1 **<u>SUPPLEMENTARY INFORMATION FOR:</u>**
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3 **Chemically-Resolved Aerosol Volatility Measurements from Two Megacity Field**
4 **Studies**
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Appendix A

List of terms and acronyms:

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

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

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

HOA: Hydrocarbon-like organic aerosol estimated from factor analysis of AMS spectra. Composed of reduced species, and typically dominated by combustion emissions. HOA is typically used as a surrogate of POA due to the similarity of its spectra with those from primary sources, and the strong correlation of its time series with those of primary tracers (CO, NOx, EC, etc.) (Zhang et al., 2005a; Zhang et al., 2005b; Lanz et al., 2007; Aiken et al., 2008; Ulbrich et al., 2009).

OOA: Oxygenated organic aerosol estimated from factor analysis of AMS spectra. HOA is typically used as a surrogate of SOA due to the similarity of its spectra with those from chamber SOA, and the correlation of its time series with those of secondary tracers (ozone, Ox, ammonium nitrate, ammonium chloride, ammonium sulfate, etc.) (Zhang et al., 2005a; Zhang et al., 2005b; Lanz et al., 2007; Aiken et al., 2008; Ulbrich et al., 2009).

OOA-1: More aged and oxygenated, less volatile fraction of OOA, estimated from factor analysis of AMS spectra in several studies (Lanz et al., 2007; Aiken et al., 2008; Nemitz et al., 2008; Ulbrich et al., 2009).

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

44   **BBOA:** Biomass burning organic aerosol. In Mexico City BBOA originated mostly from

45   wildfire and agricultural burning, but wood-fired stoves can also be important in the

46   winter at some locations (Lanz et al., 2007).

47   **LOA:** Local organic aerosol. So named because it is characterized by short (<10 min)

48   spikes of aerosol concentration that indicates a local source. Separated by PMF in both

49   SOAR-1 and MILAGRO campaigns.

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

51   **IVOC:** Intermediate-volatility organic compound, with volatility just above that of

52   undiluted POA (Robinson et al., 2007).

53   **SVOC:** Semi-volatile organic compound, which may be of primary origin (evaporated

54   POA material (Robinson et al., 2007)) of secondary origin.

Figure Captions

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

Figure S2: Thermograms for additional ions for SOAR-1 and MILAGRO. Panel **(a)** shows nitrogen-containing ions: CH_4N^+, $C_3H_8N^+$, $C_5H_{12}N^+$, and NO^+. Panel **(b)** shows sulfur-containing ions: CHS^+, $CH_3SO_3^+$, $CH_3SO_2^+$, and SO^+. $C_3H_5^+$ is also shown in each plot for visual comparison

Figure S3: Average OA mass spectra at ambient and five heated TD temperatures. HR MS are averaged over entire MILAGRO campaign and show ion groups of $C_xH_y^+$, $C_xH_yO_z^+$, $C_xH_yN_z^+$, and $C_xH_yO_zN_w^+$ in different colors.

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

Figure S5: Average SMPS size distributions from periods used in Figure 8d (high HOA, high BBOA and high OOA-2) shown as dV/dlogdP vs mobility diameter.

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

Figure S7: Average HR MS for recombined PMF factors for MILAGRO: **(a)** OOA_{Total} (sum of OOA-1 and OOA-2), **(b)** OOA-1, **(c)** OOA-2, **(d)** HOA, **(e)** BBAO, **(f)** LOA. Mass fraction of each ion group to total OA shown as inset table in each panel.
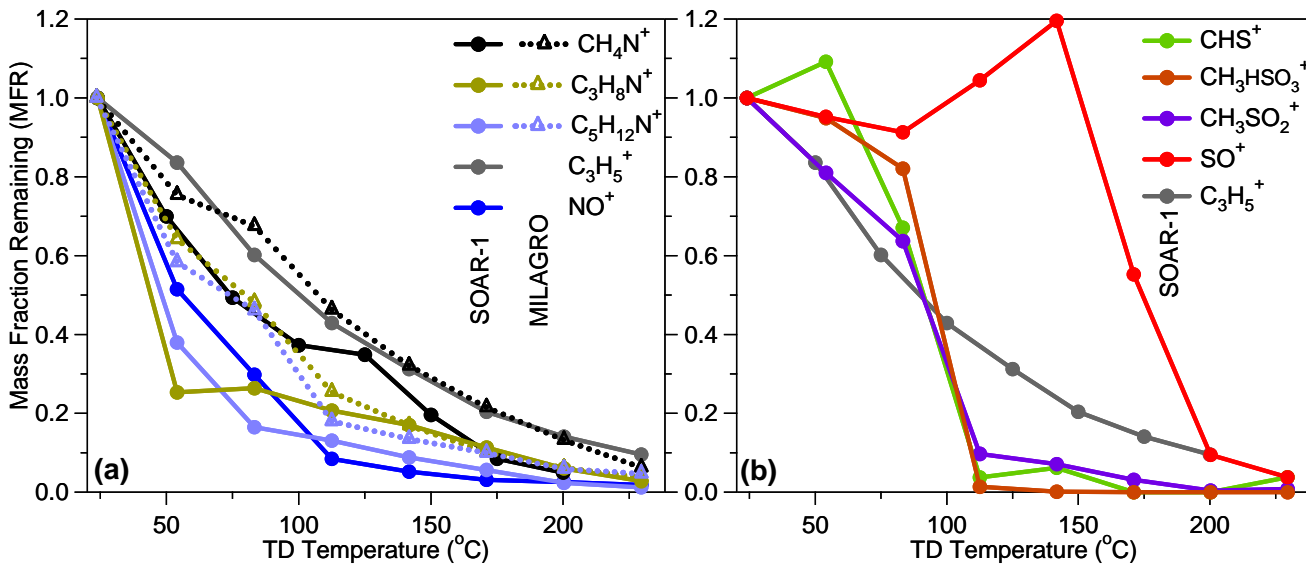
Figure S8: Fraction of the total aerosol mass contained in each PMF component shown as a function of temperature for: **(a)** SOAR-1 and **(b)** MILAGRO.
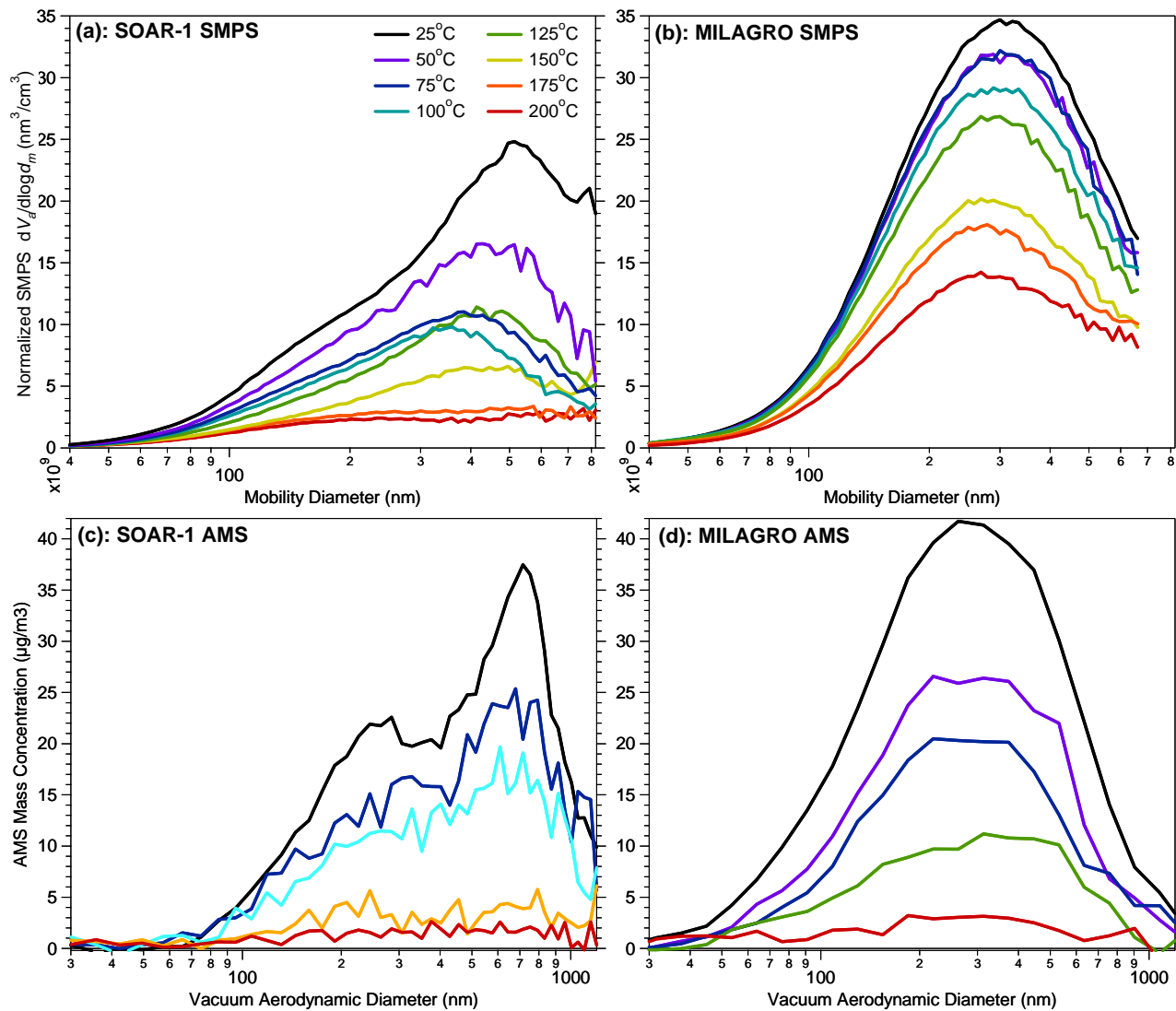
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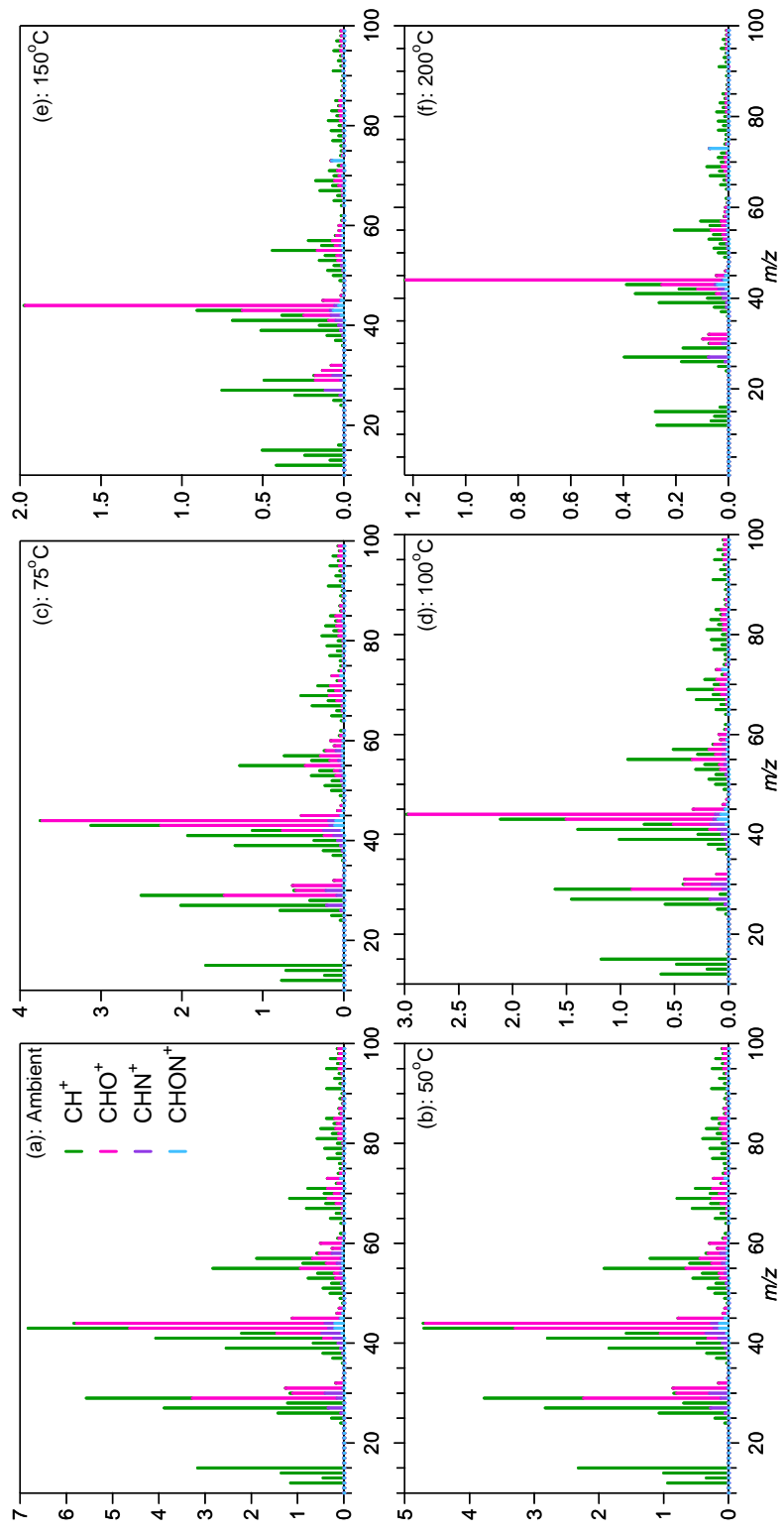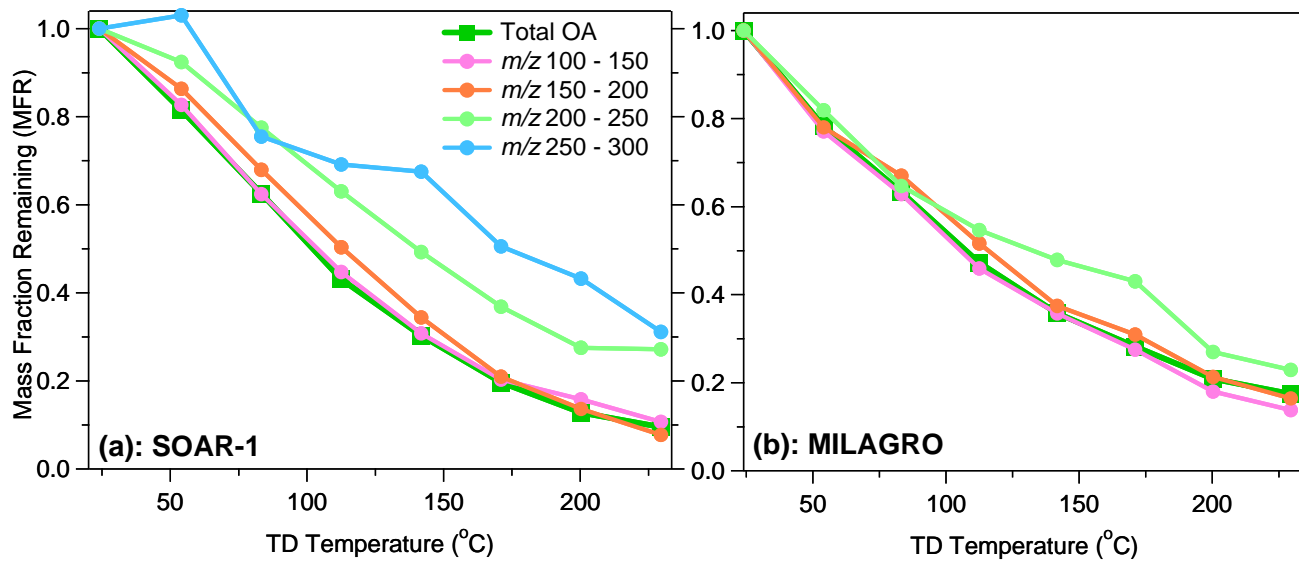128
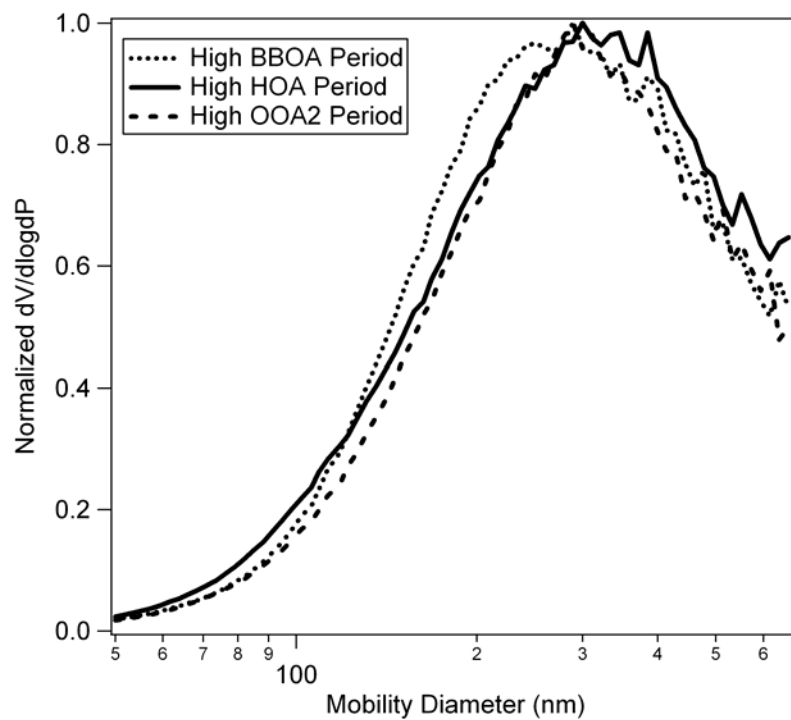129
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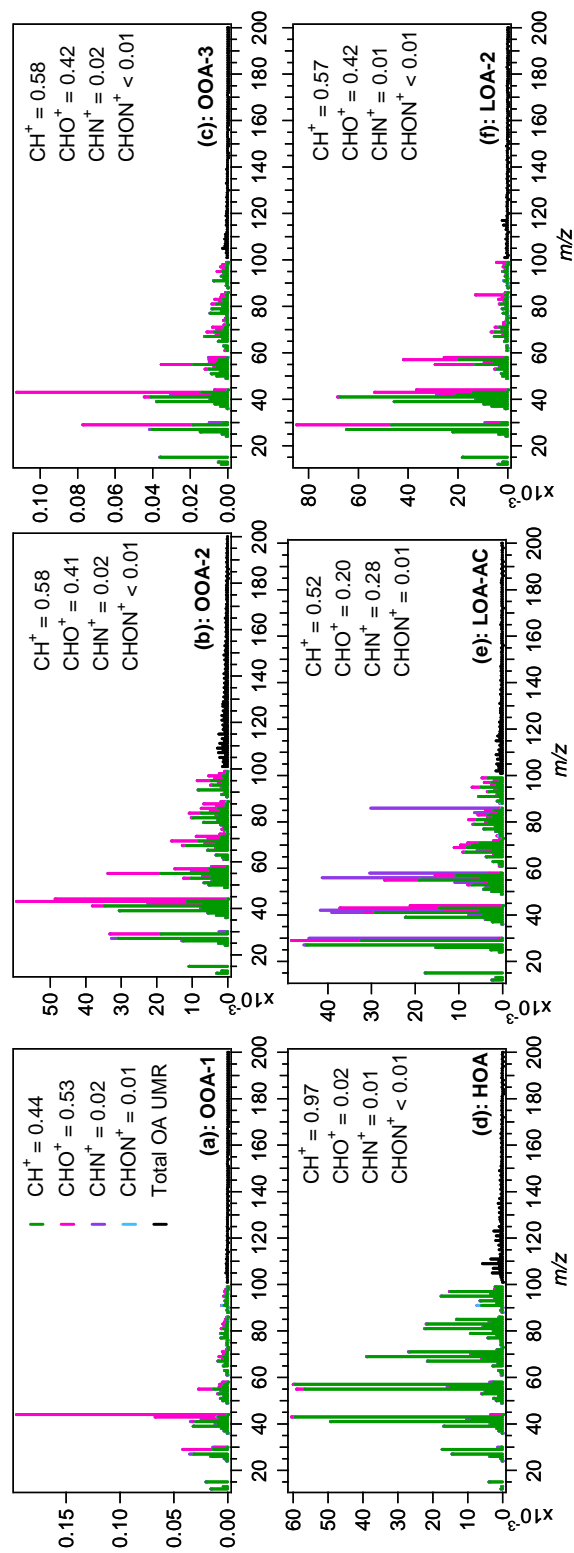193
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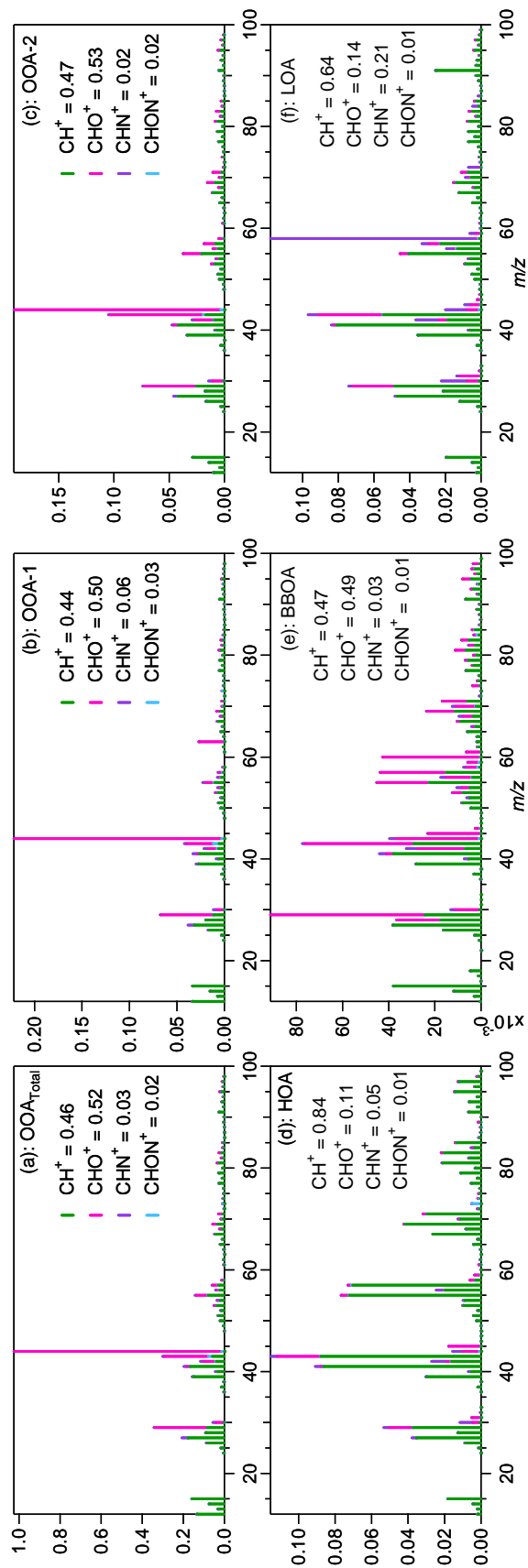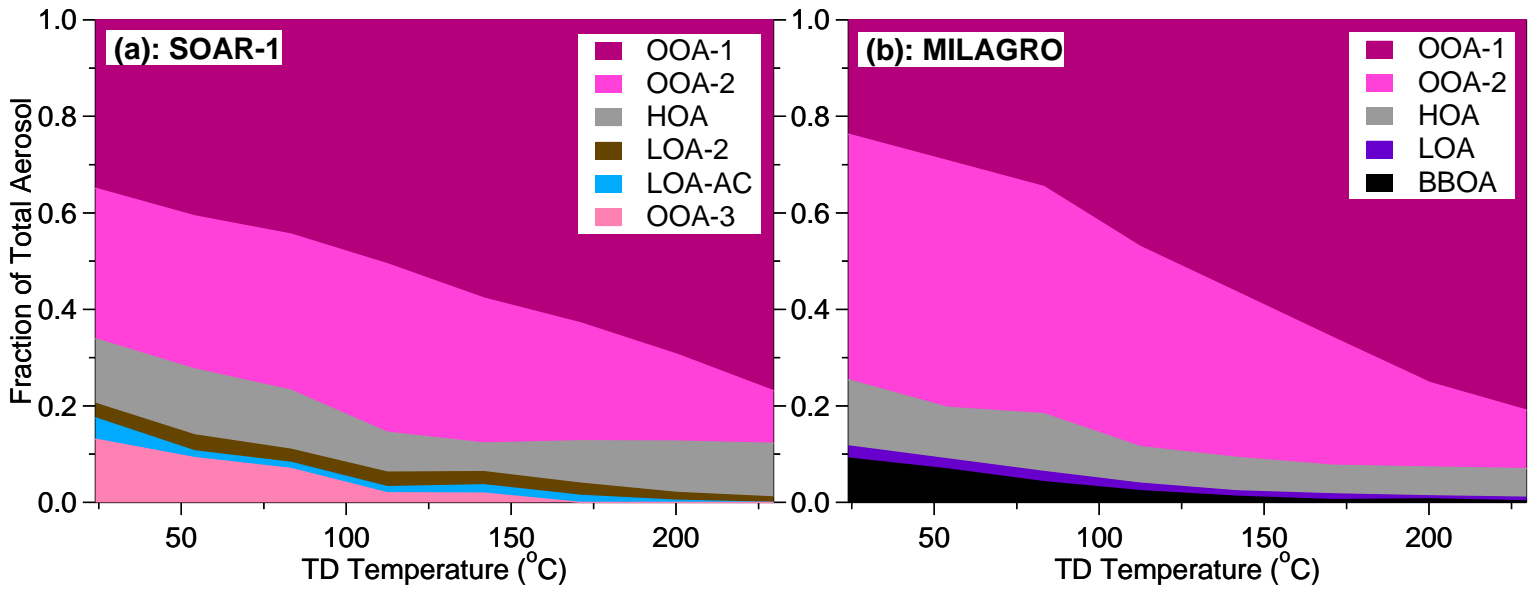239
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