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Drying-Induced Evaporation of Secondary Organic Aerosol during Summer

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S Supporting Information

ABSTRACT: This study characterized the effect of drying on the concentration of atmospheric secondary organic aerosol (SOA). Simultaneous measurements of water-soluble organic carbon in the gas ($WSOC_g$) and particle ($WSOC_p$) phases were carried out in Baltimore, MD during the summertime. To investigate the effect of drying on SOA, the $WSOC_p$ measurement was alternated through an ambient channel ($WSOC_p$) and a "dried" channel ($WSOC_{p,dry}$) maintained at ~35% relative humidity (RH). The average mass ratio between $WSOC_{p,dry}$ and $WSOC_p$ was 0.85, showing that significant evaporation of the organic aerosol occurred due to drying. The average amount of evaporated water-soluble organic matter ($WSOM = WSOC \times 1.95$) was 0.6 μg m^{-3}; however, the maximum evaporated WSOM concentration exceeded 5 μg m^{-3}, demonstrating the importance of this phenomenon. The systematic difference between ambient and dry channels indicates a significant and persistent source of aqueous SOA formed through reversible uptake processes. The wide-ranging implications of the work are discussed, and include: new insight into atmospheric SOA formation; impacts on particle measurement techniques; a newly identified bias in PM$_{2.5}$ measurements using the EPA's Federal Reference and Equivalent Methods (FRM and FEM); atmospheric model evaluations; and the challenge in relating ground-based measurements to remote sensing of aerosol properties.
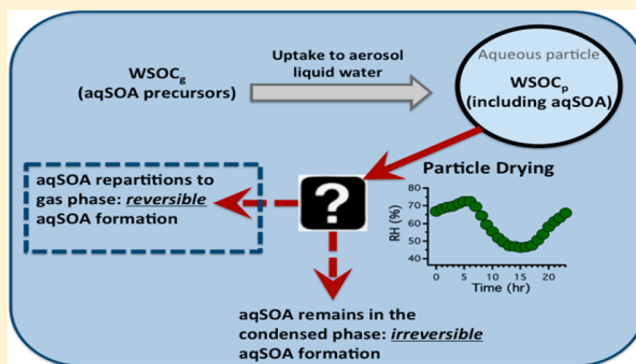
I. INTRODUCTION

Organic aerosol (OA) is a ubiquitous and highly abundant component of fine particulate matter.[1] A majority of this OA is secondary (SOA), even in urban areas where primary emissions are high.[2] State-of-the-art models are challenged to predict OA concentrations in most locations.[3,4] Further, model treatment of SOA has derived from laboratory experiments, but there are systematic differences in SOA composition commonly observed between laboratory and ambient studies.[5] This indicates that significant progress is still required to develop a complete understanding of the sources and formation of SOA. The uptake of water-soluble organic gases into atmospheric liquid water has been identified as a major route for SOA formation that could help to close the model-measurement discrepancy in many locations.[6,7]

The formation of SOA through the uptake of water-soluble organic gases can occur in cloud and fog droplets and in aerosol liquid water. A key point is that this aqueous SOA formation (aqSOA) involves the uptake of gases that are too volatile to otherwise partition to the aerosol phase without liquid water. There is mounting evidence for the important contribution of aqSOA to the global OA budget. For example, isoprene is the nonmethane hydrocarbon emitted into the atmosphere in the greatest abundance,[8] and liquid water plays a critical role in the amount of SOA formed from isoprene oxidation.[9] Several isoprene oxidation products, notably glyoxal and isoprene-derived expoxides (IEPOX), are important aqSOA precursors.[10] Neither IEPOX[11] nor glyoxal[12] partition to dry particles, but both readily form aqSOA in aerosol water (and presumably cloud and fogwater, as well). Based on the high atmospheric emissions of isoprene, IEPOX and glyoxal may be among the most abundant SOA precursors on regional and global scales.[10,13]

While aqSOA is thought to be an important contributor to global OA levels, many uncertainties remain in understanding aqSOA on a fundamental level.[7] Among the largest uncertainties is the relative contribution of reversible and irreversible uptake processes to aqSOA formation. The initial uptake of water-soluble organic gases into atmospheric water occurs through reversible, equilibrium partitioning.[7] We use the terms "reversible aqSOA" and "irreversible aqSOA" to indicate the fate of the dissolved organic gases under conditions of liquid water evaporation. A reversible process implies that

organic compounds taken up into liquid water repartition back to the gas phase upon liquid water evaporation, such as after a cloud cycle or with changes in ambient RH. An irreversible process implies that the same organics remain in the condensed phase with the evaporation of liquid water. The abundance of aqSOA can differ by orders of magnitude depending on which process—reversible or irreversible—is primarily responsible for the uptake of organic gases.[14]

Laboratory studies find evidence for both reversible and irreversible uptake of glyoxal and IEPOX. Seed particle composition is a critical factor that affects the relative split between reversible and irreversible uptake. Glyoxal uptake is enhanced by inorganic aerosol components due to a "salting in" effect.[15] While some glyoxal remains in the condensed phase under pure glyoxal-water droplet evaporation experiments,[16] ammonium (NH_4^+) greatly enhances the amount of glyoxal remaining in the aerosol phase under drying conditions.[17] Sulfate appears to play a critical role in catalyzing the ammonium-glyoxal reactions in particles undergoing drying.[18]

The relative contributions of reversible and irreversible uptake of IEPOX are also strongly affected by inorganic aerosol composition.[19] Nguyen et al.[11] observed entirely reversible uptake of β-IEPOX to aqueous sodium chloride (NaCl) or sodium sulfate (Na_2SO_4) particles, while substitution of NH_4^+ for Na^+ resulted in significant irreversible uptake. There was also an effect from nucleophile substitution, as irreversible β-IEPOX uptake to aqueous $(NH_4)_2SO_4$ was an order of magnitude greater than to aqueous NH_4Cl.[11] These experiments are qualitatively consistent with ambient observations in the southeastern U.S., where isoprene-SOA is strongly associated with sulfate.[20,21] Note that the organic aerosol composition can also affect the uptake of glyoxal, for example, by altering equilibria and condensed-phase reaction kinetics.[22,23] However, the effect of organic composition on IEPOX SOA has not been investigated.

To date, there are no ambient measurements to quantify or constrain the relative contributions of reversible and irreversible aqSOA. This is important, as it directly affects the impact of aqueous multiphase processes on the total OA budget.[16] It also has consequences for the fate and lifetime of many organic compounds in the atmosphere. This may have implications for global climate, as well, beyond the general contribution to the OA budget: reactions under conditions of water evaporation can rapidly form aqSOA that contains light-absorbing "brown carbon" species.[18]

The purpose of this study was to characterize the behavior of ambient SOA under conditions of drying. A recently developed method was deployed to cycle the measurement of water-soluble organic carbon in the particle phase ($WSOC_p$) between a dry channel and an unperturbed ambient channel.[24] A surrogate for SOA, $WSOC_p$ concentrations were unaffected by drying during a previous deployment of the system during the summer—fall transition in the eastern United States.[24] There was evidence for aqSOA formation during this time, suggesting that the uptake of water-soluble organic gases to aerosol water occurred through an irreversible process.[24] Measurements for the present study were carried out across July and August, a time period that was characterized by higher OA concentrations and warmer temperatures than our previous study, and potential differences in precursor VOC emissions and inorganic aerosol levels. If differences in the behavior of $WSOC_p$ were observed due to drying, it would represent the first direct evidence for reversible aqSOA in the atmosphere.

II. MATERIALS AND METHODS

Ambient measurements were carried out in Baltimore, MD from 6 July to 15 August 2015. A schematic of the experimental setup is provided in the Supporting Information (Figure S1). Details of the experimental setup are described elsewhere.[24] Briefly, water-soluble organic carbon was measured in the gas- and particle phases ($WSOC_g$ and $WSOC_p$, respectively). $WSOC_g$ was measured using a mist chamber (MC) coupled with a total organic carbon (TOC) analyzer (model 900 Turbo, GE Analytical).[25] $WSOC_p$ concentrations were measured using a particle into-liquid sampler (PILS, Brechtel Manufacturing) coupled with the same TOC analyzer used above, according to the method of Sullivan et al.[26] All components were housed in a temperature-controlled environmental enclosure (EKTO, Inc.) placed on the rooftop of the Engineering Building at the University of Maryland, Baltimore County (UMBC).

To characterize the effect of drying on $WSOC_p$, the particle measurement was alternated between a channel maintained at ambient relative humidity (RH) and a "dried" channel maintained at ~35% RH ± 2.6% (Supporting Information Table S1) using a 3-way valve (Brechtel Manufacturing). The goal for the $WSOC_{p,dry}$ measurement was not to remove all particle bound water, but rather to approximate the lowest RH that particles may be exposed to in ambient air during the study period to simulate "natural" drying processes (Supporting Information Figure S2). The dried channel included a silica gel diffusion dryer, which was made in-house similar to commercial models (e.g., TSI model 3062). $WSOC_p$ losses through the 3-way valve and through the dried channel were evaluated prior to the start of the sampling period and were found to be negligible (Supporting Information Figure S3). The dryer was replaced daily and its efficiency was checked with an orange silica gel color-indicator as well as an RH sensor (Omega, RH-USB) that measured the RH of air exiting the dryer. The total residence time at the reduced RH, which includes time inside the dryer and in the downstream carbon denuder, was ~7 s.

The fully automated system ran in cycles that were completed every 14 min. The three samples ($WSOC_g$, $WSOC_p$ and $WSOC_{p,dry}$) were measured every cycle with sampling times of 4, 5, and 5 min, respectively. These sampling times were averaged to provide a single measurement for each 14 min cycle. Dynamic blanks for both gases and particles were measured every 2 days when the DI water reservoirs were filled. The limits of detection (LOD) were calculated as 3× the standard deviation of the dynamic blanks and were 0.34 μg-C m^{-3} and 0.30 μg-C m^{-3} for $WSOC_g$ and $WSOC_p$, respectively. The relative uncertainty for the $WSOC_g$ measurement is 7%[25] while that for the $WSOC_p$ measurement is 8% + 0.3 μg-C m^{-3}.[26] The evaporated $WSOC_p$ concentration (i.e., reversible aqSOA) was calculated as the difference between the $WSOC_p$ and $WSOC_{p,dry}$ concentrations for each cycle. The uncertainty in the reversible aqSOA concentration is the greater of 11% or 8% + 0.1 μg-C m^{-3} (Supporting Information). This is based upon the combined uncertainties of (1) the difference in the raw TOC analyzer signal between successive dry and ambient measurements, (2) the PILS air and liquid flow rates, and(3) the PILS dilution factor. In this case, the blank measurement does not contribute to the uncertainty in the evaporated $WSOC_p$ concentration since the same background value is subtracted from the raw TOC data to calculate the concentrations of $WSOC_p$ and $WSOC_{p,dry}$ in air. The uncertainty and the LOD are largely determined by our ability
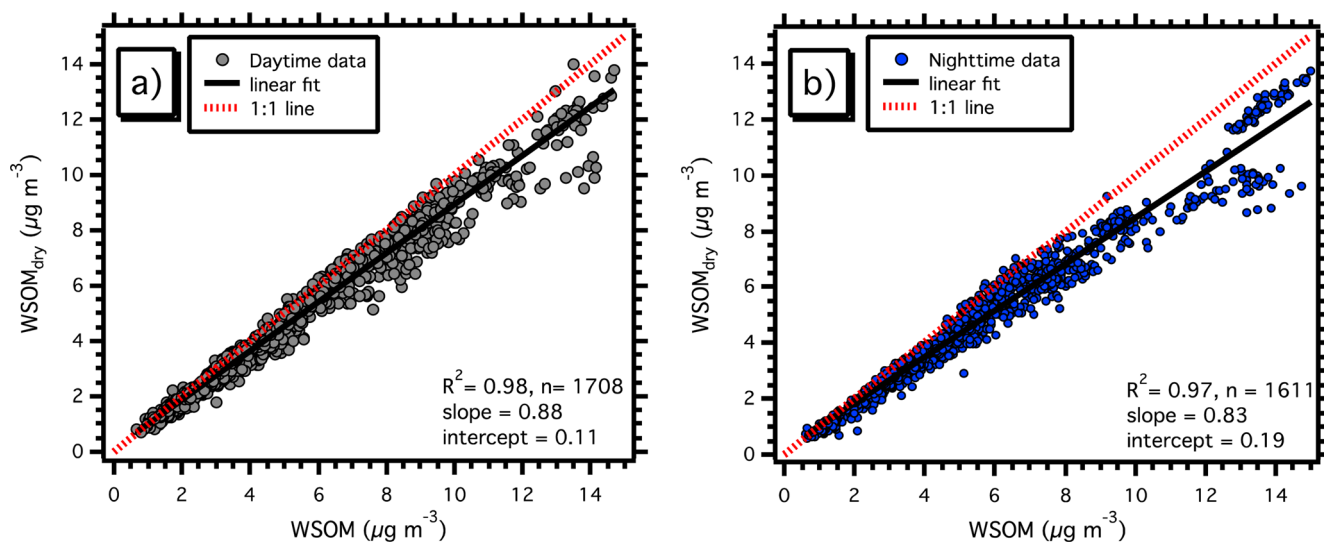
Figure 1. (a) Scatter plots of $WSOM_{dry}$ versus WSOM for (a) daytime and (b) nighttime periods. The solid black lines in (a) and (b) represent the linear fits to the data using least-squares regression analysis; the fit parameters are given in each panel.
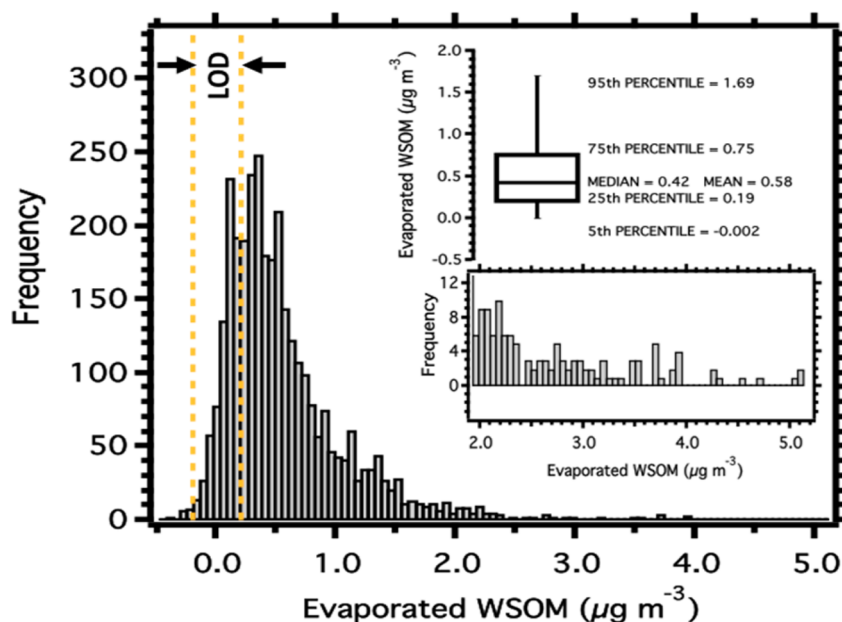

Figure 2. Histogram of evaporated WSOM. Figure on the lower right corner is a zoom-in of the histogram between $2-5.1$ μg m^{-3}. Figure on the upper right corner is a boxplot of the evaporated WSOM concentrations showing median value (horizontal line), 25th and 75th percentiles (lower and upper box values), as well as 5th and 95th percentiles (vertical lines). The dotted orange lines at evaporated WSOM equal to ± 0.2 μg m^{-3} represent the range of the method detection limits.

to measure a small difference in the TOC concentration of the aqueous PILS sample. The smallest concentration difference that can be distinguished between successive PILS samples is 0.71 ppb-C, which corresponds to an LOD for the evaporated $WSOC_p$ concentration of 0.086 μg-C m^{-3}. This indicates that the LOD for the evaporated $WSOC_p$ concentration is smaller than the LOD for either the $WSOC_p$ or $WSOC_{p,dry}$ concentrations. Again, this is due to our method of interpolating between the periodic blank measurements (approximately daily) to estimate the background concentration for each $WSOC_p$ and $WSOC_{p,dry}$ sample, while the evaporated $WSOC_p$ concentration is based upon a difference in the TOC analyzer signal, which is measured for each 14 min cycle. The $WSOC_p$ and $WSOC_{p,dry}$ method LODs could be improved by performing more frequent blank measurements,

but this was unnecessary for the summertime period: greater than 99% of the $WSOC_p$ measurements were above the 0.3 μg-C m^{-3} LOD. The $WSOC_p$ concentrations were converted from organic carbon (μg-C m^{-3}) to organic mass (μg m^{-3}) using a WSOM:WSOC ratio of 1.95. This ratio was obtained for a prior study carried out during the summertime in the northeastern U.S.[27] The total organic matter concentration corresponding to $WSOC_p$ measurement is denoted as "WSOM" while that corresponding to $WSOC_{p,dry}$ is denoted as "$WSOM_{dry}$".

III. RESULTS AND DISCUSSION

Effect of Particle Drying on SOA. An overview of the WSOC measurements and the meteorological data for the entire study period are summarized in Supporting Information

Table S3. The WSOC data were segregated into daytime (08:00 to 19:00, local time) and nighttime (20:00 to 07:00, local time) periods in order to characterize different processes that may affect reversible aqSOA formation. Figures 1a and 1b show a comparison between the WSOM concentrations measured through the two different channels. During both daytime and nighttime periods, $WSOM_{dry}$ concentrations were systematically lower than WSOM concentrations, indicating that the evaporation of aerosol water also led to the evaporation of condensed-phase organics. The estimated range for the slopes shown in Figure 1 were 0.873−0.890 (daytime) and 0.818−0.841 (nighttime) at the 99% Confidence Interval. Such narrow intervals at a high confidence level indicate that these values are tightly constrained, and are statistically different from a value of 1. This is further supported by a comparison of the $WSOM_{dry}/WSOM$ mean ratios, which were statistically different from a $WSOM_{dry}/WSOM$ ratio of 1 during the day and the night (Supporting Information Table S2).

Similar measurements carried out during a different season[24] as well as control experiments (Supporting Information Figure S3) showed no difference between WSOM concentrations through the dry and ambient channels. It is also important to note that the channel for the $WSOM_{dry}$ measurement does not employ sample heating to achieve drying, thereby avoiding any organic aerosol evaporation due to a change in vapor pressure. These factors clearly demonstrate that the differences observed in Figure 1 were caused by the loss of WSOM due to aerosol water evaporation. Numerous studies have shown that the $WSOC_p$ measurement (converted to WSOM in this study) is a surrogate for SOA in diverse environments.[25,28−31] This holds when biomass burning influence is low, as is frequently the case in the eastern U.S. during the summer.[32] Thus, it was highly likely that SOA compounds accounted for the evaporated WSOM observed during the present study.

The concentration of the evaporated SOA was calculated as the difference between the ambient and dried particle concentrations ($WSOM - WSOM_{dry}$). Figure 2 shows a histogram of the evaporated WSOM. The average amount of evaporated WSOM was 0.6 μg m^{-3}; however, the maximum evaporated value exceeded 5 μg m^{-3}, demonstrating the importance of this phenomenon. Negative evaporated WSOM values indicate measurements where $WSOM_{dry} > WSOM$. These cases accounted for less than 5% of the total observations, and were below the minimum concentration difference that could be detected for the majority of cases (indicated by the orange dotted lines and the "LOD" label in Figure 2). The systematic difference between WSOM and $WSOM_{dry}$ was observed consistently during day and night periods indicating the important role of aerosol water in summertime SOA formation.

WSOC Partitioning to Aerosol Water. The paired gas and particle WSOC measurements have provided detailed insight into the formation of aqSOA in aerosol water.[6,24,25,33] During the present study, the fraction of WSOC in the particle phase ($F_p = WSOC_p/(WSOC_p + WSOC_g)$) showed a strong increase with increasing RH during the night (Supporting Information Figure S5). The increase in F_p at higher RH levels during the night was statistically significant at the 95% confidence level.

This RH dependence has been observed in other locations, and is due to the uptake of water-soluble organic gases into aerosol water.[25] In prior measurements by our group carried out in the fall, we observed irreversible aqSOA formation: the

$WSOC_g$ taken up into aerosol water remained in the condensed phase with aerosol water evaporation.[24] For the summertime measurements of the present study, the loss of WSOM back to the gas phase upon drying indicates that some fraction of the aqSOA was formed reversibly. These observations represent, to our knowledge, the first direct atmospheric evidence for reversible aqSOA formation. In a previous study in Mexico City, the observation of reversible aqSOA was hypothesized, based upon strong daytime correlations between $WSOC_p$ and aerosol nitrate.[34] In that study, thermodynamic equilibrium modeling showed that aerosol nitrate rapidly volatilized during a daytime transition period that was characterized by the evaporation of a significant amount of aerosol liquid water, as well.[34] However, the volatilization of $WSOC_p$ (i.e., SOA) due to increasing ambient temperature or dilution could not be ruled out, since the temperature increase and boundary layer expansion were coincident with the evaporation of aerosol water. Here, we provide unambiguous evidence for the evaporation of SOA that comes about as a result of particle drying.

The difference between the current results and our prior study[24] is somewhat puzzling. Conditions that promote reversible aqSOA formation were clearly present during July and August (2015), but not during the month of September (2014). Further studies are needed to characterize the actual reason for the differences, which may include precursor VOC emissions,[35] inorganic aerosol composition,[11,17] and organic aerosol matrix effects.[22]

Sources of Reversible aqSOA. The amount of evaporated WSOM showed a statistically significant increase with increasing RH (Figure 3a). This is highly consistent with the F_p-RH relationship (Supporting Information Figure S5a) and further demonstrates the observation of reversible aqSOA. Aerosol liquid water content increases with increasing RH, enabling greater uptake of $WSOC_g$.[23,25] Some fraction of the $WSOC_g$ uptake to aerosol water during the summer was reversible, explaining the increase in evaporated WSOM with RH. This point is also illustrated in the diurnal profile of evaporated WSOM during the study period (Figure 4), which shows that higher concentrations of evaporated WSOM were observed during the night when RH was generally higher (Supporting Information Figure S2).

There are two additional points that should be noted from Figures 3a and 4. First, the evaporation of WSOM was observed even during daytime periods when the enhanced partitioning of $WSOC_g$ to aerosol water was not pronounced (Supporting Information Figure S5b). This suggests that the uptake of $WSOC_g$ to aerosol water occurred throughout the day, with some uptake proceeding reversibly, but the magnitude of the uptake was reduced during the day given lower aerosol water content. Second, it is important to note that WSOM evaporation was observed even at RH levels between 30 and 40% (Figure 3a). This suggests that the aerosol in Baltimore contained liquid water during the summer even at the lowest RH levels, consistent with observations in other locations.[36] Khlystov et al.[37] showed that aerosol in Pittsburgh, which is very similar to Baltimore in climatology and aerosol composition, likely contains water during the summer at these low RH levels, as well. Overall, this observation demonstrates that even small amounts of aerosol water ($<1−2$ μg m^{-3}) can be important for aqSOA. As discussed above, the evaporated WSOM represents a proxy measurement of aqSOA formed through a reversible pathway, so Figure 3a shows that

Figure 4. Boxplot of the diurnal profile of evaporated WSOM concentrations. For each bin, median values (horizontal line), 25th and 75th percentiles (lower and upper box values), as well as 5th and 95th percentiles (vertical lines) are shown.
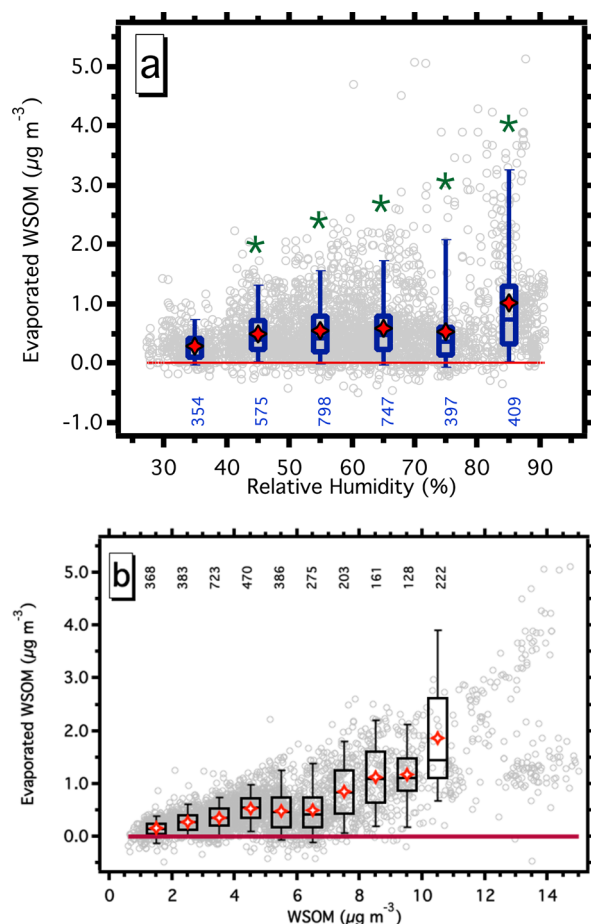
Figure 3. (a) Scatter and box plots of the evaporated WSOM as a function of RH. Data were binned according to the ambient RH: bins were defined as 0−40%, 40−50%, 50−60%, 60−70%, 70−80%, and 80−100%. For each bin, mean (red marker), median (horizontal black line), 25th and 75th percentiles (lower and upper box values), as well as 5th and 95th percentiles (vertical lines) are shown. Numbers at the bottom represent the number of points within each bin. The red dotted line at evaporated WSOM = 0 is for visual reference. The green asterisk on top of bins points to those bins that show a statistically significant increase in comparison to the first bin (i.e., 30−40% RH) at the 95% confidence level. (b) Scatter and box plots of the particulate evaporated WSOM as a function of WSOM concentrations. Data were binned according to the WSOM concentrations: bins were defined as 0−2, 2−3, 3−4, 4−5, 5−6, 6−7, 7−8, 8−9, 9−10, and 10−15 $\mu g\ m^{-3}$. For each bin, mean (red marker), median values (horizontal line), 25th and 75th percentiles (lower and upper box values), as well as 5th and 95th percentiles (vertical lines) are shown. Numbers at the top represent the number of points within each bin. The red line at evaporating WSOM = 0 is for visual reference.

aerosol water makes a significant contribution to summertime SOA formation in the study region. In addition to a relationship with RH, the amount of evaporated WSOM increased as the total WSOM concentration increased (Figure 3b). This shows that the source or sources of reversible aqSOA were highly related to those that had a dominant impact on overall SOA formation. In Maryland, as in much of the eastern U.S., it is expected that SOA derives predominantly from biogenic emissions.[32] Isoprene is the dominant biogenic VOC in this region, and contributes substantially to SOA formation during summer. We hypothesize that the reversible uptake of IEPOX and glyoxal were responsible for the majority of evaporated
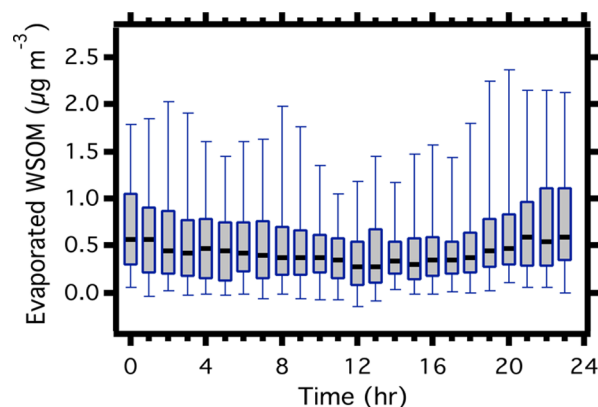
WSOM observed during our study. Together, IEPOX and glyoxal are predicted to account for ~85−90% of aqSOA formed from isoprene oxidation in the eastern U.S.[10] IEPOX-SOA has been measured in high concentrations in the eastern U.S. during summer,[20,21] and both reversible and irreversible processes contribute to IEPOX uptake in fine particle water.[11,19] Although direct evidence for glyoxal SOA is elusive due to the lack of specific molecular tracers, models predict significant glyoxal production from isoprene.[10,38] Since glyoxal readily undergoes reversible and irreversible uptake to aqueous particles,[17,23,39] it is also a likely contributor to reversible aqSOA concentrations during our study. Further atmospheric measurements, which include speciated VOCs and aerosol chemical components, are needed to test these hypotheses.

Implications. These results, which represent the first atmospheric observations of reversible aqSOA formation, have a number of important implications. It should be noted that these measurements represent a lower-bound on the reversible aqSOA concentrations observed during summer. First, aerosol water was not completely evaporated since the sample was only dried to ~35% RH, and almost certainly contained residual water. Second, the experimental setup employed a 7 s residence time within and downstream of the dryer before particle collection in the PILS. This amount of time far exceeds the equilibration time scale for water evaporation;[40] however, it may not be enough time for evaporating organic compounds to reach equilibrium.[35,41] If we have systematically underestimated the reversible aqSOA concentration, then our conclusions, and the implications discussed below, may be further amplified.

Atmospheric Chemistry. Laboratory studies find evidence for both reversible and irreversible aqSOA formation. The present results, combined with our prior observations,[24] underscore the importance of accounting for both reversible and irreversible aqueous-phase processes.[7] Although reversible aqSOA partitions between the gas and particle phases, like other semivolatile compounds, it contributes to aerosol effects on health and climate when in the condensed phase. Our results suggest that there are seasonal differences which underlie the split between reversible and irreversible aqSOA pathways, but significant work is needed to characterize these processes on a fundamental level so that they can be effectively implemented into models. Nevertheless, models that treat aqSOA formation as entirely irreversible may overstate the

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contribution of this process to the SOA burden in many environments. Conversely, certain instruments may underestimate the concentration of aqSOA if sample drying occurs as part of the measurement (see detailed Discussion below). This implies, for example, that IEPOX (and glyoxal) may make an even greater contribution to ambient OA concentrations than prior studies have reported.[20,21,42]

Atmospheric Measurements and Modeling. The present results also have implications for a wide range of atmospheric particle measurements that employ drying. For example, f(RH) measurements compare aerosol light scattering at ambient or humid conditions to light scattering under dry conditions (typically ≤20% RH).[43] The difference in light scattering is attributed to aerosol liquid water content; however, our results indicate that evaporated organic aerosol likely contributes to this difference in many environments, as well. Particles also undergo drying in the inlet of two widely used aerosol mass spectrometers[44]—the Aerodyne aerosol mass spectrometer (AMS)[45] and various laser-based single particle mass spectrometers[46]—and are thus subject to the loss of reversible aqSOA during sampling. Indeed, Kampf et al.[15] inferred the loss of glyoxal taken up reversibly to aqueous particles during sampling with an AMS. The extent of water evaporation in the aerodynamic lens inlet varies from ~50−80%,[36,44] suggesting that the loss of reversible aqSOA is of the same magnitude. However, systematic studies are needed to characterize this effect under both laboratory and ambient sampling conditions with varied inorganic and organic aerosol composition and liquid water content. Other instruments and methods that implement sample predrying, such as the Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA), are also subject to this effect.[36] It is unknown how the present observation may affect OA measurements using thermal-optical analyzers. Factors such as filter handling and storage for offline (laboratory) analysis, or minor variations in filter collection temperature during semicontinuous sampling may impart significant differences in the evaporation of reversible aqSOA by these methods. Note that complete drying (i.e., efflourescence) is not required for reversible aqSOA to undergo evaporation.

If certain measurements are subject to WSOM losses during sampling, then that could also affect the evaluation of models, especially those that implement aqueous SOA formation schemes. Models are typically judged in comparison to measurements, which are taken as the "truth", but a systematic bias due to the evaporation of WSOM could lead to incorrect interpretations of model performance. Similarly, the present results may help to reconcile some of the challenges in relating aerosol measurements from the ground with those from remote sensing platforms. There is a known RH dependence in the relationship between aerosol optical depth (AOD) and in situ $PM_{2.5}$ mass,[47−49] which is thought to be a product of aerosol water. However, the evaporation of WSOM by in situ measurements could also contribute to this observation, since reversible aqSOA contributes to AOD when it is in the particle phase. Our results suggest this effect is important in the eastern U.S., where previous discrepancies between surface and remote sensing measurements have been identified.[48,50]

Regulation and Health. These results also have implications for the EPA's Federal Reference and Federal Equivalent Methods (FRM and FEM) for measuring $PM_{2.5}$. The FRM and FEM employ drying to 35 ± 5% RH to eliminate the contribution of aerosol water to measured PM mass.[51] These methods are likely subject to a bias from the evaporation of WSOM that accompanies the filter or sample conditioning. Based on a comparison to measurements at the closest Maryland Department of the Environment ambient monitoring station to UMBC (Oldtown, ~ 10 km distance), we infer an average bias in hourly $PM_{2.5}$ concentrations measured with FEM method 127 (BAM monitor) of −5%. However, the largest inferred bias during the study period, calculated as the ratio of the evaporated WSOM concentration to the measured $PM_{2.5}$ concentration, exceeded −20%. The negative bias indicates that the FEM (and FRM) systematically undermeasure the actual concentration of $PM_{2.5}$ due to the evaporation of WSOM that occurs with the evaporation of particle-bound water. Our results suggest that this phenomenon is important in the eastern U.S. during summer, but significant work is needed to fully understand the spatial scale and magnitude of this effect. The potential for a systematic bias in FRM and FEM determinations of $PM_{2.5}$ has implications for compliance with the National Ambient Air Quality Standards (NAAQS). While the evaporation of other semivolatile compounds, notably ammonium nitrate, has been well documented for the FRM and FEM,[52] the present results identify a new bias not previously considered. The evaporation of reversible aqSOA during sampling may also have implications for health effects, beyond the general contribution to PM mass. Future studies should assess the potential of this reversible aqSOA to generate reactive oxygen species (ROS), which is thought to underlie many of the adverse health outcomes that result from exposure to PM.[53] This recommendation is based upon the strong correlation between reversible aqSOA and the overall $WSOC_p$ in this study (Figure 3b), and close associations between $WSOC_p$ and ROS observed in diverse locations,[53] including in the southeastern U.S.[54]

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b06002.

> Figures S1−S5, Tables S1−S3, and additional method details (PDF)

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Notes
The authors declare no competing financial interest.

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