Atmospheric Environment 129 (2016) 142–154

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Water uptake by organic aerosol and its influence on gas/particle partitioning of secondary organic aerosol in the United States

Shantanu H. Jathar [a], Abdullah Mahmud [b], Kelley C. Barsanti [b], William E. Asher [c], James F. Pankow [b, d], Michael J. Kleeman [a, *]

[a] *Civil and Environmental Engineering, University of California, Davis, CA, USA*
[b] *Civil and Environmental Engineering, Portland State University, Portland, OR, USA*
[c] *Applied Physics Laboratory, University of Washington, Seattle, WA, USA*
[d] *Chemistry, Portland State University, Portland, OR, USA*

HIGHLIGHTS

- Organic-phase water is predicted in eastern US and California using the same model.
- Organic-phase water enhances SOA formation in the eastern US.
- Organic-phase water has small effect on SOA formation in California.
- Different behavior is driven by regional emissions profiles.
- Particle mixing state changes the impact of organic-phase water.

ARTICLE INFO

Article history:
Received 20 January 2015
Received in revised form
28 August 2015
Accepted 4 January 2016
Available online 7 January 2016

Keywords:
Organic-phase water
Secondary organic aerosol
California
Eastern United States
Source-oriented external mixture

ABSTRACT

Organic aerosol (OA) is at least partly hygroscopic, i.e., water partitions into the organic phase to a degree determined by the relative humidity (RH), the organic chemical composition, and the particle size. This organic-phase water increases the aerosol mass and provides a larger absorbing matrix while decreasing its mean molecular weight, which can encourage additional condensation of semi-volatile organic compounds. Most regional and global atmospheric models account for water uptake by inorganic salts but do not explicitly account for organic-phase water and its subsequent impact on gas/particle partitioning of semi-volatile OA. In this work, we incorporated the organic-phase water model described by Pankow et al. (2015) into the UCD/CIT air quality model to simulate water uptake by OA and assessed its influence on total OA mass concentrations. The model was run for one summer month over two distinct regions: South Coast Air Basin (SoCAB) surrounding Los Angeles, California and the eastern United States (US). In SoCAB where the OA was dominated by non-hygroscopic primary OA (POA), there was very little organic-phase water uptake (0.1–0.2 $\mu g\ m^{-3}$) and consequently very little enhancement (or growth) in total OA concentrations (OA + organic-phase water): a 3% increase in total OA mass was predicted for a 0.1 increase in relative humidity. In contrast, in the eastern US where secondary OA (SOA) from biogenic sources dominated the OA, substantial organic-phase water uptake and enhancement in total OA concentrations was predicted, even in urban locations. On average, the model predicted a 20% growth in total OA mass for a 0.1 increase in relative humidity; the growth was equivalent to a 250 nm particle with a hygroscopicity parameter (κ) of 0.15. Further, for the same relative humidity, the exact extent of organic-phase water uptake and total OA enhancement was found to be dependent on the particle mixing state. When the source-oriented mixing state of aerosols was considered, generally, less organic-phase water uptake was predicted than when simple internal mixing approximations were made. Overall, the results indicated that organic-phase water can significantly influence predicted total OA concentrations under certain conditions. Regional models applied in areas with high humidity and significant SOA formation should include calculations for organic-phase water in order to capture this effect.

---

* Corresponding author.
E-mail address: mjkleeman@ucdavis.edu (M.J. Kleeman).

http://dx.doi.org/10.1016/j.atmosenv.2016.01.001
1352-2310/

1. Introduction

Organic aerosol (OA) accounts for a third of the ambient submicron aerosol mass (Jimenez et al., 2009) globally with significant implications for the energy budget of the earth (Pachauri et al., 2014) and human health (IHME, 2013). Despite its abundance, OA is one of the least understood components of atmospheric aerosol (Hallquist et al., 2009).

Although less hygroscopic than inorganic salts like sodium chloride and ammonium sulfate, laboratory-generated and ambient OA has been shown to be hygroscopic, i.e. depending on the particle size, the OA composition and the ambient relative humidity (RH) OA, will absorb water.[1] This organic-phase water (defined to be water in the organic phase) can alter the thermodynamic, reactive and optical behavior of OA and in turn affect the climate and health–relevant properties of OA (Kanakidou et al., 2005). OA is a complex mixture of thousands of different compounds (Goldstein and Galbally, 2007) that arise from numerous sources and reaction pathways, each with a different set of physical and chemical properties. Hence, individual constituents of OA exhibit varying levels of hygroscopicity when present as pure compounds. The hygroscopicity parameter (κ) is a measure of the ability of a molecule/mixture to absorb water; inorganic acids and salts like sodium chloride and ammonium sulfate have κ values larger than 0.6 (Koehler et al., 2009). Small acids found in ambient OA like malonic and glutaric acid or oxygenated organic compounds found in biomass burning emissions like levoglucosan are modestly hygroscopic, with pure-compound κ values of 0.44, 0.2 and 0.165 respectively (Koehler et al., 2009). In contrast, κ values less than 0.01 have been measured for primary organic aerosol (POA) from diesel exhaust (Weingartner et al., 1997). Further, constituents of OA constantly evolve in the atmosphere (e.g., via photochemical aging), changing their hygroscopic properties. For example, Jimenez et al. (2009) showed that the hygroscopicity of secondary organic aerosol (SOA) formed from the gas-phase oxidation of aromatic and biogenic volatile organic compounds (VOC) increased as the SOA become increasingly oxidized. Overall, it is expected that ambient OA will display a wide range of water uptake characteristics that will change as the chemical composition of OA evolves.

Petters and Kreidenweis (2007) used surrogate organic molecules to demonstrate that the effective hygroscopicity of OA can be estimated using a mixing rule that weights constituent hygroscopicities by their volume fractions in the OA mixture. This mixing rule provides a simple representation to model the hygroscopicity or water uptake (and cloud condensation nuclei activity) of OA (and other aerosols) in large-scale models (Liu and Wang, 2010; Pringle et al., 2010). However, the mixing rule assumes that the constituents of OA and water do not interact with each other at a molecular level (i.e., thermodynamically). Over the past decade, several studies have used activity coefficient models like UNIFAC (UNIquac Functional-group Activity Coefficient; Fredenslund et al. (1975)) to model water uptake based on the molecular interaction of aerosol constituents and water (Ansari and Pandis, 2000; Clegg et al., 2001; Seinfeld et al., 2001; Peng et al., 2001; Ming and Russell, 2002; Bowman and Karamalegos, 2002; Griffin et al., 2005; Barley et al., 2009; Zuend et al., 2010; Zuend and Seinfeld, 2012). Most found that water uptake by the OA fraction was limited compared to that by the inorganic fraction. However, the water uptake was sufficient to modify the activity of the SOA species and the mass and mean molecular weight of the absorbing organic phase. This altered the gas/particle partitioning and enhanced SOA mass concentrations by 10–100% at an RH of 80% for a wide range of precursor/oxidant systems (Seinfeld et al., 2001; Barley et al., 2009). At lower OA mass concentrations, Pankow and Chang (2008) found that the SOA enhancements were as high as a factor of 5 and an RH of 80% for the α-pinene/O_3 and isoprene/OH system.

Most large-scale models, supported by ambient observations of a well-mixed aerosol, assume that SOA is “miscible” with POA and can absorptively partition into POA. However, laboratory studies probing the miscibility of POA and SOA are equivocal. It has been suggested that fresh emissions of POA from diesel exhaust (Asa-Awuku et al., 2009) and biomass burning (Kanakidou et al., 2005) can mix with SOA while model compounds/surrogates for POA like dioctyl phthalate, adipic and fulvic acid, diesel fuel and lubricating oil do not (Asa-Awuku et al., 2009; Song et al., 2007, 2011). The miscibility of POA and SOA will determine not only the total uptake of water but will also modify the influence water has on the gas/particle partitioning of OA. For an activity coefficient model like UNIFAC, the modeled molecular interactions within an OA and water system will, hence, be sensitive to assumptions made about the miscibility of POA and SOA and contribute to uncertainty in model predictions of OA and organic-phase water. Further, almost all large-scale models assume that ambient aerosol is internally mixed, which might not always be a good assumption for urban aerosol (Schwarz et al., 2008) where differences in OA composition across particle types will lead to varying water uptake and subsequent effects on gas/particle partitioning of OA. Model predictions of OA and organic-phase water will, hence, be sensitive to assumptions about the mixing state of aerosol. These assumptions about POA-SOA miscibility and the aerosol mixing state add uncertainty to model predictions of OA and organic-phase water and, in the context of the current work (i.e., role of water on OA), have not previously been explored in large-scale models.

Examples of the explicit treatment of water uptake by OA and its influence on gas/particle partitioning of semi-volatile OA in a chemical transport or a climate model are limited mostly because of the computational expense of running an activity coefficient model in a three-dimensional framework. In fact, we are only aware of two studies that used activity coefficient models to predict the effects of organic-phase water. The first is by Pun (2008) where a single day was simulated in the eastern United States (US) for the summer of 2002. This work used a simpler model (Wilson equation) to calculate activity coefficients for the OA-organic-phase water mixture and did not represent important processes such as “oligomerization” (aka accretion reactions). The second is the work by Pankow et al. (2015) – a companion paper to this work – that simulates the influence of organic-phase water on SOA partitioning over a 10-day episode in the eastern US. We build on the latter study to explore the sensitivity of water uptake by OA and subsequent SOA gas/particle partitioning in different geographical domains (South Coast Air Basin (SoCAB) versus eastern US) to assumptions about the miscibility of POA and SOA and the mixing state of the aerosol (internally versus source-oriented externally mixed aerosol).

2. Methods

2.1. Chemical transport model

We used the UCD/CIT (University of California/California Institute of Technology) air quality model to simulate organic-phase water uptake and its influence on the gas/particle partitioning of OA. The UCD/CIT model is a regional chemical transport model

---

[1] In this manuscript, the word “organic-phase water” is exclusively used to refer to the water associated with the organic fraction of ambient aerosol. This “organic-phase water” is separate from the water associated with the inorganic fraction of ambient aerosol.