



## **Effect of photochemical aging on the partitioning and oxidation state of atmospheric organic carbon**

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The multigenerational oxidative processing (“aging”) of atmospheric organic species is likely to have a major influence on organic aerosol (OA). However, due to the difficulty in simulating such processes in the laboratory, the effects and underlying chemistry of these aging processes are poorly understood. This limits our ability to accurately predict the loadings, composition, and properties of OA, representing a major uncertainty in the effects of atmospheric aerosol on climate. Here we describe laboratory experiments aimed at better constraining the key chemical changes that organics undergo upon multigenerational aging. Two sets of experiments are carried out: chamber studies of the gas-phase oxidation of simple alkanes (in which some fraction of the organic carbon partitions into the particle phase), and flow-tube studies of the heterogeneous oxidation of single-component particulate organics (in which some fraction of the organic carbon escapes to the gas phase). In all experiments, the organics are exposed to elevated levels of OH, in order to access the equivalent of several days’ worth of atmospheric oxidation. A scanning mobility particle sizer (SMPS) and an Aerodyne high-resolution aerosol mass spectrometer (HR-AMS) are used for measurements of the mass and elemental composition of the particles as a function of OH exposure.

These measurements enable the accurate determination of two key quantities for describing OA chemistry, the absolute amount of particulate carbon and the average carbon oxidation state of the OA. Changes in these quantities during both gas-phase oxidation reactions (chamber experiments) and heterogeneous oxidation reactions (flow-tube experiments) provide strong evidence for the increasingly important role of carbon-carbon bond-breaking reactions as organic species age. Such fragmentation reactions are among the most efficient pathways for the formation of highly oxidized carbon; however, the fragmentation of organic species into smaller molecules is also expected to offset any decreases in volatility that occur when new functional groups are added. The net result is that particulate organics will likely have increasingly lower carbon numbers as they become more oxidized, with the continual escape of oxidized carbon to the gas phase during aerosol aging. Such effects are generally not included in most current models of aerosol aging. Implications of these results for our understanding of the lifecycle of organic compounds in the atmosphere will be discussed.