

Chemical composition of atmospheric aerosols resolved via positive matrix factorization

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Atmospheric particulate matter is a complex mixture of various chemical species such as organic compounds, sulfates, nitrates, ammonia, chlorides, black carbon and sea salt. As aerosol chemical composition strongly influences aerosol climate effects (via cloud condensation nucleus activation, hygroscopic properties, aerosol optics, volatility and condensation) as well as health effects (toxicity, carcinogenicity, particle morphology), detailed understanding of atmospheric fine particle composition is widely beneficial for understanding these interactions. Unfortunately the comprehensive, detailed measurement of aerosol chemistry remains difficult due to the wide range of compounds present in the atmosphere as well as for the miniscule mass of the particles themselves compared to their carrier gas. Aerosol mass spectrometer (AMS; Canagaratna et al., 2007) is an instrument often used for characterization of non-refractive aerosol types: the near-universal vaporization and ionisation technique allows for measurement of most atmospheric-relevant compounds (with the notable exception of refractory matter such as sea salt, black carbon, metals and crustal matter). The downside of the hard ionisation applied is extensive fragmentation of sample molecules. However, the apparent loss of information in fragmentation can be partly offset by applying advanced statistical methods to extract information from the fragmentation patterns.

In aerosol mass spectrometry statistical analysis methods, such as positive matrix factorization (PMF; Paatero, 1999) are usually applied for aerosol organic component only, to keep the number of factors to be resolved manageable, to retain the inorganic components for solution validation via correlation analysis, and to avoid inorganic species dominating the factor model. However, this practice smears out the interactions between organic and inorganic chemical components, and hinders the understanding of the connections between primary and secondary aerosols via atmospheric physicochemical processes (e.g. condensation and evaporation of gases) and on the other hand the potential non-linear summation (Spracklen et al., 2011 2011) of anthropogenic and biogenic aerosol emissions. From the perspective of statistical analysis there is no definite reason why inorganics could not be included, as long as their uncertainties are estimated correctly and their influence is properly weighted in the factor model. For result validation, external, additional information available from most measurement sites, such as correlations with trace gas concentrations or size distribution derived, mode-specific mass loadings can be used instead of AMS inorganics. In recent analyses, nitrate compounds have already been added to PMF analyses and shown to interact with organic semi-volatile compounds (Hao et al., 2014).

In this study we tested including all the default AMS chemical species, i.e. organics, sulfates, nitrates, ammonia and chlorides, in a PMF analysis, and present potential interpretations of the results with regard to aerosol sources and the chemical processes shaping the aerosol types. In addition to resolving organic-dominated aerosol classes, the results shed light on inorganic salt formation and may imply formation of organics salts.

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