

Chemically-resolved aerosol volatility measurements from two megacity field studies

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Keywords: Volatility, Thermodenuder, Aerosol Mass Spectrometry, Field Measurements, Submicron Particles

The volatilities of different chemical species within ambient aerosols are important in order to be able to more accurately understand their reaction and deposition rates, but also remain poorly characterized. The coupling of a recently modified rapid, temperature-stepping thermodenuder (TD, operated in the range 54–230°C, ~21s heated residence time) with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) during field studies in two polluted megacities has enabled the first direct characterization of chemically-resolved urban particle volatility on a timescale shorter than most changes in ambient particle composition. Measurements were conducted for approximately two weeks each in Riverside, CA as a part of the SOAR-1 study (Study of Organic Aerosols in Riverside – Phase 1, July-August 2005) and Mexico City as a part of MILAGRO (Megacity Initiative: Local And Global Research Observations, March-April 2006). Volatility measurements are generally consistent and show ambient nitrate as having the highest volatility of any AMS aerosol species while sulfate showed the lowest volatility. Total organic aerosol (OA) showed volatility intermediate between nitrate and sulfate, with an evaporation rate of $0.6\% \cdot K^{-1}$ near ambient temperature, although OA dominates the residual species at the highest temperatures. Different types of OA were characterized with marker ions, diurnal cycles, and positive matrix factorization (PMF) and show significant differences in volatility. Reduced hydrocarbon-like OA (HOA, a surrogate for primary OA, POA), oxygenated OA (OOA, a surrogate for secondary OA, SOA), and biomass-burning OA (BBOA) separated with PMF were all determined to be semi-volatile. The most aged OOA-1 and its dominant ion, CO_2^+ , consistently exhibited the lowest volatility, with HOA, BBOA, and associated ions for each among the highest. The similar or higher volatility of HOA/POA compared to OOA/SOA contradicts the current representations of OA volatility in most atmospheric models and has important implications for aerosol growth and

lifetime. Our results strongly imply that all OA types should be considered semivolatile in models.

The study in Riverside identified organosulfur species (e.g. $CH_3HSO_3^+$ ion, likely from methanesulfonic acid), while both studies identified ions indicative of amines (e.g. $C_5H_{12}N^+$) with very different volatility behaviors than inorganic-dominated ions. The oxygen-to-carbon ratio of OA in each ambient study was shown to increase both with TD temperature and from morning to afternoon, while the hydrogen-to-carbon ratio showed the opposite trend.

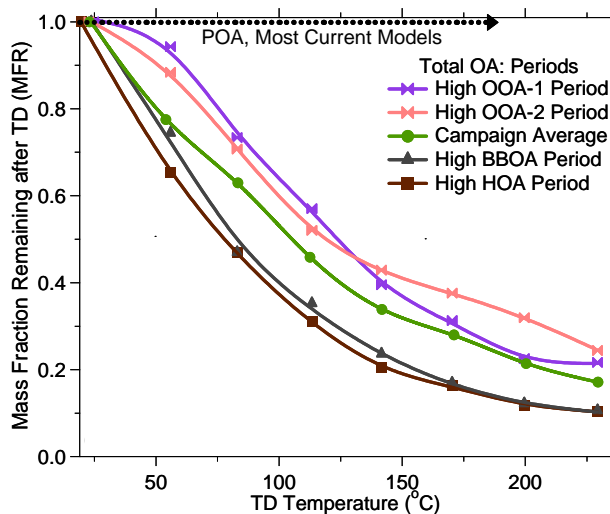


Figure 1. Particle mass fraction remaining (MFR) after passing through TD is shown as a function of TD-processing temperature (“thermogram”-style plots). As temperature increases, MFR decreases from a defined value of unity at ambient temperature with a larger negative slope showing more rapid evaporation. Aerosol from periods (1-2 hours) during MILAGRO when different OA types were dominant are shown as different colored lines. HOA and BBOA are shown to decrease more rapidly with increasing temperature than the average OA or than periods of OA dominated by aged, oxygenated aerosol.