Computational tools for functional group analysis of organic aerosols

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The molecular diversity of compounds in atmospheric organic aerosol (OA) poses challenges for measurement and modeling of these complex mixtures. Common methods to interpret OA composition in atmospheric or laboratory measurements and numerical simulation include speciated molecule concentrations and atomic ratios. Functional group (FG) abundance in OA provides an intermediate chemical resolution that retains source class fingerprints, capability for OA mass estimation, and physicochemical properties such as hygroscopicity, volatility, and reactivity. However, extracting FG content from measurements such as infrared (IR) absorption spectra or numerical models have been impeded by our lack of computational tools required to harvest this information. We therefore present two sets of tools we have recently developed to accomplish model and measurement interpretation through FGs, which we make available to the aerosol community.

First, we describe a tool based on chemoinformatic algorithms for reducing a set of molecular abundances to their corresponding proportions in FG space. Through this tool, we introduce a novel method of formulating and validating a set of patterns which apportion all atoms in a mixture to one of several predefined FGs, thereby bridging the gap between molecular specificity and atomic composition (Ruggeri and Takahama, 2015). We demonstrate its application to molecularly speciated mixture composition of primary OA measured with gas chromatography with mass spectrometry, and secondary OA formed from anthropogenic and biogenic precursors by simulation with the Master Chemical Mechanism (MCM) v3.2 (Jenkin et al., 1997) with dynamic gas/particle partitioning (Figure 1) (Ruggeri et al., 2016). These results are compared with available IR spectroscopy measurements of FG composition in chamber studies and comparable systems.

We further present chemometric tools for FG estimation of OA using IR spectroscopy. While the sample collection and signal acquisition can be relatively simple, the processing of the IR spectrum requires one of several algorithms to correct for substrate interferences, and relate the remaining analyte absorbance to abundances of vibrational modes present in the organic mixture. We describe a new interface that allows experimentalists and practitioners to access our algorithms (e.g., Takahama et al., 2013; Kuzmiakova et al. 2016). The FG composition obtained by this tool can then be used for comparison against model simulation and other measurements; estimation of organic carbon (OC) and organic matter (OM) mass, OM/OC ratios, and atomic ratios. We briefly demonstrate the scalability of such FG analysis to short-term field campaign and large-scale monitoring network measurements.

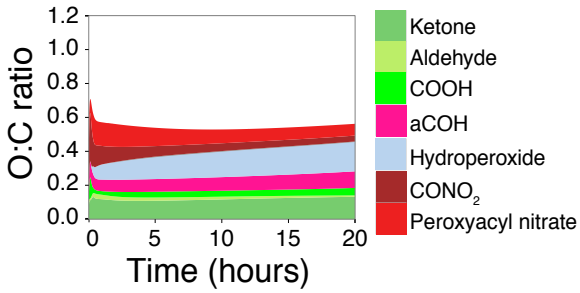

Figure 1. Simulated O:C ratio from MCMv3.2 apportioned to contributing functional groups.

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