



Photochemical Aging of Organic Aerosols: A Laboratory Study

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Organic aerosols (OA) are either emitted directly (primary OA) or formed (secondary OA) in the atmosphere and consist of an extremely complex mixture of thousands of organic compounds. Although the scientific community has put significant effort, in the past few decades, to understand organic aerosol (OA) formation, evolution and fate in the atmosphere, traditional models often fail to reproduce the ambient OA levels. Secondary organic aerosol (SOA) formed, in traditional laboratory chamber experiments, from the gas phase oxidation of known precursors, such as α -pinene, is semi-volatile and with an O:C ratio of around 0.4. In contrast, OA found in the atmosphere is significantly less volatile, while the O:C ratio often ranges from 0.5 to 1. In conclusion, there is a significant gap of knowledge in our understanding of OA formation and photochemical transformation in the atmosphere. There is increased evidence that homogeneous gas phase aging by OH radicals might be able to explain, at least in part, the significantly higher OA mass loadings observed and also the oxidation state and volatility of OA in the atmosphere.

In this study, laboratory chamber experiments were performed to study the role of the continued oxidation of first generation volatile and semi-volatile species by OH radicals in the evolution of the SOA characteristics (mass concentration, volatility, and oxidation state). Ambient air mixtures or freshly formed SOA from α -pinene ozonolysis were used as the source of organic aerosols and semi-volatile species. The initial mixture of organic aerosols and gas phase species (volatile and semi-volatile) was then exposed to atmospheric concentrations of OH radicals to study the aging of aerosols. Experiments were performed with various OH radical sources (H_2O_2 or HONO) and under various NO_x conditions. A suite of instruments was employed to characterize both the gas and the aerosol phase. A Scanning Mobility Particle Sizer (SMPS) and a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) were used to measure the organic aerosol mass production and oxidation degree (O:C ratio) following OH aging. A thermodenuder system was used to measure the volatility distribution change as organic aerosol aged upon continuous oxidation. Organic gas phase species were characterized with a Proton Transfer Reaction - Mass Spectrometer (PTR-MS) while NO_x and O_3 were measured with the use of corresponding analyzers.

Results from this study show that organic mass production occurs upon exposure to OH radicals indicating that continuous OH aging of semi-volatile is probably responsible for at least some of the gap between observed and modeled OA levels in the atmosphere. Additionally, this chemical aging process leads to a decrease in volatility and an increase in O:C ratio while the level of change in both properties depends on OH exposure. The atmospheric implications of this study are discussed.