text{N}^+$, $\text{C}_5\text{H}_{12}\text{N}^+$, and NO^+ . Panel (b) shows
62 sulfur-containing ions: CHS^+ , CH_3SO_3^+ , CH_3SO_2^+ , and SO^+ . C_3H_5^+ is also shown in each
63 plot for visual comparison

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65 **Figure S3:** Average OA mass spectra at ambient and five heated TD temperatures. HR
66 MS are averaged over entire MILAGRO campaign and show ion groups of C_xH_y^+ ,
67 $\text{C}_x\text{H}_y\text{O}_z^+$, $\text{C}_x\text{H}_y\text{N}_z^+$, and $\text{C}_x\text{H}_y\text{O}_z\text{N}_w^+$ in different colors.

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69 **Figure S4:** Thermograms of high m/z ratios for SOAR-1 (a) and MILAGRO (b)
70 averaged into 50 m/z bins. Thermograms of total OA from each campaign shown for
71 comparison

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73 **Figure S5:** Average SMPS size distributions from periods used in Figure 8d (high HOA,
74 high BBOA and high OOA-2) shown as $dV/d\log d_P$ vs mobility diameter.

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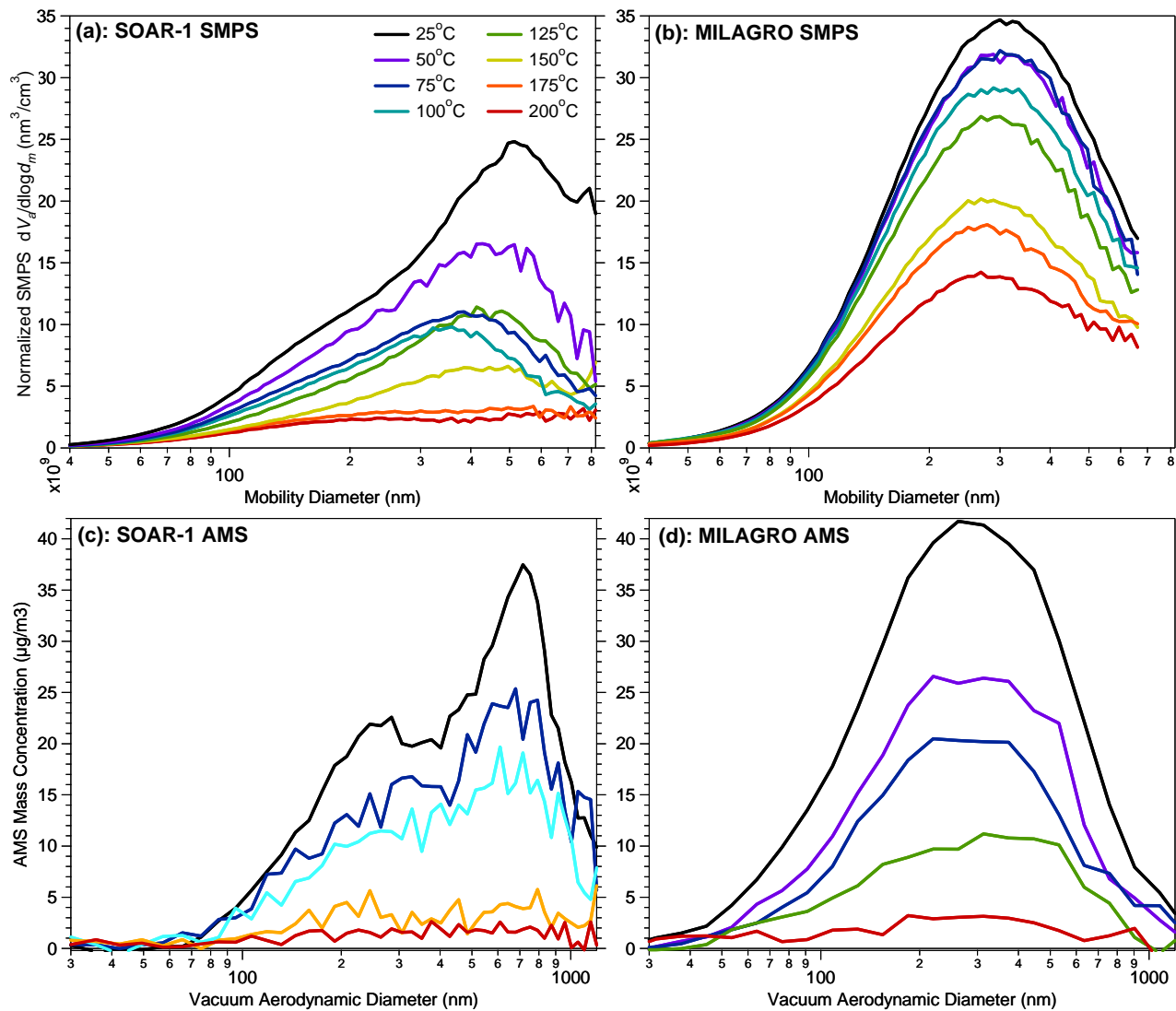
76 **Figure S6:** Average HR MS for recombined PMF factors for SOAR-1: (a) OOA-1, (b)
77 OOA-2, (c) OOA-3, (d) HOA, (e) LOA-AC, (f) LOA-2. Mass fraction of each ion group
78 to total OA shown as inset table in each panel.

79

80 **Figure S7:** Average HR MS for recombined PMF factors for MILAGRO: (a) $\text{OOA}_{\text{Total}}$
81 (sum of OOA-1 and OOA-2), (b) OOA-1, (c) OOA-2, (d) HOA, (e) BBAO, (f) LOA.
82 Mass fraction of each ion group to total OA shown as inset table in each panel.

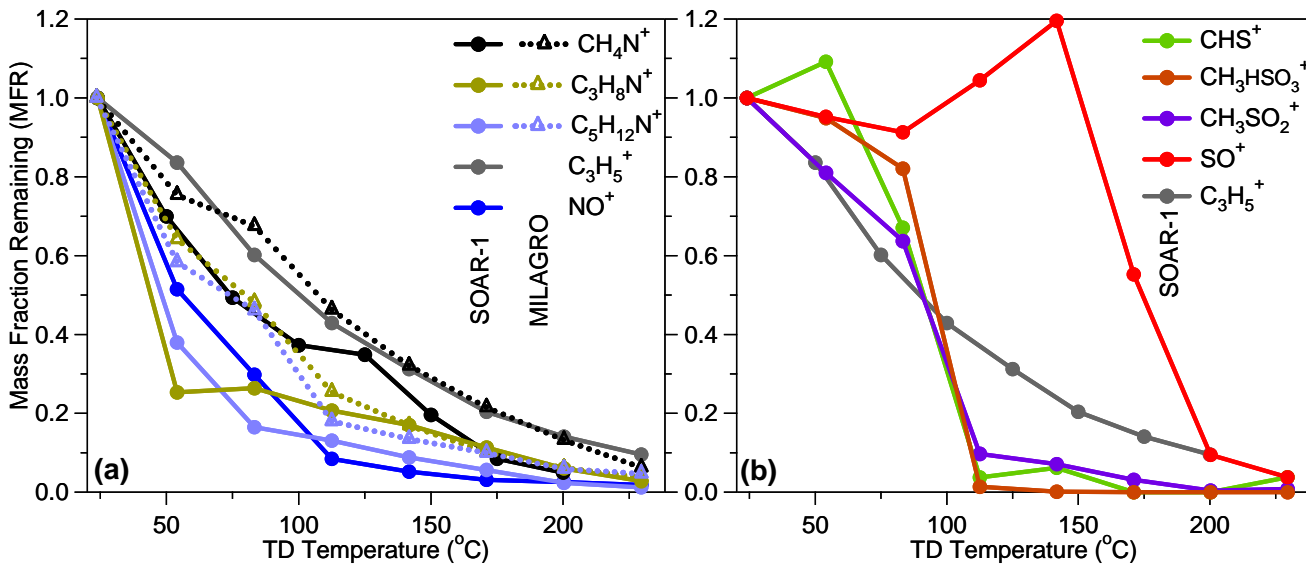
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84 **Figure S8:** Fraction of the total aerosol mass contained in each PMF component shown
85 as a function of temperature for: (a) SOAR-1 and (b) MILAGRO.



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87 **Figure S1**



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Figure S2

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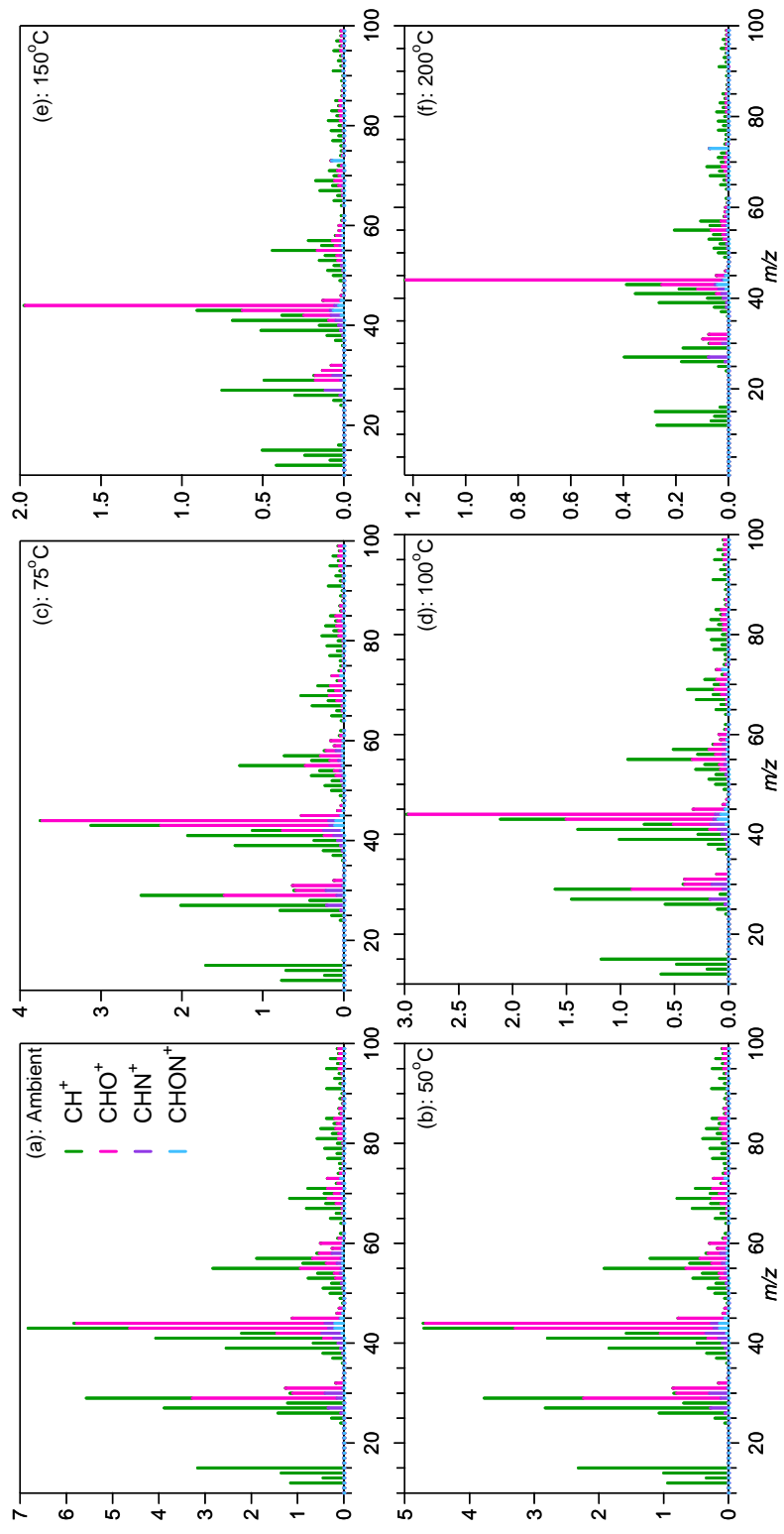
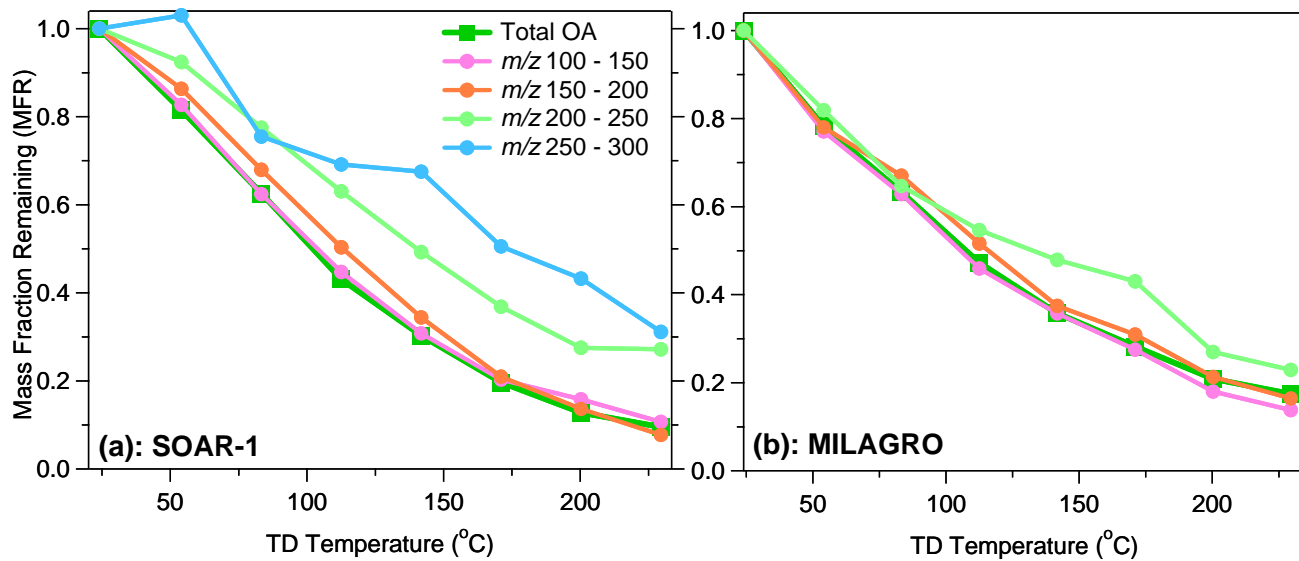


Figure S3



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137 **Figure S4**

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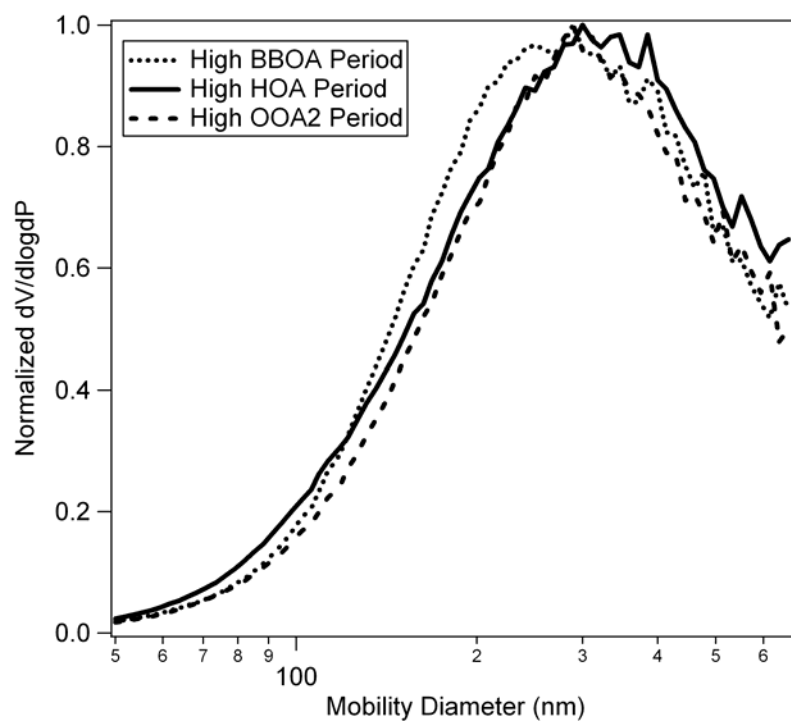


Figure S5

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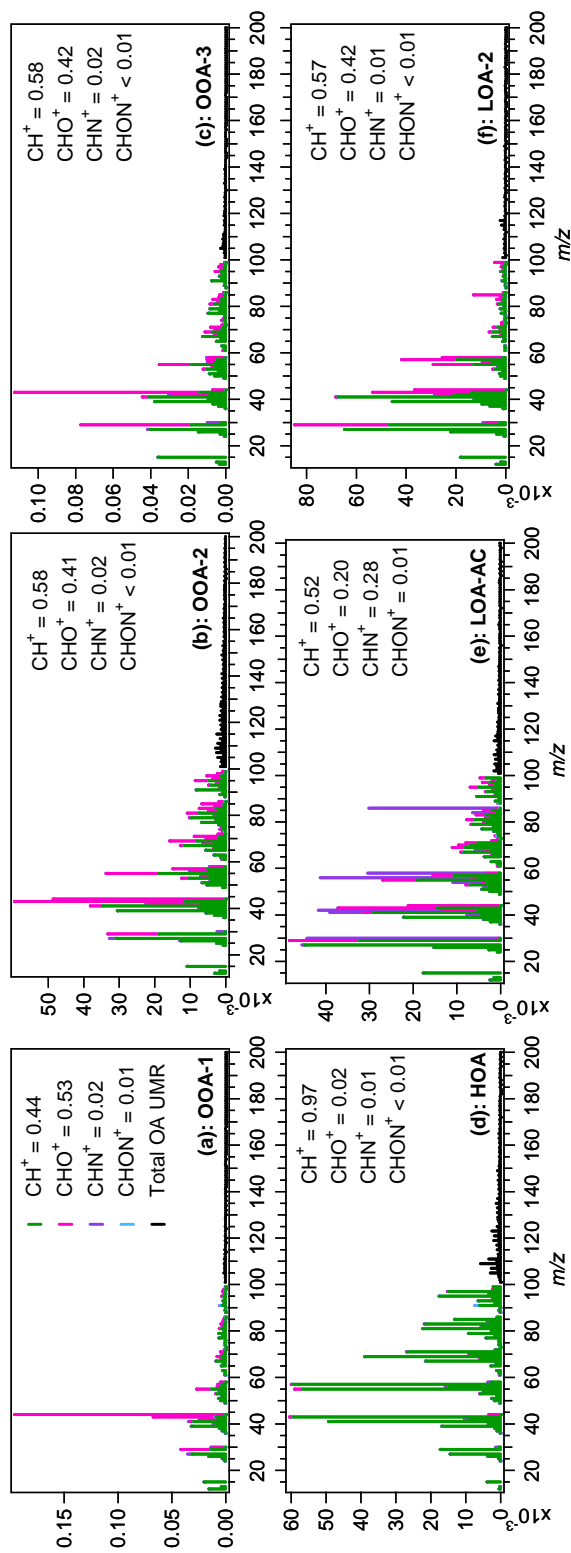


Figure S6

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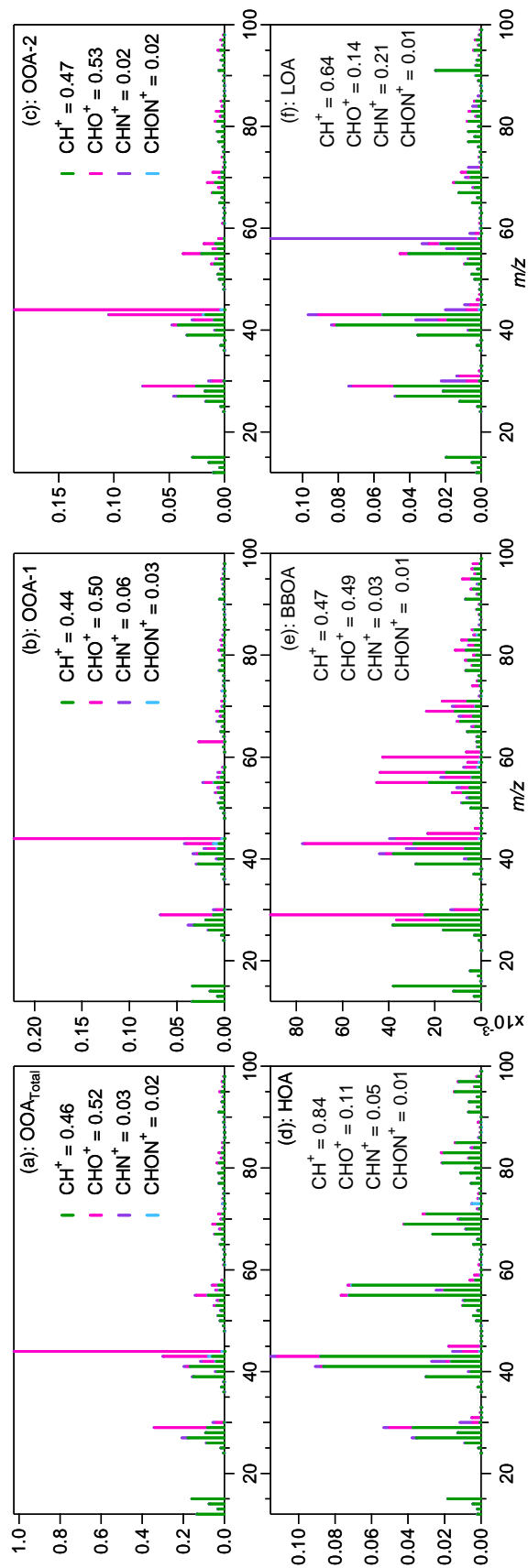
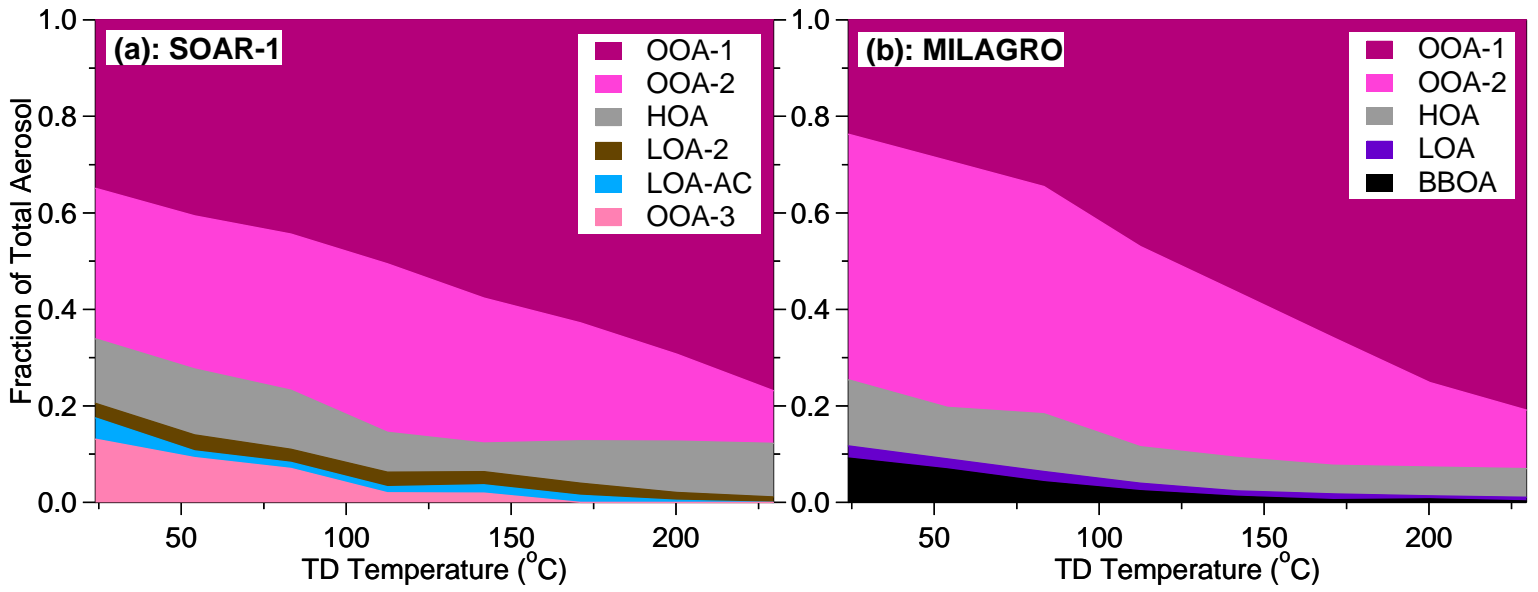


Figure S7



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Figure S8

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