



Modeling secondary organic aerosol formation from xylene and aromatic mixtures using a dynamic partitioning approach incorporating particle aqueous-phase chemistry (II)

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ABSTRACT

Formation of secondary organic aerosol (SOA) is simulated for 14 outdoor smog chamber experiments using condensed gas-phase regulatory mechanisms and a new SOA framework. This framework is based on empirical parameterizations of independent chamber experiments and includes role of glyoxal and methylglyoxal in formation of particle aqueous-phase. To evaluate for regulatory applications, the chamber experiments include an urban non-SOA VOC mixture and NO_x, with either injections of *o/p*-xylenes or toluene. The experiments are performed under varying conditions of relative humidity (RH) and in the presence of low initial background seed. Gas-particle partitioning of semi-volatile products into particle organic-phase is modeled using a dynamic partitioning approach with reactive uptake coefficient as the principal transport and kinetic parameter. Aqueous-phase SOA is predicted using formulations that describe the irreversible loss of both glyoxal and methylglyoxal to particle aqueous-phase. The predicted SOA mass in the new framework is evaluated using two regulatory gas-phase mechanisms – CB05 or SAPRC07 and, two regulatory parameterization schemes to predict semi-volatile product formation – an Odum-type two-product model and volatility basis-set (VBS). Predictions from the new SOA framework reproduce SOA mass within the uncertainty range of observations, irrespective of the choice of gas-phase mechanism and SOA parameterization scheme (root mean square error [RMSE] range of 0.18–3.08 μg m⁻³). Further, model results suggest strong possibility of dominance of bulk-process under low seed conditions and surface-uptake process under high seed for aqueous-phase SOA formation. Sensitivity analysis to the hygroscopic nature of aqueous-phase SOA indicates an uncertainty of a factor of 2 in bulk-process and surface-uptake rates. In summary, the results strongly point to considering mass-transfer and kinetic limitations in regulatory air quality models at low ambient seed concentrations and highlight the importance of aqueous-phase SOA for aromatics under high-RH conditions.

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1. Introduction

Atmospheric aerosols play a crucial role in climate by influencing the radiative balance in Earth's atmosphere and also through modification of cloud optical properties and lifetimes

(I.P.C.C., 2007). Further, high concentrations of particulate matter (PM) adversely affect human health due to respiratory and cardiovascular complications (Lazaridis, 2011). Secondary organic aerosol (SOA) forms a substantial component of PM. It is therefore important to accurately represent the potential SOA precursors and formation processes in predictive regulatory air quality models (AQMs).

SOA forms in the atmosphere from complex and multi-generational reactions of a variety of volatile organic compounds (VOCs) and intermediate oxidation products that form semi-volatile products capable of absorbing into a particle liquid-phase (Donahue et al., 2006; Pankow, 1987). Current AQMs used to

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formulate policy predict SOA using simpler empirical parameterization schemes (Carlton et al., 2010). These parameterization schemes are based on smog chamber experiments used to compute mass-based stoichiometric yields to represent some degree of gas-phase oxidation. Two such schemes include a 2-product model (2P) with VOC specific saturation vapor pressures (Odum et al., 1996), or a volatility basis-set (VBS) modeling approach in which semi-volatile oxidation products are distributed in logarithmically spaced volatility bins (Donahue et al., 2006). Both 2P and VBS use NO_x -dependent values of stoichiometric yield coefficients (Hildebrandt et al., 2009; Ng et al., 2007), representing effects of gas-phase RO_2 chemistry (i.e., predominance of $\text{RO}_2 + \text{NO}$ or $\text{RO}_2 + \text{HO}_2$, respectively) on PM mass (Lane et al., 2008). Additionally, the SOA framework in AQMs assume instantaneous thermodynamic equilibrium for gas-particle partitioning and have been shown to be sensitive to assumed enthalpy of vaporization (ΔH) values for the semi-volatile products (Henze et al., 2008).

Recent laboratory and field studies have also highlighted the importance of aqueous-phase SOA formation though major role of glyoxal and methylglyoxal in formation of particle aqueous-phase (Liggio et al., 2005; Sareen et al., 2010; Volkamer et al., 2009). Research studies with inclusion of aqueous-phase SOA in AQMs have helped close the gap between observed and predicted SOA (Li et al., 2011) and improved the O/C ratio of predicted SOA when compared to observations (Dzepina et al., 2009). Yu et al. (2011) recently studied the reactions and interactions between glyoxal and salts in aqueous solution and concluded the importance of strong interaction between glyoxal and sulfate ions, contributing to observed enhancement of the effective Henry's law coefficient for glyoxal. Ervens and Volkamer (2010) provide a detailed discussion on the mechanism of glyoxal loss process and subsequent SOA formation on various organic and inorganic seeds. More recently Nakao et al. (2011) reported that that role of glyoxal in SOA formation is minor when the surface (and near-surface) of aerosols are primarily composed of secondary organic compounds. Further, Galloway et al. (2011) observed in their experiments that $(\text{NH}_4)_2\text{SO}_4$ particles only show dark-type reactions and no enhancement in SOA formation from photochemical processes as found by Volkamer et al. (2009). The authors attribute this discrepancy to an organic coating on $(\text{NH}_4)_2\text{SO}_4$ seed, formed due to chamber background-aerosol or glyoxal oligomers formed at the injection port, which may have prevented fast photochemical reactive surface-uptake but not slower dark-type bulk-limited process of glyoxal.

The dynamic approach to describe partitioning of semi-volatile species in particle organic-phase has also been previously used before in laboratory experiments (Bowman et al., 1997) and field study (Koo et al., 2003). The dynamic approach by Parikh et al. (2011) also included aqueous-phase SOA production at varying relative humidity (RH) conditions using a simplified bulk-process particle aqueous-phase rate for glyoxal and methylglyoxal. Ultimately the goal is to implement the approach described by Parikh et al. (2011) into a regulatory air quality model. Prior to implementation the framework requires further testing under urban conditions. This is accomplished in this study with evaluation of the dynamic approach and inclusion of aqueous-phase SOA pathway to new xylene and aromatic mixture (toluene and xylene) experiments and detailed sensitivity analysis to model and parameter choices.

The experiments were modeled using either CB05 (Yarwood et al., 2005) or SAPRC07 (Carter, 2009), both of which are condensed gas-phase mechanisms used widely in regional-scale regulatory modeling. Gas-phase predictions of the decay of toluene and/or xylene leads to corresponding prompt production of semi-volatile species that can partition to the particle organic-phase. The gas-phase predictions of glyoxal and methylglyoxal play an important role in determining the contribution of SOA in

particle aqueous-phase. We evaluate the new SOA framework with two gas-phase mechanisms to compare the differences in SOA predictions due to the underlying prediction differences for toluene, xylene, glyoxal and methylglyoxal.

In the new modeling framework we evaluated, two approaches to SOA parameterization are tested: 2P and VBS. Further, we evaluated the use of two aqueous-phase SOA formation models; one using an assumed bulk-process rate and another using surface-uptake formulation from Liggio et al. (2005). Although the organic-phase SOA is assumed to be non-hygroscopic (Jang and Kamens, 1998; Kleindienst et al., 1999), recent studies have shown that the aqueous-phase SOA is highly oxidized and can contribute to additional water uptake for the duration of the experiment (Ervens and Volkamer, 2010; Petters and Kreidenweis, 2007). A sensitivity analysis is performed, where the aqueous-phase SOA in the model is assumed to be hygroscopic and the impacts of this assumption on different experiments and the assumed bulk-process rate are provided to account for this uncertainty. Lastly, we evaluated the sensitivity of the model results to the assumed reactive uptake coefficient to particle organic-phase. This reactive uptake coefficient represents both mass-transfer and kinetic limitations in multigenerational toluene oxidation chemistry that arise due to low OH concentrations in the presence of non-SOA-forming mixture (HCmix) (Parikh et al., 2011). In summary, we evaluate the SOA framework under a variety of regulatory modeling choices and sensitivity scenarios which provides guidance for future implementation of these SOA updates in a regulatory air quality model.

2. Materials and methods

2.1. Experimental section

Table 1 shows the list of experiments modeled in this study, experimental conditions and initial injections. Chamber and instrument details are provided in the supplementary material.

The initial seed aerosol for each experiment consists of rural background particles (called background particles) and depends on the level of drying and outdoor conditions for that experiment. The background seed composition is measured to be 25% sulfate and bisulfate, 10% nitrates and the rest is primary and aged organic material (Kamens et al., 2011). Also, a field study by Tolocka et al. (2001) measures the average sulfate and nitrate concentrations in the Research Triangle Park, NC area to be approximately 35% of the total $\text{PM}_{2.5}$ mass concentration. Since the water uptake of NH_4NO_3 is very similar to $(\text{NH}_4)_2\text{SO}_4$, the water-uptake capacity of background seed aerosol is assumed to be 35% pure $(\text{NH}_4)_2\text{SO}_4$ seed. The absorption of water from aged organics has been shown to be insignificant and is neglected (Engelhart et al., 2011). Particle liquid water content (LWC) is then computed from RH in the chamber using the $(\text{NH}_4)_2\text{SO}_4$ water-uptake vs. RH relationship given in the supplementary information of Parikh et al. (2011) in Section S1 (Figure S1-1). This relationship is specifically based on the water uptake data of $(\text{NH}_4)_2\text{SO}_4$ particles containing toluene SOA, for descending RH (Kleindienst et al., 1999). It is reasonable to assume this relationship, since it has been shown in our chamber that for background seed experiments, where particles contain a certain fraction of aged organics and elemental carbon, temperatures over a range of 11 °C–28 °C do not influence water uptake, with RH being the only controlling factor (Vartiainen et al., 1994). One point to note is that the chamber RH may change as the temperature of the chamber changes over the duration of the experiment. Kleindienst et al. (1999) additionally observed that toluene SOA did not contribute to LWC and that all of the LWC could be ascribed to water uptake by $(\text{NH}_4)_2\text{SO}_4$ seed. This is supported by Jang and Kamens

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