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Characterization of Hydrocarbon-like and Oxygenated Organic Aerosols Based on Aerosol Mass Spectrometry—Method Development and Application to the Pittsburgh Dataset

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A new data analysis technique has been developed to deconvolve and quantify hydrocarbon-like and oxygenated organic aerosol (HOA and OOA) using highly time-resolved organic mass spectral data obtained with an Aerodyne Aerosol Mass Spectrometer (AMS). The core of this technique is an iterative customized principal component analysis (PCA) algorithm that is initialized with two AMS mass spectral tracers—m/z 57 (mostly $\mathrm{C_4H_9^+}$) for hydrocarbon-like organic aerosols (i.e., HOA) and m/z 44 (mostly $\mathrm{CO_2^+}$) for oxygenated (i.e., OOA). This technique was applied to the AMS organic aerosol data acquired at the Pittsburgh Supersite during September 2002 to determine the mass concentrations, size distributions, and mass spectra of HOA and OOA. The reconstructed organic concentrations (= HOA + OOA) agree very well with the measured values (r^2 = 0.997, slope = 0.998) and the reconstructed organic data matrix (3199 time steps $\times$ 300 m/z's) explains 99% of the variance in the measured time series. The extracted mass spectrum of HOA is remarkably similar to that of directly sampled vehicle exhaust, while the spectrum of OOA closely resembles that of highly processed organic aerosols sampled from a rural location.

Analysis of the mass spectra, size distributions, and diurnal variations of HOA and OOA and their correlations to gas phase and particulate tracer compounds, including

CO, NO_x, EC and sulfate indicates that the majority of HOA is primary OA from local emissions (likely from combustion processes) and the OOA is mostly secondary OA that present on a regional scale. On average, hydrocarbon-like compounds represent 34% of the organic aerosol mass in Pittsburgh while oxygenated compounds account for 66%. Strong evidence of the direct correspondence of OOA to SOA was observed during an intense new particle formation and growth event, when condensational growth of OOA was observed. The mass spectrum of OOA during this period is very similar to that of the entire study. We examined the correlation between OOA and O_3 and found O_3 a poor indicator for OOA concentration while SO_4^{2-} is a relatively good surrogate for this dataset.

Based on extracted mass spectra and the likely elemental compositions of major m/z's, the organic mass to organic carbon ratios (OM:OC) of HOA and OOA are estimated at 1.2 and 2.2μg/μgC, respectively, leading to an average OM:OC ratio of 1.8 for submicron OA in Pittsburgh during September. The C:O ratio of OOA is estimated at 1:0.8. The carbon contents in HOA and OOA estimated accordingly correlate well to primary and secondary organic carbon, respectively, estimated by the OC/EC tracer technique (assuming POC-to-EC ratio=1). In addition, the total carbon concentrations estimated from the AMS data agree well with those measured by the Sunset Laboratory Carbon analyzer (r^2=0.87; slope=1.01±0.11). Our results represent the first direct estimate of the OM:OC ratio from highly time-resolved chemical composition measurements.