Geophysical Research Abstracts, Vol. 11, EGU2009-6549-1, 2009 EGU General Assembly 2009 © Author(s) 2009



O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry

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A recently developed method to rapidly quantify the elemental composition of bulk organic aerosols (OA) using a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) is improved and applied to ambient measurements. Atomic oxygen-to-carbon (O/C) ratios characterize the oxidation state of OA, and O/C from ambient urban OA ranges from 0.2 to 0.8 with a diurnal cycle that decreases with primary emissions and increases because of photochemical processing and secondary OA (SOA) production. Regional O/C approaches approximately 0.9. The hydrogen-to-carbon (H/C, 1.4–1.9) urban diurnal profile increases with primary OA (POA) as does the nitrogen-to-carbon (N/C, approximately 0.02). Ambient organic-mass-to-organic-carbon ratios (OM/OC) are directly quantified and correlate well with O/C (R2 = 0.997) for ambient OA because of low N/C. Ambient O/C and OM/OC have values consistent with those recently reported from other techniques. Positive matrix factorization applied to ambient OA identifies factors with distinct O/C and OM/OC trends. The highest O/C and OM/OC (1.0 and 2.5, respectively) are observed for aged ambient oxygenated OA, significantly exceeding values for traditional chamber SOA, while laboratory-produced primary biomass burning OA (BBOA) is similar to ambient BBOA, O/C of 0.3–0.4. Hydrocarbon-like OA (HOA), a surrogate for urban combustion POA, has the lowest O/C (0.06–0.10), similar to vehicle exhaust. An approximation for predicting O/C from unit mass resolution data is also presented.