

Molecular Insights on the Aqueous Phase Processing of Ambient Biomass Burning Emissions Influenced Fog and Aerosol using Ultrahigh Resolution Orbitrap Elite Mass Spectrometry

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Ambient samples of fog water and PM1 aerosol were collected in the Italian Po Valley over 5 consecutive days in the winter of 2015. The Po Valley has an established history of regional biomass burning emissions influence and aqueous aging processes resulting in significant concentrations of brown carbon. Five samples of fog water and ten samples of extracted PM1 aerosol filters (day and night samples) were analyzed by ultrahigh resolution Orbitrap mass spectrometry using both electrospray ionization and atmospheric pressure photoionization methods. The water-soluble organic matter of the samples was fractionated prior to analysis using a 2-step solid phase extraction procedure for HULIS. This fractionation method facilitated the observation of additional less easily ionized condensed aromatic species. Thousands of distinct molecular formulas were assigned to the monoisotopic masses of each sample and were categorized into elemental groups and sub-classes based on the observed number of oxygen, nitrogen and/or sulfur atoms in the formulas. An atypically large frequency of molecular formulas containing nitrogen and sulfur were observed. Many of which could be attributed to multifunctional organonitrates and organosulfates, however a wide array of aromatic species with lower numbers of oxygen observed using atmospheric pressure photoionization were not. In general, higher numbers of CHNO species were observed in aerosol samples and higher numbers of CHOS species were found in fog water. The observed molecular trends were related to the atmospheric conditions to determine their likely origins. The overlapping collection time periods between the two sample types, and the progressive chronological sampling allowed for a unique perspective on chemical transformations within this humid atmosphere.