

This report is organized into three sections. Section A provides highlights of selected publications. Section B lists participation in ASR focus or working groups related to the grant. Section C lists publications supported by grant.

A. Highlights

1. Highlights of Y. Liu, M. Kuwata, B. Strick, F.M. Geiger, R.J. Thomson, K.A. McKinney*, S.T. Martin*, "Uptake of epoxydiol isomers account for half of the particle-phase material produced from isoprene photooxidation via the HO₂ pathway," *Environmental Science & Technology*, 2015, 49, 250-258.

Secondary organic material (SOM) accounts for a large and sometimes dominant fraction of the mass concentration of submicron atmospheric particles. SOM is produced as a result of the oxidation of volatile organic compounds (VOCs). There are multiple parallel production pathways, including gas- and condensed-phase processes. Because of the complexity of the processes involved, a quantitative and predictive understanding of SOM production is a major challenge in atmospheric chemistry research. The reaction pathways of a single species, isoprene, are estimated to contribute at least 25 to 50% of the annual global average of SOM production. Predominantly emitted by vegetation, isoprene is the single largest source of non-methane VOCs to the atmosphere.

A quantitative understanding of the multiple reaction pathways that contribute to SOM production from isoprene photooxidation is a critical step in the formulation of accurate models of atmospheric particle mass concentrations. Isoprene epoxydiol (IEPOX) isomers, which are produced by the further reactions of the population of RO₂ intermediates with hydroperoxyl and then hydroxyl radicals, serve as at least one set of important products to produce SOM, especially by reactive uptake to acidic sulfate particles. Although the IEPOX pathway had been suggested as an important pathway for SOM production from isoprene photooxidation, definitive quantitative evidence nevertheless remained lacking, and other

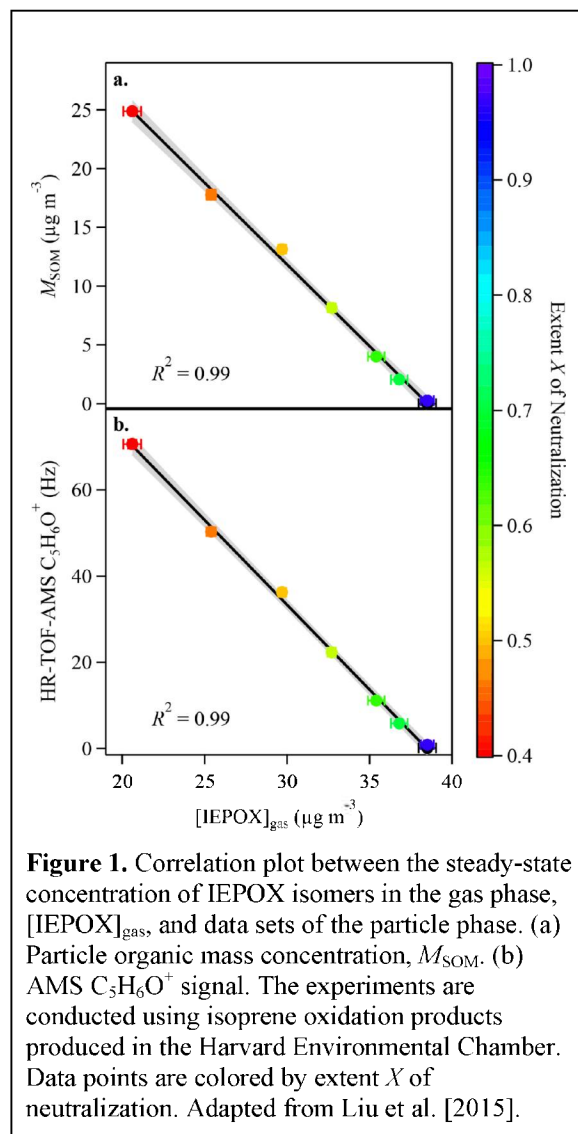


Figure 1. Correlation plot between the steady-state concentration of IEPOX isomers in the gas phase, $[\text{IEPOX}]_{\text{gas}}$, and data sets of the particle phase. (a) Particle organic mass concentration, M_{SOM} . (b) AMS $\text{C}_3\text{H}_6\text{O}^+$ signal. The experiments are conducted using isoprene oxidation products produced in the Harvard Environmental Chamber. Data points are colored by extent X of neutralization. Adapted from Liu et al. [2015].

reaction pathways might also be quantitatively important. Quantitative determination of the relative contribution of the IEPOX pathway to SOM production from isoprene photooxidation was the goal of the conducted experiments.

SOM production from isoprene photooxidation was studied under hydroperoxyl-dominant conditions for <5% relative humidity and at 20 °C in the presence of highly acidic to completely neutralized sulfate particles. Isoprene photooxidation was separated from SOM production by using two continuously mixed flow reactors connected in series and operated at steady state. Two on-line mass spectrometers separately sampled the gas and particle phases in the reactor outflow. The loss of specific gas-phase species as contributors to the production of SOM was thereby quantified as well as the overall mass balance between gas-phase loss and particle-phase production.

Figure 1a shows a scatter plot between the steady-state mass concentration of IEPOX isomers in the gas phase, $[\text{IEPOX}]_{\text{gas}}$, and the mass concentration of SOM, M_{SOM} , of Reactor #2. The plot shows that the production of M_{SOM} correlated ($R^2 = 0.99$) with the loss of gas-phase IEPOX isomers for the whole range of X investigated. The correlation confirms that the reactive uptake of IEPOX isomers, which were present in the suite of isoprene photooxidation products produced in the HEC, was a contributing process to SOM production. The relative contribution of IEPOX isomers to SOM production, compared to other possible contributors, was estimated by comparing on a mass basis the gas-phase loss of IEPOX isomers to SOM production. By this analysis, the decrease in gas-phase IEPOX mass concentration corresponded to $(46 \pm 11)\%$ of the produced organic mass concentration (including wall-loss correction) across the experiments. Within the stated uncertainties, this result of a contribution of $(46 \pm 11)\%$ by consideration of gas-phase mass loss and particle-phase mass increment was consistent with the estimate of an IEPOX contribution of $(59 \pm 21)\%$ (molecular counts) based on the total loss of gas-phase species. The conclusion is that the reactive uptake of IEPOX isomers accounted for half of the produced SOM, demonstrating the dominant role of these isomers for SOM production from isoprene photooxidation under HO_2 -dominant conditions in the presence of acidic particles.

Figure 1b shows a scatter plot between the gas-phase concentration of IEPOX isomers and the corresponding intensity of the $\text{C}_5\text{H}_6\text{O}^+$ signal measured by the HR-TOF-AMS. The decrease of the gas-phase IEPOX concentration and the increase of HR-TOF-AMS $\text{C}_5\text{H}_6\text{O}^+$ were correlated ($R^2 = 0.99$), suggesting that the HR-TOF-AMS $\text{C}_5\text{H}_6\text{O}^+$ signal of isoprene-derived SOM was directly related to the reactive uptake of IEPOX isomers. Given the hard ionization by electron impact in the AMS (in contrast to the soft ionization of the SRI-TOF-MS), the $\text{C}_5\text{H}_6\text{O}^+$ ion in AMS spectra should however not itself be interpreted as indicative of the direct presence of IEPOX isomers in the particle phase but rather of the possible presence of IEPOX isomers, their derivatives, and other oxidation products having similar base structures that can all fragment to $\text{C}_5\text{H}_6\text{O}^+$. The correlation apparent in Figure 1b provides further positive support of the link between isoprene photooxidation products (in particular IEPOX isomers) and the HR-TOF-AMS $\text{C}_5\text{H}_6\text{O}^+$ signal (m/z 82). This signal has recently emerged in the literature as a suggested tracer fragment ion of isoprene-derived SOM in the atmosphere.

Atmospheric models of SOM production have recently begun to incorporate isoprene-derived SOM production via reactive uptake, with a focus on IEPOX isomers. An uncertainty in these models has been the importance of IEPOX relative to other products of isoprene photooxidation for SOM production. The results of the present study support the validity of the recent developments of atmospheric models by finding that IEPOX isomers account for half of SOM

produced under laboratory conditions and demonstrating that SOM production in the particle phase is proportional to IEPOX loss from the gas phase.

2. Highlights of **M. Kuwata, Y. Liu, K.A. McKinney, S.T. Martin***, "Physical state and acidity of inorganic sulfate can regulate the production of secondary organic material from isoprene photooxidation products," *Physical Chemistry Chemical Physics*, 2015, 17, 5670-5678.

Atmospheric SOM production occurs by several parallel pathways, such as gas-to-particle condensation as well as multiphase reactions in cloud hydrometeors and haze particles. The production pathways, including anthropogenic-biogenic interactions, must be adequately understood and quantified to serve as a basis for accurate modeling of climate- and health-relevant properties of particles. Several laboratory experiments have demonstrated that isoprene SOM production is enhanced in the presence of acidic sulfate particles, suggesting the role of particle-phase reactions. Two leading facts, namely the importance both of phase and acidity for SOM production from IEPOX, motivated the closer scrutiny in the present study of the detailed relationship between the phase diagram of partially to wholly neutralized sulfate particles and isoprene SOM production.

The dependence of the produced SOM mass concentration M_{org} on the extent X of neutralization is shown in Figure 2a. For $X < 0.7$, M_{org} decreases for increasing X , and SOM production becomes insignificant for $X > 0.7$. This threshold value of 0.7 is related to the solid or liquid phase of the sulfate particles. For sufficiently low values of RH, the solids ammonium sulfate ($X_{\text{solid}} = 1.0$; AS) and letovicite ($X_{\text{solid}} = 0.75$; LET) crystallize from aqueous solution for $X > 0.7$ (Figure **Error!** **Reference source not found.**). By comparison, for submicron particles at room temperature the solid ammonium bisulfate ($X_{\text{solid}} = 0.5$; AHS) does not crystallize from aqueous solution by homogeneous nucleation even at low RH, meaning that the liquid phase is metastable. For $0.6 < X < 0.7$, within a population of particles, some individual sulfate particles can crystallize completely as two crystals (i.e., LET + AHS) whereas others can remain aqueous. For $X > 0.7$, all particles in the population crystallize. The data set of Figure 2a for the dependence of M_{org} on X , in conjunction with the dependence of phase on X , leads to the

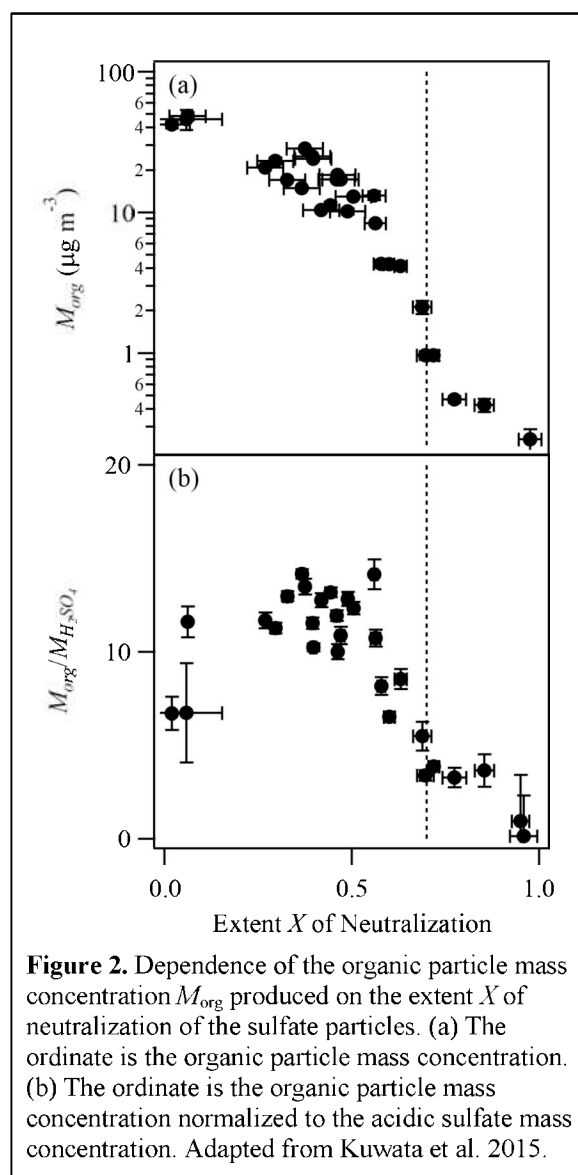


Figure 2. Dependence of the organic particle mass concentration M_{org} produced on the extent X of neutralization of the sulfate particles. (a) The ordinate is the organic particle mass concentration. (b) The ordinate is the organic particle mass concentration normalized to the acidic sulfate mass concentration. Adapted from Kuwata et al. 2015.

inference that SOM production is greatly inhibited in the presence of solid compared to aqueous particles.

An alternative presentation of the results is shown in Figure 2b. Literature results suggest that isoprene SOM production correlates with proton concentration.¹⁹ For the present experiments, this possibility is explored by using the quantity $M_{\text{org}}/M_{\text{H}_2\text{SO}_4}$ as the ordinate Figure 2b in place of M_{org} as the ordinate in Figure 2a. As for the plot of M_{org} with X (Figure 2a), the plot of $M_{\text{org}}/M_{\text{H}_2\text{SO}_4}$ with X (Figure 2b) shows a threshold point for $X < 0.7$, which is related to the solid or liquid phase of the sulfate particles.

These results can underpin treatments of phase-dependent SOM production within chemical transport models, thereby improving the accuracy of simulations of biogenic-anthropogenic interactions in the atmosphere and the associated impacts of aerosol particles on climate and air quality. The phase of atmospheric particles can fluctuate between solid and liquid depending on local and prior relative humidity, particle composition, and other factors. The current study finds that there is a discontinuous function in the produced SOM mass concentration at a threshold value of 0.70 for X , at least for low RH. The implication is that an aqueous phase is needed for isoprene SOM production by particle-phase reactions. Moreover, isoprene SOM production, the oligomer fraction, and the organosulfate fraction all steadily increase for increasingly acidic particles. Chemical transport models of atmospheric organic mass concentration have begun to simulate isoprene SOM production from the reactive uptake of known photooxidation products, such as the IEPOX family. The current experimental results imply that updated models should also treat the phase and extent of neutralization of the reactive medium.

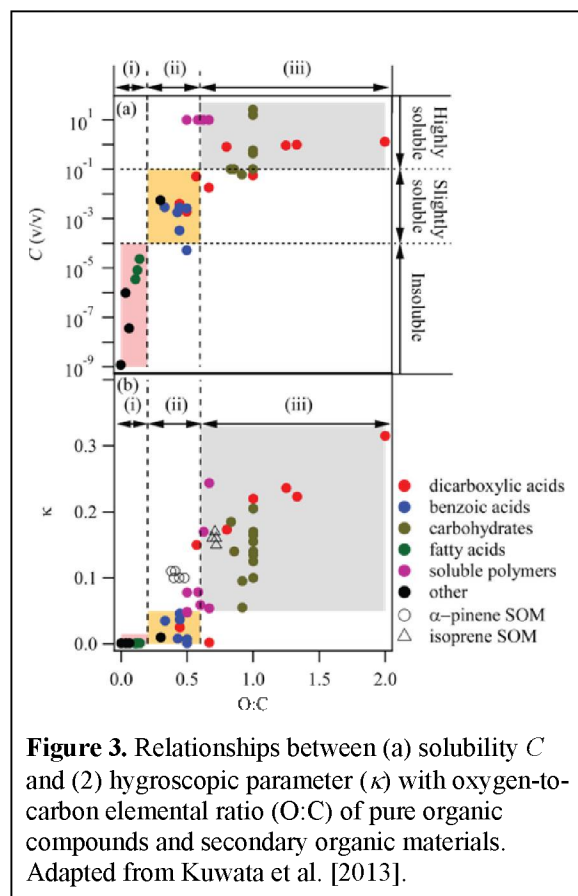


Figure 3. Relationships between (a) solubility C and (b) hygroscopic parameter (κ) with oxygen-to-carbon elemental ratio (O:C) of pure organic compounds and secondary organic materials. Adapted from Kuwata et al. [2013].

3. Highlights of M. Kuwata, W. Shao, R. Lebouteiller, S.T. Martin*, "Classifying organic materials by oxygen-to-carbon elemental ratio to predict the activation regime of cloud condensation nuclei (CCN)," *Atmospheric Chemistry Physics*, 2013, 13, 5309-5324.

This work focused on the cloud condensation nuclei (CCN) activity of organic aerosol particles in the context of the links between aerosol and cloud life cycles. Previous studies had demonstrated empirical correlations between oxygen-to-carbon elemental ratios (O:C) with the effective hygroscopic parameter κ of CCN activity. The underlying explanation of the observed relationship, however, had not been clarified, and the absence of an explanation limited confidence in applicability beyond calibrated domains.

CCN activities of both pure and secondary organic aerosol particles were investigated to tackle this issue. SOM particles were produced in the Harvard Environmental Chamber both by isoprene photo-oxidation and α -pinene dark ozonolysis. The CCN activity of the SOM particles was quantified using a CCN counter coupled with a differential mobility analyzer. Elemental ratios, including O:C ratio, were measured using a high-resolution aerosol mass spectrometer. Crystalline particles of pure organic compounds were generated by homogeneous nucleation of gaseous vapor to minimize contamination. The tested compounds included adipic, pimelic, suberic, azelaic, and pinonic acids. Experimental results were combined with literature data on other pure compounds to compile a dataset on the relationship between O:C elemental ratio and CCN activity.

Figure 3 shows the relationships among solubility C , hygroscopicity κ , and elemental ratio O:C. A positive correlation was observed between C and O:C, separating organic materials as insoluble (O:C < 0.2), slightly soluble (0.2 < O:C < 0.6), and highly soluble (O:C > 0.6). Those categories were tightly related to CCN activity. Depression of equilibrium vapor pressure of water induced by mixing of solute was therefore a key mechanism of cloud activation. In agreement, κ was nearly 0.0 for O:C < 0.2, relatively low (0.9 < κ < 0.05) for 0.2 < O:C < 0.6, and higher (κ > 0.1) for O:C > 0.6. SOM was further tested. Organic aerosol particles formed from isoprene had an O:C of 0.7, and they were highly CCN active. For α -pinene SOM, relatively high κ was observed, even though the values of O:C ratio was intermediate (0.45).

The study demonstrated how CCN activity of pure organic aerosol particles could be related to a measurable chemical property, which is necessary as a step in developing a quantitative methods to predict climate impacts of organic aerosol particles in modeling studies.

4. Highlights of **L. Renbaum-Wolff, J.W. Grayson, A.P. Bateman, M. Kuwata, M. Sellierc, B.J. Murray, J.E. Shilling, S.T. Martin*, A.K. Bertram***, "Viscosity of α -pinene secondary organic material and implications for particle growth and reactivity," *Proceedings of the National Academy of Sciences USA*, 2013, *110*, 8014-8019.

Global chemical transport models largely assume that equilibrium is achieved rapidly between the gas and particle phases for organic compounds. Evidence is accumulating, however, that SOM particles can be semisolid or solid with low diffusion coefficients. The phase-state of SOM particles and thus molecular diffusion and rates of equilibration within a particle is expected to depend on relative humidity. This study provided quantitative measurements of that dependence for the viscosity of α -pinene SOM, setting a stage for the possibility of quantitative modeling of the heterogeneous chemistry of this SOM. Molecular diffusion is a parameter controlling reactivity, growth rate, and partitioning of semi-volatile organic compounds.

Two techniques were employed to measure the RH-dependent viscosity of the water-soluble component of α -pinene SOM. The first measured the speed of small beads (1 μm) inserted into the SOM particles (30-50 μm). At each RH, images were recorded using an optical microscope, and the average bead speed was calculated. The second technique involved poking the SOM particles and thus deforming them to a non-equilibrium shape. The experimental time required for the shape to reform to its equilibrium shape was obtained by analysis of the image time series. The two techniques were used to measure the RH-dependent viscosity over a wide range of RH values (30 - 90% RH) (Figure 4). The experimentally determined viscosities of α -pinene

SOM correspond to a liquid phase for $RH \geq 80\%$, semisolid phase for $40 \leq RH \leq 80\%$, and solid phase for $RH \leq 30\%$.

Most models estimate the effect of SOM particles on air quality and/or climate by assuming that particle growth occurs instantaneously in conjunction with fast equilibration partitioning from the gas to particle phase. The mixing time of particle can be calculated from the experimentally determined viscosities, as show in Figure 4 for a 100 nm particle. The mixing time for particles in an environment of 70 to 90% RH is 0.01 to 1 s, and instantaneous partitioning therefore appears valid in this regime. However, for $RH \leq 30\%$, the mixing time exceeds 2.5 days. Therefore the growth mechanism of these particles cannot be explained using instantaneous partitioning. These experimental findings have important consequences for accurate modeling of the particle number-diameter distribution and hence for the scattering and absorption of solar radiation as well as the tendency for the particles to act as cloud condensation nuclei.

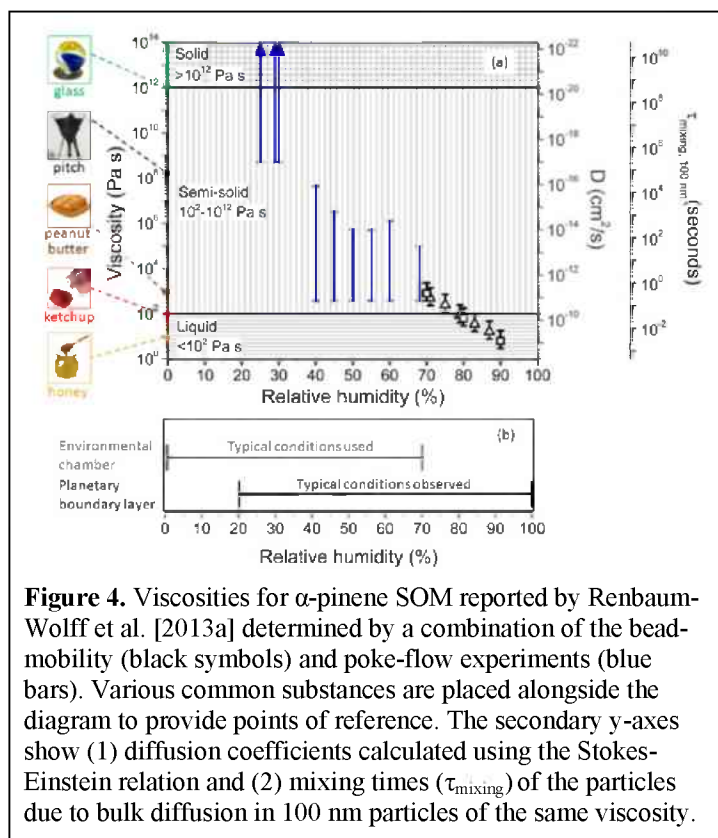


Figure 4. Viscosities for α -pinene SOM reported by Renbaum-Wolff et al. [2013a] determined by a combination of the bead-mobility (black symbols) and poke-flow experiments (blue bars). Various common substances are placed alongside the diagram to provide points of reference. The secondary y-axes show (1) diffusion coefficients calculated using the Stokes-Einstein relation and (2) mixing times (τ_{mixing}) of the particles due to bulk diffusion in 100 nm particles of the same viscosity.

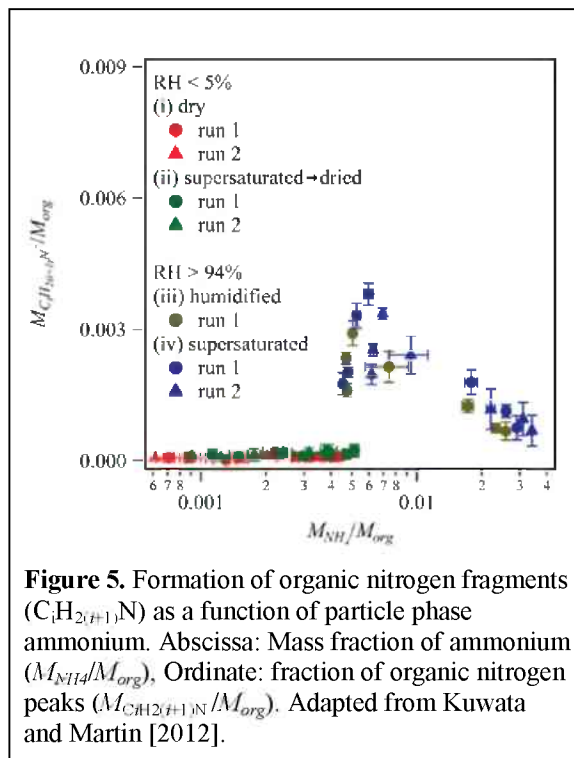
5. Highlights of **M. Kuwata and S.T. Martin***, "Phase of atmospheric secondary organic material affects its reactivity," *Proceedings of the National Academy of Sciences USA*, 2012, **109**, 17354-17359.

Chemical aging of organic aerosol particles is a key process in the aerosol life cycle because it changes climatically important characteristics such as cloud nucleation ability and optical properties. Studies had shown that SOM particles in the atmosphere are sufficiently viscous to be treated as semisolid, contrasting with conventional understanding that SOM particles behave thermodynamically as liquid. However, the influence of particle phase on chemical aging of SOM particles had not yet been clarified.

The reactive uptake of ammonia by α -pinene SOM was investigated to address this issue. The particles were treated by water vapor in different ways to control particle phase and viscosity. Subsequently, the particles were exposed to gaseous ammonia in dry (relative humidity $RH < 5\%$) or humidified ($RH > 94\%$) environments. A high resolution time-of-flight aerosol mass spectrometer monitored ammonium concentration as well as organic nitrogen species. High-resolution mass spectrometry was advantageous in the study because of its capabilities (1) to identify ammonium peaks from other isobaric species and (2) to clearly separate organic nitrogen species such as CH_4N^+ (m/z 30.034) from other peaks such as NO^+ (m/z 29.998). Reactive uptake

of ammonia was not observed at dry conditions. In contrast, SOM particles took up significant ammonia following exposure in humidified environments. The implication is that a phase transition occurred from semisolid to liquid, induced by water uptake, and that this transition plays a critical role in determining the chemical reactivity of SOM particles.

In addition, as shown in Figure 5, organic nitrogen species were produced in the particle phase following ammonia exposure. Organic nitrogen is an important contributor to atmospheric light-absorbing species, with important influences on radiative transfer. The present result suggests that water-induced phase transitions influence particle-phase SOM reactions, with important implications for quantitative modeling of transformation processes in aerosol life cycle.



B. Participation in ASR Focus or Working Groups

- S.T. Martin and J. Thornton, co-leaders for Workshop Session: “Secondary Organic Aerosol: Condensed Phase Processes,” ASR Working Group Meeting, November 2012
- S.T. Martin, J.E. Shilling, R. Zaveri, P. Ziemann, co-leaders for “Secondary Organic Aerosol: Anthropogenic-Biogenic Interactions” Focus Group, ASR Science Team Meeting, March 2013
- S.T. Martin, J.E. Shilling, co-leaders for Workshop Session: “Secondary Organic Aerosol,” ASR Working Group Meeting, November 2013
- J.E. Shilling, S.T. Martin, co-leaders for “Secondary Organic Aerosol” Focus Group, ASR Science Team Meeting, March 2014.
- S.T. Martin, A. Zelenyuk, “Secondary Organic Aerosol: Viscosity/Phase,” ASR Working Group Meeting, November 2014
- J.E. Shilling, S.T. Martin, co-leaders for “Secondary Organic Aerosol” Focus Group, ASR Science Team Meeting, March 2015.
- Service on Executive Committee for “Secondary Organic Aerosol” Focus Group from 2012 to date.

C. List of Publications Supported by Grant

1. M. Kuwata, Y. Liu, K.A. McKinney, S.T. Martin^{*}, "Physical state and acidity of inorganic sulfate can regulate the production of secondary organic material from isoprene photooxidation products," *Physical Chemistry Chemical Physics*, **2015**, *17*, 5670 - 5678.
2. Y. Liu, M. Kuwata, B. Strick, F.M. Geiger, R.J. Thomson, K.A. McKinney^{*}, S.T. Martin^{*}, "Uptake of epoxydiol isomers account for half of the particle-phase material produced from isoprene photooxidation via the HO₂ pathway," *Environmental Science & Technology*, **2015**, *49*, 250-258.
3. S.T. Martin^{*}, M. Kuwata, M.L. Smith, "An analytic equation for the volume fraction of condensationally grown mixed particles and applications to secondary organic material produced in continuously mixed flow reactors," *Aerosol Science & Technology*, **2014**, *48*, 803-812.
4. M. Kuwata, W. Shao, R. Lebouteiller, S.T. Martin^{*}, "Classifying organic materials by oxygen-to-carbon elemental ratio to predict the activation regime of cloud condensation nuclei (CCN)," *Atmospheric Chemistry Physics*, **2013**, *13*, 5309-5324.
5. L. Renbaum-Wolff, J.W. Grayson, A.P. Bateman, M. Kuwata, M. Sellierc, B.J. Murray, J.E. Shilling, S.T. Martin^{*}, A.K. Bertram^{*}, "Viscosity of α -pinene secondary organic material and implications for particle growth and reactivity," *Proceedings of the National Academy of Sciences USA*, **2013**, *110*, 8014-8019.
6. M. Kuwata and S.T. Martin^{*}, "Phase of atmospheric secondary organic material affects its reactivity," *Proceedings of the National Academy of Sciences USA*, **2012**, *109*, 17354-17359.
7. Y. You, L. Renbaum-Wolff, M. Carreras-Sospedra, S.J. Hanna, N. Hiranuma, S. Kamal, M.L. Smith, X. Zhang, R.J. Weber, J.E. Shilling, D. Dabdub, S.T. Martin^{*}, and A.K. Bertram^{*}, "Images reveal that atmospheric particles can undergo liquid-liquid phase separations," *Proceedings of the National Academy of Sciences USA*, **2012**, *109*, 13188-13193.
8. M. Kuwata and S.T. Martin^{*}, "Particle size distributions following condensational growth in continuous flow aerosol reactors as derived from residence time distributions: Theoretical development and application to secondary organic aerosol," *Aerosol Science & Technology*, **2012**, *46*, 937-949.
9. M. Kuwata, S.R. Zorn, S.T. Martin^{*}, "Using elemental ratios to predict the density of organic material composed of carbon, hydrogen, and oxygen," *Environmental Science & Technology*, **2012**, *46*, 787-794.
10. Q. Chen, Y. Li, K.A. McKinney, M. Kuwata, and S.T. Martin^{*}, "Particle mass yield from β -caryophyllene ozonolysis," *Atmospheric Chemistry and Physics*, **2012**, *12*, 3165-3179.