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Simulating the Oxidative Aging of Ambient Organic Compounds Using the 2-D Volatility Basis Set

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Organic compounds are subject to continued oxidation (aging) throughout their atmospheric lifetime. These complex reactions change the volatility and degree of oxygenation of the compounds, thus affecting the concentrations and chemical composition of atmospheric organic aerosols. We employ a regional-scale, Lagrangian model with a volatility basis-set module that explicitly tracks oxidation state (or O/C ratio) as well as vapor pressure (or saturation concentration) to simulate aging and evaluate predictions with observations made at several sites within the European Integrated Project on Aerosol Cloud Climate Air Quality Interactions (EUCAARI).

Traditional chemical transport models simulate secondary organic aerosol (SOA) formation as the condensation of semivolatile gases produced by volatile organic precursor oxidation. Most large-scale models that treat SOA formation, though, do not consider the additional chemistry that may change the properties of those products. However, chamber studies have found that, under a variety of conditions for longer experiment durations (several hours), the total organic aerosol concentration and the O/C ratio do continue to evolve. Since organic aerosols tend to experience an atmospheric lifetime on the order of one week, representing this phenomenon accurately could be an important feature for the development of reliable atmospheric organic aerosol modules. There are significant uncertainties in this process though, including the aging reaction rates, the volatility and O/C ratio distributions of the product species and the roles of functionalization versus fragmentation pathways.

Organic species gas/particle partitioning has been described in recent lab- and large-scale models using the volatility basis set approach, which tracks the saturation concentration of organic vapor and particle mass. We have extended this model to describe variations in O/C ratio so the degree of oxygenation can be tracked explicitly. The model simulates 3 days of transport for each parcel arriving at a measurement site and takes into account emissions, chemical processing, wet deposition, dry deposition, and gas/particle equilibrium of pollutant species. This model can therefore predict the organic aerosol concentration as well as quantify the volatility and O/C ratio distributions through time. These metrics are compared to thermodenuder and aerosol mass spectrometer measurements taken at various EUCAARI sites including Finokalia, Cabauw, Melpitz and K-Puszta. Combining the Lagrangian model application with the available measurements allows us to evaluate the reasonableness of a variety of homogeneous gas-phase organic aerosol aging configurations and probe the effects of more complicated aging pathways such as heterogeneous OH uptake and oligomerization. The results from this explicit model will improve the way large-scale 3-dimensional models treat organic aerosol aging.