Molecular view modeling of atmospheric organic particulate matter: Incorporating molecular structure and co-condensation of water

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HIGHLIGHTS

- Current 3-D transport models use anonymized view modeling of organic particulate matter (OPM).
- Anonymized view modeling assigns only a volatility (vapor pressure) to each OPM constituent.
- Anonymized view modeling cannot consider effects of water uptake on OPM levels.
- Molecular view modeling assigns structural features to each OPM constituent.
- Molecular view modeling can consider effects of water uptake on OPM levels and OPM properties.

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ABSTRACT

Most urban and regional models used to predict levels of organic particulate matter (OPM) are based on fundamental equations for gas/particle partitioning, but make the highly simplifying, anonymized-view (AV) assumptions that OPM levels are not affected by either: a) the molecular characteristics of the condensing organic compounds (other than simple volatility); or b) co-condensation of water as driven by non-zero relative humidity (RH) values. The simplifying assumptions have allowed parameterized chamber results for formation of secondary organic aerosol (SOA) (e.g., "two-product" (2p) coefficients) to be incorporated in chemical transport models. However, a return towards a less simplistic (and more computationally demanding) molecular view (MV) is needed that acknowledges that atmospheric OPM is a mixture of organic compounds with differing polarities, water, and in some cases dissolved salts. The higher computational cost of MV modeling results from a need for iterative calculations of the composition-dependent gas/particle partition coefficient values. MV modeling of OPM that considered water uptake (but not dissolved salts) was carried out for the southeast United States for the period August 29 through September 7, 2006. Three model variants were used at three universities: CMAQ-RH-2p (at PSU), UCD/CIT-RH-2p (at UCD), and CMAQ-RH-MCM (at TAMU). With the first two, MV structural characteristics (carbon number and numbers of functional groups) were assigned to each of the 2p products used in CMAQv.4.7.1 such that resulting predicted $K_{p,i}$ values matched those in CMAQv.4.7.1. When water uptake was allowed, most runs assumed that uptake occurred only into the SOA portion, and imposed immiscibility of SOA with primary organic aerosol (POA). (POA is often viewed as rather non-polar, while SOA is commonly viewed as moderately-to-rather polar. Some runs with UCD/CIT-RH-2p were used to investigate the effects of POA/SOA miscibility.) CMAQ-RH-MCM used MCM to generate oxidation products, and assumed miscibility of SOA and POA. In a ~500 km wide band from Louisiana through to at least North Carolina, CMAQ-RH-2p and UCD/CIT-RH-2p predicted that water uptake can increase SOA levels by as much as 50—100% (from a range of ~1—2 μg m^{-3} to a range of ~1—4 μg m^{-3}). CMAQ-RH-MCM predicted much lower effects of water uptake on SOA levels (<10% increase). The results from CMAQ-RH-2p and UCD/CIT-RH-2p are considered more reflective of reality. In the Alabama/Georgia

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hotspot, both CMAQ-RH-2p and UCD/CIT-RH-2p predicted aerosol water levels that are up to nearly half the predicted SOA levels, namely ~0.5–2 $\mu g\ m^{-3}$. Such water levels in SOA will affect particle optical properties, viscosity, gas/particle partitioning times, and rates of hydrolysis and water elimination reactions.

1. Introduction

Most current 3D chemical transport models use primitive approaches for predicting levels of organic particulate matter (OPM) in the atmosphere: they incorporate only the barest aspects of the chemistry of the complex mixes of organic compounds that may occur, ignore the role of co-condensing water, and usually do not attempt to consider the time-dependent oxidation reactions that continually transform organic compounds in the atmosphere. This is problematic: 1) aerosol particles are known to have direct and indirect effects on climate (Ramanathan et al., 2001; Kanakidou et al., 2005); 2) ambient levels of fine PM are associated with increases in human morbidity and mortality (Pope and Dockery, 2006); and 3) atmospheric PM is often 20–60% organic material (Kanakidou et al., 2005). In those contexts, the composition of the OPM can strongly affect light absorption (Andreae and Gelencsér, 2006; Updyke et al., 2012; and Song et al., 2013), cloud condensation (Petters and Kreidenweis, 2007), and particle deposition rates (composition affects hygroscopicity (Petters and Kreidenweis, 2007) and hygroscopicity affects deposition rates (Vong et al., 2010)).

While views vary regarding the advantages and deficiencies of different modeling approaches, there is scientific consensus at least that in the general case: 1) a portion of ambient OPM has some volatility, and so is in active evaporation/condensation (*i.e.*, gas/particle) exchange with the gas phase; and 2) a second portion is essentially non-volatile at the ambient temperature *T*. Both the exchanging and non-volatile fractions can be subdivided as anthropogenic or biogenic, and further as primary (directly emitted) or secondary. For a neutral species, an inherently low volatility is always ascribable to the combined effects of molecular weight (MW), polarity, and temperature *T*. Temperature plays its role through vapor pressure, which sets the volatility for every particular pure liquid compound *i*. Atmospheric OPM, however, is never a single pure compound, so the effective volatility of each constituent compound is lowered by dilution, and changed by non-ideal solution effects (Pankow, 1994a). Regarding acidic and basic species (*i.e.* organic carboxylic acids can be deprotonated to form carboxalate ions, and organic amines can be protonated to form aminium ions), charge alone is enough to prevent volatilization at ambient *T* values (*cf.* protonation of ammonia to form ammonium ion) (Pankow, 2003).

Chemical transport models in current use for atmospheric OPM modeling such as CMAQ and PMCAMx (Carlton et al., 2010; Robinson et al., 2007) suffer from two deficiencies that affect OPM predictions. *First*, they both utilize a severely *anonymized view* (AV) in which a limited number (20 or less) of "hypothetical lumped compounds" is invoked. The "compounds" vary only by inherent volatility, with no other characteristics such as polarity. Examples of the AV approach include the two-product (2p) view of Odum et al. (1996, 1997) as used in CMAQ (Carlton et al., 2010), and the 1-D volatility basis set (VBS) of Donahue et al. (2006). In fact, contrary to the AV assumption, both low polarity and polar constituents are always present in atmospheric OPM, and those differences will affect the levels and properties of the OPM. Low polarity constituents include plant wax materials, cooking oils, and petroleum hydrocarbons (Schauer et al., 1999, 2002; Conte and Weber, 2002); polar constituents include secondary compounds with functional groups such as hydroxyl and carboxyl (e.g., Yu et al., 1999; Zhang et al., 2007). Each OPM phase will therefore be a mix with a mixture-average polarity that is between non-polar and highly polar. For each exchanging compound *i*, the gas/particle partitioning is affected by the polarity match or mismatch between the compound and the OPM mixture. A high mismatch (relative to condensation into a liquid in which $\zeta_i = 1$) causes $\zeta_i > 1$ which reduces the condensation tendency (*viz.* increases the volatility) (Pankow, 1994a, 2003). When the condensed material includes both non-polar and rather polar compounds in similar abundance, phase separation in the OPM becomes certain (Erdakos and Pankow, 2004; Zuend et al., 2010; Donahue et al., 2011), as when within the miscibility gap of a partially miscible binary system. While anonymized models ignore these complexities, a *molecular view* (MV) can assign functionalities to each OPM compound to allow consideration of non-ideality effects, and phase separation.

Second, AV modeling precludes consideration of water uptake: there is no character of the OPM that can be used to estimate hygroscopicity. However, theory (e.g., Pankow, 1994a, 2010; Pankow and Chang, 2008; Chang and Pankow, 2010), and applications with the 3D sesqui-MADRID model (Pun, 2008), predict that important effects on OPM levels are possible. Indeed, although water is far more volatile than "condensable" organic compounds, it is also always vastly more abundant in the atmosphere than the sum of all condensable organic compounds (~10^7 $\mu g/m^3$ water at 20 °C, 50% relative humidity (RH), and 1 atm total pressure). In addition to the importance of the effects of water on OPM levels and that of hygroscopicity itself (e.g., Massoli et al., 2010; Duplissy et al., 2011), there are expected significant effects of absorbed water on viscosity (Iwata and Shimada, 2013) and thus gas/particle equilibration times (Shiraiwa et al., 2011; Bones et al., 2012), and reaction rates within organic liquids (Vollhardt and Schore, 2007). Fortunately, once an adequately flexible MV model is built for considering compounds with varying polarity and molecular weight, inclusion of water as a fully-interacting partitioning compound is simple. With the 2-D VBS of Donahue et al. (2011), while some measure of MV effects amongst the partitioning organic compounds can be considered, only O:C ratio and carbon number are available as measures of molecular variability, and water is not included in the basis set so it is not predicted to be present in, or have an effect on the levels of, the modeled OPM. We are interested in modeling carried out considering specific functionalities (alcohol groups, aldehyde groups, carboxylic acid groups, etc.) assigned to partitioning organic molecules, and allowing water uptake.

Herein we provide an overview of the OPM model development required for a simple consideration of MV effects for non-ionic organic compounds, with water uptake into a single OPM phase; the effects of ionization and multiple OPM phases (*i.e.*, phase separation) are beyond the scope of this work. Simulations are described for the southeast United States for the period August 29 through September 7, 2006 using three chemical transport models modified to include MV features for OPM calculations. The implications of water uptake for OPM phase characteristics are considered.