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Potential of Aerosol Liquid Water to Facilitate Organic Aerosol Formation: Assessing Knowledge Gaps about Precursors and Partitioning

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S *Supporting Information*

ABSTRACT: Isoprene epoxydiol (IEPOX), glyoxal, and methylglyoxal are ubiquitous water-soluble organic gases (WSOGs) that partition to aerosol liquid water (ALW) and clouds to form aqueous secondary organic aerosol (aqSOA). Recent laboratory-derived Setschenow (or salting) coefficients suggest glyoxal's potential to form aqSOA is enhanced by high aerosol salt molality, or "salting-in". In the southeastern U.S., aqSOA is responsible for a significant fraction of ambient organic aerosol, and correlates with sulfate mass. However, the mechanistic explanation for this correlation remains elusive, and an assessment of the importance of different WSOGs to aqSOA is currently missing. We employ EPA's CMAQ model to the continental U.S. during the Southern Oxidant and Aerosol Study (SOAS) to compare the potential of glyoxal, methylglyoxal, and IEPOX to partition to ALW, as the initial step toward aqSOA formation. Among these three studied compounds, IEPOX is a dominant contributor, ~72% on average in the continental U.S., to potential aqSOA mass due to Henry's Law constants and molecular weights. Glyoxal contributes significantly, and application of the Setschenow coefficient leads to a greater than 3-fold model domain average increase in glyoxal's aqSOA mass potential. Methylglyoxal is predicted to be a minor contributor. Acid or ammonium - catalyzed ring-opening IEPOX chemistry as well as sulfate-driven ALW and the associated molality may explain positive correlations between SOA and sulfate during SOAS and illustrate ways in which anthropogenic sulfate could regulate biogenic aqSOA formation, ways not presently included in atmospheric models but relevant to development of effective control strategies.
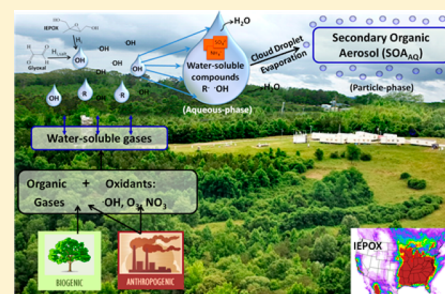
INTRODUCTION

Biogenic and anthropogenic volatile organic compounds (VOCs) are oxidized in the gas-phase to form small, water-soluble organic gases (WSOGs) that are abundant and ubiquitous in the atmosphere.[1−5] WSOGs are absorbed by cloud droplets, fog waters, or aqueous aerosol particles and react to form secondary organic aerosol (aqSOA)[6−11] and impact aerosol properties such as droplet acidity, surface tension, and cloud condensation nuclei activation.[12−15] Secondary organic aerosol (SOA) formation processes are a leading source of uncertainty in estimates of aerosol forcing in global climate models.[16−18] Both global and regional models used in air quality and climate applications tend to underestimate particulate organic carbon (OC), an important constituent of $PM_{2.5}$, both at the surface and aloft.[19−21] The modeling deficiency may be related to an incomplete attribution of SOA precursor sources[22] and formation processes, such as reactive uptake of WSOGs to cloud/fog and aerosol liquid water (ALW).[23−25] Aqueous SOA (aqSOA) pathways are a consequence of complex anthropogenic−biogenic interactions that may be mediated by sulfate, nitrate, chloride, and ALW.[26,27] Failure to understand anthropogenic drivers of biogenic aqSOA and include them in models hampers the development of effective air quality management strategies for $PM_{2.5}$, particularly in areas where ALW is high, such as the eastern US.[28]
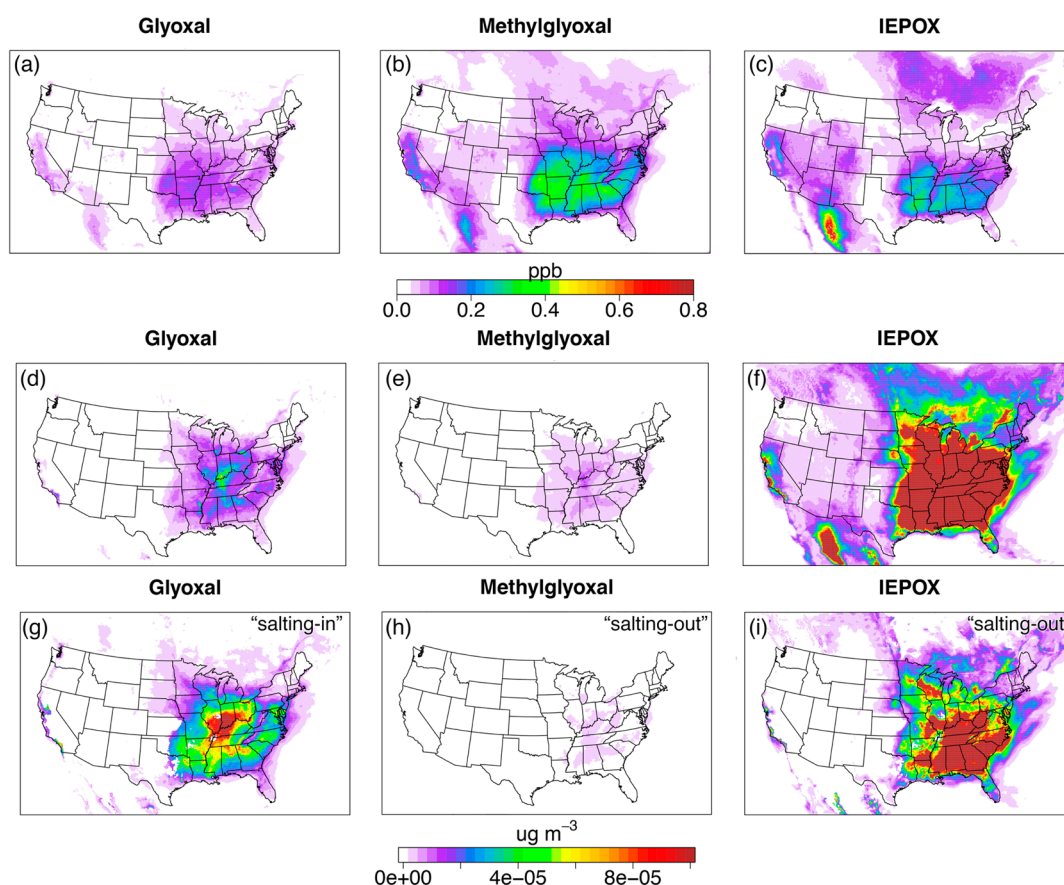
Figure 1. CMAQ modeled gas-phase concentrations over the continental U.S. from June 6−15, 2013 of (a) glyoxal, (b) methylglyoxal, and (c) IEPOX. Particle-phase concentrations for (d) glyoxal, (e) methylglyoxal, and (f) IEPOX calculated using CMAQ-modeled gas-phase concentrations of the WSOGs, ALW, and Henry's Law constants for the species, (g) glyoxal, calculated using the "salting-in" effects of particulate inorganic ion concentration as measured by Kampf et al. EST 2013,[26] (h) methylglyoxal, calculated using the "salting-out" effects of particulate inorganic ion concentration as measured by Waxman et al. EST 2015,[27] and (i) IEPOX calculated using the "salting-out" effects of particulate inorganic ion concentration as measured by Waxman et al. 2015.[67]

Recent field, modeling, and experimental studies highlight the role of isoprene in global SOA formation.[23,29−36] Isoprene emissions are estimated to be ∼600 Tg year^{-1} globally, the largest of all nonmethane VOCs.[37] Glyoxal, methylglyoxal, and isoprene epoxydiol (IEPOX) are water-soluble gas-phase oxidation products of isoprene. They undergo aqueous processing in cloud waters, fogs, and aerosols to form compounds that contribute to the SOA burden.[17,23,38−50] The relative importance of individual WSOG contributions to the atmospheric burden of SOA mass is dependent on their gas-phase mixing ratios, colocation in time and space with the aqueous partitioning medium, affinity for the condensed-phase, and the gas-particle partitioning of condensed-phase reaction products, that is, volatility and effective Henry's Law partitioning coefficient. Preference for the condensed-phase is a function not only of gas, but particle properties,[51−56] including salt molality in ALW.[26,27,57] Molality is defined as the concentration of the inorganic salt per mass of aerosol liquid water. Mass concentrations of WSOGs in the condensed-phase are often measured at higher concentrations than estimated based on current understanding of gas-particle partitioning processes including dissolution according to Henry's Law.[24,40,58] The Henry's Law partitioning coefficient for IEPOX is highly uncertain, and varies by up to 3 orders of magnitude.[48,59,60] Recent evaluations comparing the Community Multiscale Air Quality (CMAQ) model simulations to

IEPOX aerosol positive matrix factorization (PMF) of field measurements predict 10-fold lower IEPOX-derived SOA mass.[25] However, previous filter-based measurements of tetrols have shown good agreement with CMAQ simulations,[60] primarily because IEPOX-derived SOA mass in CMAQ is attributed to tetrols, organosulfates, organonitrates, and oligomers from IEPOX, which are only a subset of the IEPOX-OA PMF factor used for comparison in the former study where CMAQ under-predicts IEPOX-SOA. One possible explanation for this disagreement is a lack of aerosol molality impacts on effective uptake of IEPOX and other collocated molecules in the model, in addition to missing condensed-phase reactions.

Partitioning of polar organic compounds to an aqueous solution with inorganic ions can lead to interactions that increase the solubility of the organic compounds beyond that predicted by Henry's Law; this is called "salting-in".[61] Recent laboratory experiments indicate enhanced glyoxal partitioning to aqueous aerosol in the presence of ammonium sulfate and other inorganic salts.[26,27] A modified Setschenow relationship (Figure 1 in Kampf et al.[26]) exhibits an exponential increase in glyoxal partitioning with increasing aqueous phase ammonium sulfate molalities up to 12 mol kg^{-1}. The mechanism is attributed to the formation of sulfate−glyoxal−hydrate complexes.[57] Additionally, the presence of salts can decrease the solubility of the organic, known as "salting-out". Whether a

molecule "salts in" or "salts out" of an inorganic salt solution is determined by the interactions between the organic molecule and the salt(s) in solution. For example, glyoxal was found experimentally to salt in to a number of inorganic solutions including ammonium sulfate, ammonium nitrate, sodium nitrate, and sodium chloride as well as ammonium sulfate and ammonium sulfate/fulvic acid aerosols.[26,27] Quantum mechanical calculations showed that this "salting-in" was due to strong interactions of the OH groups on hydrated glyoxal molecules with sulfate ions in the hydration shell.[57] On the other hand, methylglyoxal which is only one carbon larger than glyoxal has been found to salt out of solutions of ammonium sulfate, ammonium nitrate, sodium nitrate, and sodium chloride.[27] This is presumably because its increased size adds steric hindrance to fit in the ion hydration shell. Indeed, most molecules have been found to salt out of solutions.[62,63] This is likely due to a combination of the functional groups found on the molecules and their size. These "salting-in" and "salting-out" effects are not typically accounted for when calculating partitioning and uptake coefficients for WSOGs other than glyoxal in models.[64,65] Recent field evidence suggests that isoprene–SOA is directly modulated by an abundance of sulfate in the southeastern U.S.[66] Sulfate-induced molality impacts on partitioning and uptake of isoprene oxidation products,[27,67] the subsequent rate of their multiphase reactions,[46,48] partitioning of reaction products, or a combination of these effects is consistent with these field observations. However, the dominant reason(s) for the strong associations between sulfate and this significant portion of ambient SOA remains elusive.

In this work, we explore the relative importance of glyoxal, methylglyoxal, and IEPOX partitioning to ALW as the starting point to quantify in a relative sense the ability of individual species to form SOA through aerosol water-mediated chemistry and contribute appreciably to organic aerosol mass. We employ CMAQ version 5.0.1 with isoprene updates to evaluate the significance of IEPOX in relation to other WSOGs, mainly glyoxal and methylglyoxal. CMAQ simulations were conducted for a 10-day period from June 6−15, 2013, coinciding with the Southern Oxidant and Aerosol Study (SOAS). We study SOAS using the newest model version with the latest meteorology and emissions inputs as a way to guide our (and the community's) focus and topic areas when delving into the large SOAS data set. Additionally, we apply the Setschenow coefficient derived by Kampf et al.[26] for glyoxal, and Waxman et al. for methylglyoxal and IEPOX[27,67] partitioning as a sensitivity to determine impacts of "salting-in" and "salting-out", both in terms of amount of partitioned organic mass and spatial distribution as a function of aerosol salt molality. Through this work, we aim to inform future laboratory studies that contribute to the efficient improvement of predicted SOA formed through chemistry in wet aerosols, including inorganic molality effects.

■ MATERIALS AND METHODS

CMAQ Simulations. CMAQ is a 3D air quality model used to predict fate and transport of atmospheric trace species. CMAQ v5.0.1 with the Statewide Air Pollution Research Center (SAPRC-07) chemical mechanism to describe gas-phase photochemistry with gas-phase isoprene extensions[68] is applied here to simulate a time period from June 6−15, 2013 over the contiguous United States at 12 × 12 km horizontal resolution with 35 layers. Anthropogenic emissions are based on

information from the 2008 National Emissions Inventory v2. Mobile emissions are based on MOtor Vehicle Emission Simulator (MOVES) 2010 emission factors and 2013 meteorology. Wildfire emissions are based on 2013 specific information. Biogenic emissions are computed using the Biogenic Emission Inventory System (BEIS) v3.14 using meteorology estimated by Weather Research and Forecasting (WRF) model as input.[69] Gridded meteorological data is generated from WRF v3.3 and processed for input to CMAQ by Meteorology−Chemistry Interface Processor (MCIP) 4.0. In addition to the semivolatile partitioning scheme and simplified cloud chemistry to describe SOA formation,[21,70] we employ the monomeric IEPOX partitioning method for a single-phase aqueous aerosol.[60] Partitioning and reactions in clouds are outside the scope of this study. Herein, CMAQ is used to predict WSOGs and ALW to provide insights relevant to aqSOA formation in aerosols.

Partitioning Potential to Particle-Phase: Offline Calculations. Gas-phase concentrations of glyoxal, methylglyoxal, and IEPOX from CMAQ are postprocessed and converted into particle-phase potentials (C_{ip}) using their respective Henry's Law constant (SI Table S1) and liquid water content of the aerosol population:

$$[C_i]_p = H_i RTL C_i(g) \tag{1}$$

where $[C_i]_p$ is the concentration of WSOG species i in the particle-phase, H_i is the Henry's law constant for species i as used in CMAQ, R is the ideal gas constant, T is temperature, L is ALW concentration in air from CMAQ, and $C_{i(g)}$ is mass concentration of species i in the gas-phase (converted from mixing ratios using the ideal gas law) from CMAQ. This work focuses on gas-to-particle partitioning and not on further reactions. All predicted potentials are solely due to partitioning. Additionally, we compare potentials instead of mass concentrations since CMAQ predicts SOA trends accurately but not the absolute concentrations.[71]

A limitation and source of uncertainty in the calculations presented here is that partitioning is calculated from 10-day averaged and postprocessed CMAQ output or "offline" estimates. During the standard CMAQ simulation, IEPOX partitions to ALW and forms SOA mass as described in Pye et al.,[60] while glyoxal and methylglyoxal do not. To be consistent, in this work, the formation of IEPOX-SOA from the CMAQ simulation was disregarded and all partitioning of WSOG into ALW presented here is from offline calculations. IEPOX gas-phase mixing ratios available in the model output are in theory reduced by the amount of IEPOX that formed SOA during the standard CMAQ simulation. This limitation introduces negligible error when evaluating relative potential importance because IEPOX, glyoxal, and methylglyoxal are predominantly (∼100%) present in the atmosphere as gases (SI Figure S1), consistent with observations indicating most atmospheric organic carbon is present in the gas-phase.[72,73] Recent measurements highlight the abundance of ALW during SOAS.[74] CMAQ's predictive availability for ALW mass concentrations is not well-known. The thermodynamic partitioning model, ISORROPIA,[75,76] that predicts mass concentrations of water employed in CMAQ, includes dependence on meteorology and inorganic species; potential effects of organic species on ALW are neglected. Historical analysis in the southeastern U.S. indicates including organic effects on ISORROPIA predicted ALW mass concentrations does not perturb overall water trends.[77]

Treatment of Setschenow Salting Constants. To account for the influence of "salting-in" of glyoxal, and "salting-out" of methylglyoxal and IEPOX, experimentally derived Setschenow constants for glyoxal and methylglyoxal and estimates for IEPOX based on similar compounds in ammonium sulfate (AS), ammonium nitrate (AN), and sodium chloride (NaCl) are applied to eq 1:

$$H_{i,\text{salt}} = \frac{H_i}{e^{\sum_j K_{s,j} c_j}} \tag{2}$$

where $H_{i,\text{salt}}$ is Henry's Law constant in salt containing particles, $K_{S,j}$ is the Setschenow salting constant for the respective salts, j (AS, AN, and NaCl) shown in Table 1, c_j is aqueous-phase molality (mol kg^{-1}, m) for the salts, j, calculated as

$$cj = \frac{\text{CMAQ salt mass}}{\text{CMAQ aerosol liquid water content}} \tag{3}$$

Table 1. Setschenow Salting Constants for the Organic Gases

salt	glyoxal "salting-in"	methylglyoxal "salting-out"	IEPOX "salting-out"
	salting constants[67] [kg mol^{-1}]		
ammonium sulfate (AS)	−0.2	+0.16	+0.16
ammonium nitrate (AN)	−0.06	+0.075	+0.075
sodium chloride (NaCl)	−0.10	+0.06	+0.06

We impose a limit on molality at 12m. In dry regions, with low ALW content, the molality approaches infinity, leading to artificially high values for $H_{i,\text{salt}}$. Laboratory experiments suggest partitioning beyond values of AS molality (c_{AS}) greater than 12 m is kinetically limited; hence our calculations only use values of $c_{\text{AS}} \leq 12$ and exclude data where $c_{\text{AS}} > 12$.[26,65]

RESULTS AND DISCUSSION

CMAQ predicts that IEPOX, an isoprene oxidation product that forms SOA in wet acidic aerosols,[46,48] discovered and confirmed ~6 years ago,[42,78] has the highest potential to partition to ALW in the eastern U.S. (Figure 1(d)−(f), SI Figure S2 shows the entire range for IEPOX). The IEPOX instantaneous potential from average gas-phase mixing ratios contributes on average up to ~72% of the sum of predicted aerosol mass from glyoxal, methylglyoxal, and IEPOX in the eastern U.S. during this 10 day simulation over the continental U.S. In comparison, the average glyoxal contribution is ~27%, with the maximum occurring in the midwestern states (Figure 2). Compared to glyoxal and IEPOX, methylglyoxal is a minor contributor. Use of these calculations to estimate relative SOA contributions assumes equal particle-phase retention of the three WSOGs and their aqueous reaction products. Assuming 100% particle-phase retention of these WSOGs and their reaction products, accounting for IEPOX partitioning into ALW reduces the discrepancy between measured and modeled total organic carbon by 17% as compared to the Chemical Speciation Network (CSN) and by 34% for the IMPROVE network.[60] Further particle-phase reactions of the WSOGs, which are not considered here, may lead to the accumulation or reduction of aerosol mass owing to reservoir species of low
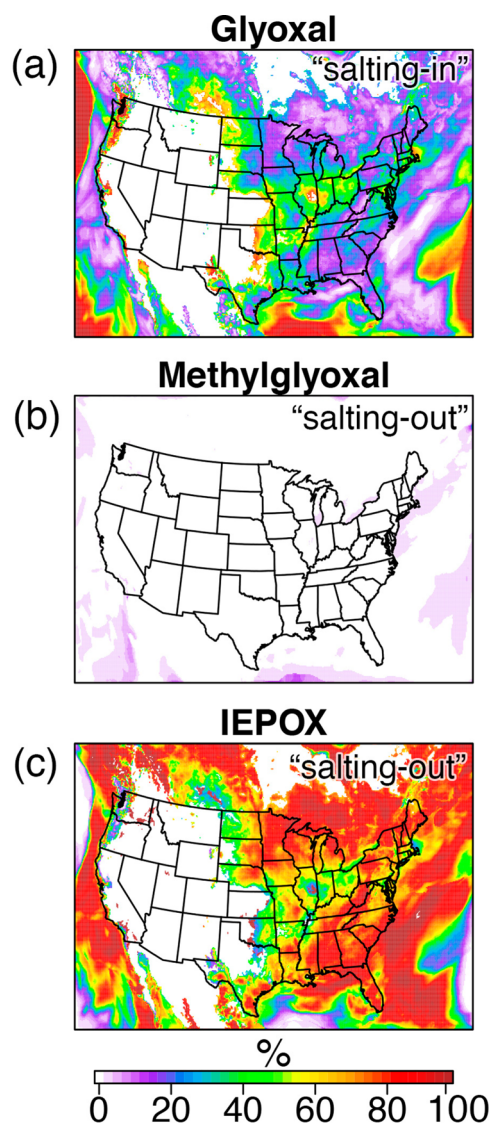
Figure 2. Percent contribution of (a) glyoxal with "salting-in" (b) methylglyoxal with "salting-out" (c) IEPOX with "salting-out" to total particle-phase concentrations due to glyoxal, methylglyoxal and IEPOX.

volatility/reactivity or repartitioning of higher volatility products.

WSOG and ALW concentrations from CMAQ were combined with Henry's Law constants for the respective WSOGs to evaluate partitioning to the particle-phase. CMAQ predicts SOA trends and patterns well, but there are still key uncertainties in predicting absolute mass concentrations[71] due to limitations in representing gas−aerosol partitioning processes, thermodynamic and volatility properties of SOA compounds, condensed-phase reactions, and influence of molality. Hence, we focus on trends in the potential of WSOGs to form SOA rather than comparing absolute concentrations. Potential is described as the amount of organic expected to partition into a particle based on Henry's Law equilibrium; it does not include condensed-phase reactions that can subsequently alter gas-particle partitioning.

IEPOX predominance is largely driven by differences in Henry's Law constants; IEPOX has a factor of at least 10 and 100 greater solubility than glyoxal and methylglyoxal,

respectively (SI Table S1). The higher molecular weight of IEPOX as compared to glyoxal or methylglyoxal also contributes to its larger aqSOA mass formation potential. Glyoxal, methylglyoxal, and IEPOX are all abundant in the gas-phase over the continental U.S. (Figure 1(a)−(c)), though IEPOX is slightly greater at the surface and dominant aloft (SI Figure S3). The geographic pattern in gas-to-particle water partitioning is highest in the southeastern U.S., the location where gas-phase mixing ratios of WSOGs and ALW are highest (Figure 1, SI Figure S4, S5). These results are consistent with model simulations suggesting SOA formed from aqueous processing of WSOG is dominant in this region.[5] The ratio of ALW to organic material is consistently greater than 5 over the eastern U.S. (SI Figure S6), suggesting that the potential for WSOGs to partition to water is greater than their potential to partition to organic matter. Higher CMAQ modeled ALW concentrations in the southeastern U.S. as compared to other U.S. regions are in line with ALW measurements during SOAS.[74] CMAQ predictions highlighting IEPOX dominance in the southeastern U.S. are consistent with field measurements in Atlanta, GA, a region heavily influenced by biogenic and anthropogenic emissions, which attribute on average 3.8 μg m^{-3}, that is, up to 30%, of urban organic aerosol to IEPOX.[47] Modeling studies suggest that glyoxal−SOA can also contribute substantially to total SOA mass, up to 15%, through water-mediated aerosol pathways.[65] It should be noted that SOA from other WSOGs than IEPOX may be underpredicted but this remains unevaluated in field studies due to absence of obvious marker molecules.

SOAS measurements highlight the need for refinement and validation of IEPOX and glyoxal chemistry in models to accurately represent the fate of these SOA precursors, and derive the overall SOA mass under varying atmospheric conditions.[66] For example, GEOS-Chem simulations over-predict IEPOX gas-phase mixing ratios in the southeastern U.S. during SOAS, likely due to missing heterogeneous loss reactions (e.g., organic aerosol transformation in anthropogeni-cally affected ALW).[79] CMAQ simulations underpredict IEPOX-derived SOA mass in Atlanta, possibly because of low uptake values that do not include salting effects and missing aerosol-phase or in-cloud reactions.[25] There exists a significant knowledge gap in understanding the influences of inorganics on modifying partitioning and rates of further reactions, and in lieu of the uncertainties surrounding IEPOX-SOA formation, it is critical to explore the effects of salts on WSOG partitioning.

Condensed-phase glyoxal potentials approximately triple in the eastern U.S. when the Setschenow coefficients to account for "salting-in" due to sulfate, nitrate, and chloride are employed (Figure 1g), and are second to IEPOX particle-phase potentials. When "salting-in" is included, glyoxal contributes up to 50% of the particle-phase mass of the three WSOG's studied here (Figure 2a). Compared to nitrate and chloride, sulfate has the largest impact on "salting-in" of glyoxal. Table 2 highlights the contribution of each salt to the "salting-in" of glyoxal and "salting-out" of methylglyoxal and IEPOX. Sulfate is the highest contributor in both cases, followed closely by nitrate, and then chloride. The highest values of glyoxal−SOA are located over Ohio/Indiana/Illinois, consistent with glyoxal−SOA dominance observed in Ohio/Pennsylvania.[65] This enhancement of condensed-phase glyoxal suggests that including salting effects may explain some of the discrepancies between predicted and measured aqueous organic mass derived from other WSOGs. However, "salting-out" may also

Table 2. Percent Contribution of Each Salt to "Salting-in" Of Glyoxal and "Salting-out" Of Methylglyoxal and IEPOX over the Continental U.S.

salt	contribution of salts to "salting-in" and "salting-out"	
	"salting-in" of glyoxal	"salting-out" of methylglyoxal and IEPOX
ammonium sulfate (AS)	43%	37%
ammonium nitrate (AN)	37%	34%
sodium chloride (NaCl)	20%	30%

occur[62,80−82] and is a critical knowledge gap. Recent laboratory measurements by Waxman et al.[27,67] of Setschenow coefficients for methylglyoxal, and IEPOX calculations indicate that unlike glyoxal, both these compounds "salt-out" leading to lower particle-phase potentials (Figure 1h−i). However, even when "salting-in" for glyoxal and "salting-out" for methylglyoxal and IEPOX are included, IEPOX is the largest contributor to total SOA mass due to these three WSOGs, followed by glyoxal, and then methylglyoxal (Figure 2).

Employing a molality factor in the Henry's Law partitioning coefficient preserves the geographic distribution and conditions that influence partitioning of organic species to the condensed-phase and captures the emission feedback critical to developing control strategies. The ALW and molality effects are largely unexplored avenues by which anthropogenic emissions can facilitate and inhibit biogenic SOA formation. A relative assessment of the abundance of glyoxal, methylglyoxal, and IEPOX in ALW is currently missing from the literature. Molality impacts on IEPOX partitioning may help to explain the gap between measured Henry's Law partitioning coefficient ($\sim$10^7−10^8 M atm^{-1})[48,59] for IEPOX and what is needed in an atmospheric model (10^6 M atm^{-1})[60] to reconcile IEPOX-SOA mass measurements with predictions,[25] in particular given that gas-phase mixing ratios are likely overpredicted.[79] Nguyen et al. measured Henry's Law partitioning of IEPOX on NaCl particles to be 3 × 10^7 M atm^{-1},[48] whereas bond contribution method calculations suggest 2.7 × 10^6 M atm^{-1} as an appropriate value.[60] Salting constants accounting for aerosol molality due to inorganic ion constituents present in the particle, and multiphase reaction products may contribute to explain these differences. For example the Henry's Law value for glyoxal in these simulations differs by approximately a factor of 20 at the highest molality compared to the nonsalting value. Molality impacts and ion-specific impacts[26,83,84] on water-mediated partitioning of WSOGs constitute a critical knowl-edge gap.

While past studies have focused on the importance of glyoxal and methylglyoxal as aqueous SOA precursors,[6] the results herein provide support for the importance of IEPOX as a dominant source of aqueous SOA in the eastern U.S., and for significant contributions also from glyoxal. Since the discovery of IEPOX as a gas-phase oxidation product of isoprene under low NO$_x$ conditions in 2009,[42] there is growing laboratory, field, and modeling evidence of the importance of IEPOX as a precursor to SOA formation via water-mediated pathways, especially in the southeastern U.S. Particle-phase liquid water, critical for IEPOX-SOA formation,[48] is abundant in the southeastern U.S.,[74] and facilitates SOA formation from WSOGs,[5] including from IEPOX. Being a low NO$_x$ product does not imply that anthropogenic impacts are not important.

On the contrary, IEPOX-SOA will only form in appreciable amounts in the presence of ALW via ring-opening chemistry when anthropogenic influence is sufficient to facilitate SOA formation. However, the role of inorganic salts on the reaction rates of ring-opening is currently not clear. In the southeastern U.S., anthropogenic sulfate is critical for ALW and IEPOX ring-opening.[46] Including salting effects enhances glyoxal–SOA concentrations, and decreases IEPOX partitioning. However, in the southeastern U.S. IEPOX partitioning potentials still dominate and contribute 40 to 90% toward particle-phase glyoxal, methylglyoxal, and IEPOX (Figure 2). The maximum concentrations of glyoxal–SOA are collocated with high-NO_x regimes in the model, and IEPOX dominance is prominent in low-NO_x regions in the continental U.S. (SI Figure S7). Previous work in Mexico City, a high-NO_x regime, attributed up to 15% of total SOA mass to glyoxal.[8] It is difficult to directly compare our results to Mexico City, where glyoxal forms primarily from anthropogenic VOCs, and isoprene mixing ratios are extremely low. In isoprene-rich environments, the latest CMAQ model version predicts that IEPOX contributes more to SOA mass under low NO_x conditions, and glyoxal is relatively more important under high NO_x conditions, consistent with findings by McNeill et al.[49] Table 3 compares the average contributions of glyoxal, methylglyoxal,

Table 3. Percent Contribution of Glyoxal ("Salting-In"), Methylglyoxal and IEPOX ("Salting-out") to Total Particle-Phase Concentrations Due to Glyoxal, Methylglyoxal and IEPOX in Various Subdivisions of the Continental U.S.

organic gas	contribution of WSOG to total SOA		
	eastern U.S.	western U.S.	southeastern U.S.
glyoxal	27%	34%	26%
methylglyoxal	1%	1%	1%
IEPOX	72%	65%	73%

and IEPOX to total particle-phase concentrations due to the three WSOGs in the eastern, western, and southeastern U.S. In all three regions, IEPOX is the largest contributor on average. Glyoxal contribution is more dominant in the western U.S. as compared to the eastern U.S. This work provides a guide as to the compounds for which it would be critical to further develop aqueous-phase chemical processing mechanisms. For the simplest representation of aqSOA chemistry from isoprene in climate models, it is essential to include both IEPOX and glyoxal as key precursors and to account for the presence of water and acidity. Further laboratory studies elucidating the molality- and ion-specific impacts of various salts on IEPOX and glyoxal partitioning and chemistry are warranted to improve model representation of these WSOGs and reconcile measurements and model results for aqSOA formation. Similar studies are also relevant under more dilute cloud and fogwater conditions.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b04540.

Table S1 and Figures S1−S8 (PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Chebbi, A.; Carlier, P. Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review. *Atmos. Environ.* **1996**, *30* (24), 4233−4249.

(2) Nolte, C. G.; Fraser, M. P.; Cass, G. R. Gas phase C2−C10 organic acids concentrations in the Los Angeles atmosphere. *Environ. Sci. Technol.* **1999**, *33* (4), 540−545.

(3) Spaulding, R. S.; Schade, G. W.; Goldstein, A. H.; Charles, M. J. Characterization of secondary atmospheric photooxidation products: Evidence for biogenic and anthropogenic sources. *J. Geophys. Res.* **2003**, *108* (D8), 4247.

(4) Hennigan, C. J.; Bergin, M. H.; Russell, A. G.; Nenes, A.; Weber, R. J. Gas/particle partitioning of water-soluble organic aerosol in Atlanta. *Atmos. Chem. Phys.* **2009**, *9* (11), 3613−3628.

(5) Carlton, A. G.; Turpin, B. J. Particle partitioning potential of organic compounds is highest in the Eastern US and driven by anthropogenic water. *Atmos. Chem. Phys.* **2013**, *13* (20), 10203−10214.

(6) Blando, J. D.; Turpin, B. J. Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility. *Atmos. Environ.* **2000**, *34* (10), 1623−1632.

(7) Carlton, A. G.; Turpin, B. J.; Altieri, K. E.; Reff, A.; Seitzinger, S.; Lim, H. J.; Ervens, B. *Atmos. Environ.* **2007**, *41*, 7588.

(8) Volkamer, R.; San Martini, F.; Molina, L. T.; Salcedo, D.; Jimenez, J. L.; Molina, M. J. A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol. *Geophys. Res. Lett.* **2007**, *34* (19), L19807.

(9) Ervens, B.; Volkamer, R. Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles. *Atmos. Chem. Phys.* **2010**, *10* (17), 8219−8244.

(10) Ervens, B.; Turpin, B. J.; Weber, R. J. Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies. *Atmos. Chem. Phys.* **2011**, *11* (21), 11069−11102.

(11) Liu, S.; Ahlm, L.; Day, D. A.; Russell, L. M.; Zhao, Y.; Gentner, D. R.; Weber, R. J.; Goldstein, A. H.; Jaoui, M.; Offenberg, J. H.; Kleindienst, T. E.; Rubitschun, C.; Surratt, J. D.; Sheesley, R. J.; Scheller, S. Secondary organic aerosol formation from fossil fuel

sources contribute majority of summertime organic mass at Bakersfield. *J. Geophys. Res., [Atmos.]* **2012**, *117* (D24), D00V26.

(12) Keene, W. C.; Galloway, J. N. The biogeochemical cycling of formic and acetic acids through the troposphere: an overview of current understanding. *Tellus, Ser. B* **1988**, *40B* (5), 322−334.

(13) Facchini, M. C.; Mircea, M.; Fuzzi, S.; Charlson, R. J. Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature* **1999**, *401* (6750), 257−259.

(14) Limbeck, A.; Kulmala, M.; Puxbaum, H. Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles. *Geophys. Res. Lett.* **2003**, *30* (19), 1996.

(15) Sareen, N.; Schwier, A. N.; Lathem, T. L.; Nenes, A.; McNeill, V. F. Surfactants from the gas phase may promote cloud droplet formation. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110* (8), 2723−2728.

(16) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; Swietlicki, E.; Putaud, J. P.; Balkanski, Y.; Fuzzi, S.; Horth, J.; Moortgat, G. K.; Winterhalter, R.; Myhre, C. E. L.; Tsigaridis, K.; Vignati, E.; Stephanou, E. G.; Wilson, J. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* **2005**, *5* (4), 1053−1123.

(17) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; Hamilton, J. F.; Herrmann, H.; Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M. E.; Jimenez, J. L.; Kiendler-Scharr, A.; Maenhaut, W.; McFiggans, G.; Mentel, T. F.; Monod, A.; Prévôt, A. S. H.; Seinfeld, J. H.; Surratt, J. D.; Szmigielski, R.; Wildt, J. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* **2009**, *9* (14), 5155−5236.

(18) Carslaw, K. S.; Lee, L. A.; Reddington, C. L.; Pringle, K. J.; Rap, A.; Forster, P. M.; Mann, G. W.; Spracklen, D. V.; Woodhouse, M. T.; Regayre, L. A.; Pierce, J. R. Large contribution of natural aerosols to uncertainty in indirect forcing. *Nature* **2013**, *503* (7474), 67−71.

(19) Heald, C. L.; Jacob, D. J.; Park, R. J.; Russell, L. M.; Huebert, B. J.; Seinfeld, J. H.; Liao, H.; Weber, R. J. A large organic aerosol source in the free troposphere missing from current models. *Geophys. Res. Lett.* **2005**, *32* (18), L18809.

(20) Volkamer, R.; Jimenez, J. L.; San Martini, F.; Dzepina, K.; Zhang, Q.; Salcedo, D.; Molina, L. T.; Worsnop, D. R.; Molina, M. J. Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected. *Geophys. Res. Lett.* **2006**, *33* (17), L17811.

(21) Carlton, A. G.; Bhave, P. V.; Napelenok, S. L.; Edney, E. O.; Sarwar, G.; Pinder, R. W.; Pouliot, G. A.; Houyoux, M. Model representation of secondary organic aerosol in CMAQv4.7. *Environ. Sci. Technol.* **2010**, *44* (22), 8553−8560.

(22) De Gouw, J.; Jimenez, J. L. Organic aerosols in the earth's atmosphere. *Environ. Sci. Technol.* **2009**, *43* (20), 7614−7618.

(23) Carlton, A. G.; Wiedinmyer, C.; Kroll, J. H. A review of secondary organic aerosol (SOA) formation from isoprene. *Atmos. Chem. Phys.* **2009**, *9* (14), 4987−5005.

(24) Volkamer, R.; Ziemann, P. J.; Molina, M. J. Secondary Organic Aerosol Formation from Acetylene (C_2H_2): seed effect on SOA yields due to organic photochemistry in the aerosol aqueous phase. *Atmos. Chem. Phys.* **2009**, *9* (6), 1907−1928.

(25) Karambelas, A.; Pye, H. O. T.; Budisulistiorini, S. H.; Surratt, J. D.; Pinder, R. W. Contribution of Isoprene Epoxydiol to Urban Organic Aerosol: Evidence from Modeling and Measurements. *Environ. Sci. Technol. Lett.* **2014**, *1* (6), 278−283.

(26) Kampf, C. J.; Waxman, E. M.; Slowik, J. G.; Dommen, J.; Pfaffenberger, L.; Praplan, A. P.; Prévôt, A. S. H.; Baltensperger, U.; Hoffmann, T.; Volkamer, R. Effective Henry's Law partitioning and the salting constant of glyoxal in aerosols containing sulfate. *Environ. Sci. Technol.* **2013**, *47* (9), 4236−4244.

(27) Waxman, E. M.; Elm, J.; Kurtén, T.; Mikkelsen, K. V.; Ziemann, P. J.; Volkamer, R. Glyoxal and Methylglyoxal Setschenow Salting Constants in Sulfate, Nitrate, and Chloride Solutions: Measurements and Gibbs Energies. *Environ. Sci. Technol.* **2015**, *49* (19), 11500−11508.

(28) Hodas, N.; Sullivan, A. P.; Skog, K.; Keutsch, F. N.; Collett, J. L.; Decesari, S.; Facchini, M. C.; Carlton, A. G.; Laaksonen, A.; Turpin, B. J. Aerosol Liquid Water Driven by Anthropogenic Nitrate: Implications for Lifetimes of Water-Soluble Organic Gases and Potential for Secondary Organic Aerosol Formation. *Environ. Sci. Technol.* **2014**, *48* (19), 11127−11136.

(29) Claeys, M.; Graham, B.; Vas, G.; Wang, W.; Vermeylen, R.; Pashynska, V.; Cafmeyer, J.; Guyon, P.; Andreae, M. O.; Artaxo, P.; Maenhaut, W. Formation of secondary organic aerosols through photooxidation of isoprene. *Science* **2004**, *303* (5661), 1173−1176.

(30) Edney, E. O.; Kleindienst, T. E.; Jaoui, M.; Lewandowski, M.; Offenberg, J. H.; Wang, W.; Claeys, M. Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_X/SO_2/air mixtures and their detection in ambient $PM_{2.5}$ samples collected in the eastern United States. *Atmos. Environ.* **2005**, *39* (29), 5281−5289.

(31) Kroll, J. H.; Ng, N. L.; Murphy, S. M.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions. *Geophys. Res. Lett.* **2005**, *32* (18), L18808.

(32) Kroll, J. H.; Ng, N. L.; Murphy, S. M.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation from isoprene photooxidation. *Environ. Sci. Technol.* **2006**, *40* (6), 1869−1877.

(33) Henze, D. K.; Seinfeld, J. H. Global secondary organic aerosol from isoprene oxidation. *Geophys. Res. Lett.* **2006**, *33* (9), L09812.

(34) Kleindienst, T. E.; Edney, E. O.; Lewandowski, M.; Offenberg, J. H.; Jaoui, M. Secondary Organic Carbon and Aerosol Yields from the Irradiations of Isoprene and α-Pinene in the Presence of NO_x and SO_2. *Environ. Sci. Technol.* **2006**, *40* (12), 3807−3812.

(35) Kleindienst, T. E.; Lewandowski, M.; Offenberg, J. H.; Jaoui, M.; Edney, E. O. Ozone-isoprene reaction: Re-examination of the formation of secondary organic aerosol. *Geophys. Res. Lett.* **2007**, *34* (1), L01805.

(36) Ng, N. L.; Kwan, A. J.; Surratt, J. D.; Chan, A. W. H.; Chhabra, P. S.; Sorooshian, A.; Pye, H. O. T.; Crounse, J. D.; Wennberg, P. O.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO_3). *Atmos. Chem. Phys.* **2008**, *8* (14), 4117−4140.

(37) Guenther, A.; Karl, T.; Harley, P.; Wiedinmyer, C.; Palmer, P. I.; Geron, C. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.* **2006**, *6* (11), 3181−3210.

(38) Carlton, A. G.; Turpin, B. J.; Altieri, K. E.; Seitzinger, S.; Reff, A.; Lim, H.-J.; Ervens, B. Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments. *Atmos. Environ.* **2007**, *41* (35), 7588−7602.

(39) Altieri, K. E.; Seitzinger, S. P.; Carlton, A. G.; Turpin, B. J.; Klein, G. C.; Marshall, A. G. Oligomers formed through in-cloud methylglyoxal reactions: Chemical composition, properties, and mechanisms investigated by ultra-high resolution FT-ICR mass spectrometry. *Atmos. Environ.* **2008**, *42* (7), 1476−1490.

(40) Galloway, M. M.; Chhabra, P. S.; Chan, A. W. H.; Surratt, J. D.; Flagan, R. C.; Seinfeld, J. H.; Keutsch, F. N. Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions. *Atmos. Chem. Phys.* **2009**, *9* (10), 3331−3345.

(41) De Haan, D. O.; Corrigan, A. L.; Smith, K. W.; Stroik, D. R.; Turley, J. J.; Lee, F. E.; Tolbert, M. A.; Jimenez, J. L.; Cordova, K. E.; Ferrell, G. R. Secondary Organic Aerosol-Forming Reactions of Glyoxal with Amino Acids. *Environ. Sci. Technol.* **2009**, *43* (8), 2818−2824.

(42) Paulot, F.; Crounse, J. D.; Kjaergaard, H. G.; Kurten, A.; St Clair, J. M.; Seinfeld, J. H.; Wennberg, P. O. Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene. *Science* **2009**, *325* (5941), 730−733.

(43) Tan, Y.; Carlton, A. G.; Seitzinger, S. P.; Turpin, B. J. SOA from methylglyoxal in clouds and wet aerosols: Measurement and prediction of key products. *Atmos. Environ.* **2010**, *44* (39), 5218−5226.

(44) Sareen, N.; Schwier, A. N.; Shapiro, E. L.; Mitroo, D.; McNeill, V. F. Secondary organic material formed by methylglyoxal in aqueous aerosol mimics. *Atmos. Chem. Phys.* **2010**, *10* (3), 997−1016.

(45) Schwier, A. N.; Sareen, N.; Mitroo, D.; Shapiro, E. L.; McNeill, V. F. Glyoxal-Methylglyoxal Cross-Reactions in Secondary Organic Aerosol Formation. *Environ. Sci. Technol.* **2010**, *44* (16), 6174−6182.

(46) Surratt, J. D.; Chan, A. W. H.; Eddingsaas, N. C.; Chan, M.; Loza, C. L.; Kwan, A. J.; Hersey, S. P.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107* (15), 6640−6645.

(47) Budisulistiorini, S. H.; Canagaratna, M. R.; Croteau, P. L.; Marth, W. J.; Baumann, K.; Edgerton, E. S.; Shaw, S. L.; Knipping, E. M.; Worsnop, D. R.; Jayne, J. T.; Gold, A.; Surratt, J. D. Real-time continuous characterization of secondary organic aerosol derived from isoprene epoxydiols in downtown Atlanta, Georgia, using the Aerodyne Aerosol Chemical Speciation Monitor. *Environ. Sci. Technol.* **2013**, *47* (11), 5686−5694.

(48) Nguyen, T. B.; Coggon, M. M.; Bates, K. H.; Zhang, X.; Schwantes, R. H.; Schilling, K. A.; Loza, C. L.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. Organic aerosol formation from the reactive uptake of isoprene epoxydiols (IEPOX) onto non-acidified inorganic seeds. *Atmos. Chem. Phys.* **2014**, *14* (7), 3497−3510.

(49) McNeill, V. F. Aqueous organic chemistry in the atmosphere: Sources and chemical processing of organic aerosols. *Environ. Sci. Technol.* **2015**, *49* (3), 1237−1244.

(50) Tan, Y.; Perri, M. J.; Seitzinger, S. P.; Turpin, B. J. Effects of Precursor Concentration and Acidic Sulfate in Aqueous Glyoxal−OH Radical Oxidation and Implications for Secondary Organic Aerosol. *Environ. Sci. Technol.* **2009**, *43* (21), 8105−8112.

(51) Mikhailov, E.; Vlasenko, S.; Martin, S. T.; Koop, T.; Pöschl, U. Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations. *Atmos. Chem. Phys.* **2009**, *9* (24), 9491−9522.

(52) Virtanen, A.; Joutsensaari, J.; Koop, T.; Kannosto, J.; Yli-Pirila, P.; Leskinen, J.; Makela, J. M.; Holopainen, J. K.; Poschl, U.; Kulmala, M.; Worsnop, D. R.; Laaksonen, A. An amorphous solid state of biogenic secondary organic aerosol particles. *Nature* **2010**, *467* (7317), 824−827.

(53) Koop, T.; Bookhold, J.; Shiraiwa, M.; Poschl, U. Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere. *Phys. Chem. Chem. Phys.* **2011**, *13* (43), 19238−19255.

(54) Bones, D. L.; Reid, J. P.; Lienhard, D. M.; Krieger, U. K. Comparing the mechanism of water condensation and evaporation in glassy aerosol. *Proc. Natl. Acad. Sci. U. S. A.* **2012**, *109* (29), 11613−11618.

(55) Song, M.; Marcolli, C.; Krieger, U. K.; Zuend, A.; Peter, T. Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles. *Atmos. Chem. Phys.* **2012**, *12* (5), 2691−2712.

(56) Song, M.; Marcolli, C.; Krieger, U. K.; Lienhard, D. M.; Peter, T. Morphologies of mixed organic/inorganic/aqueous aerosol droplets. *Faraday Discuss.* **2013**, *165*, 289−316.

(57) Kurtén, T.; Elm, J.; Prisle, N. L.; Mikkelsen, K. V.; Kampf, C. J.; Waxman, E. M.; Volkamer, R. Computational Study of the Effect of Glyoxal−Sulfate Clustering on the Henry's Law Coefficient of Glyoxal. *J. Phys. Chem. A* **2015**, *119* (19), 4509−4514.

(58) Kroll, J. H.; Ng, N. L.; Murphy, S. M.; Varutbangkul, V.; Flagan, R. C.; Seinfeld, J. H. Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds. *J. Geophys. Res.* **2005**, *110* (D23), D23207.

(59) Gaston, C. J.; Riedel, T. P.; Zhang, Z.; Gold, A.; Surratt, J. D.; Thornton, J. A. Reactive uptake of an isoprene-derived epoxydiol to submicron aerosol particles. *Environ. Sci. Technol.* **2014**, *48* (19), 11178−11186.

(60) Pye, H. O. T.; Pinder, R. W.; Piletic, I. R.; Xie, Y.; Capps, S. L.; Lin, Y. H.; Surratt, J. D.; Zhang, Z. F.; Gold, A.; Luecken, D. J.; Hutzell, W. T.; Jaoui, M.; Offenberg, J. H.; Kleindienst, T. E.; Lewandowski, M.; Edney, E. O. Epoxide pathways improve model predictions of isoprene markers and reveal key role of acidity in aerosol formation. *Environ. Sci. Technol.* **2013**, *47* (19), 11056−11064.

(61) Almeida, M. B.; Alvarez, A. M.; Miguel, E. M. D.; Hoyo, E. S. D. Setchenow coefficients for naphthols by distribution method. *Can. J. Chem.* **1983**, *61* (2), 244−248.

(62) Wang, C.; Lei, Y. D.; Endo, S.; Wania, F. Measuring and modeling the salting-out effect in ammonium sulfate solutions. *Environ. Sci. Technol.* **2014**, *48* (22), 13238−13245.

(63) Wang, C.; Lei, Y. D.; Wania, F. Effect of Sodium Sulfate, Ammonium Chloride, Ammonium Nitrate, and Salt Mixtures on Aqueous Phase Partitioning of Organic Compounds. *Environ. Sci. Technol.* **2016**, *50* (23), 12742−12749.

(64) Waxman, E. M.; Dzepina, K.; Ervens, B.; Lee-Taylor, J.; Aumont, B.; Jimenez, J. L.; Madronich, S.; Volkamer, R. Secondary organic aerosol formation from semi- and intermediate-volatility organic compounds and glyoxal: Relevance of O/C as a tracer for aqueous multiphase chemistry. *Geophys. Res. Lett.* **2013**, *40* (5), 978−982.

(65) Knote, C.; Hodzic, A.; Jimenez, J. L.; Volkamer, R.; Orlando, J. J.; Baidar, S.; Brioude, J.; Fast, J.; Gentner, D. R.; Goldstein, A. H.; Hayes, P. L.; Knighton, W. B.; Oetjen, H.; Setyan, A.; Stark, H.; Thalman, R.; Tyndall, G.; Washenfelder, R.; Waxman, E.; Zhang, Q. Simulation of semi-explicit mechanisms of SOA formation from glyoxal in aerosol in a 3-D model. *Atmos. Chem. Phys.* **2014**, *14* (12), 6213−6239.

(66) Xu, L.; Guo, H.; Boyd, C. M.; Klein, M.; Bougiatioti, A.; Cerully, K. M.; Hite, J. R.; Isaacman-VanWertz, G.; Kreisberg, N. M.; Knote, C.; Olson, K.; Koss, A.; Goldstein, A. H.; Hering, S. V.; de Gouw, J.; Baumann, K.; Lee, S.-H.; Nenes, A.; Weber, R. J.; Ng, N. L. Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (1), 37−42.

(67) Waxman, E. M. Secondary Organic Aerosol Formation from alpha-dicarbonyls in Aerosol Water: Salt interactions and multi-phase chemistry. Ph.D. Thesis, University of Colorado, 2015.

(68) Xie, Y.; Paulot, F.; Carter, W. P. L.; Nolte, C. G.; Luecken, D. J.; Hutzell, W. T.; Wennberg, P. O.; Cohen, R. C.; Pinder, R. W. Understanding the impact of recent advances in isoprene photo-oxidation on simulations of regional air quality. *Atmos. Chem. Phys.* **2013**, *13* (16), 8439−8455.

(69) Carlton, A. G.; Baker, K. R. Photochemical modeling of the Ozark isoprene volcano: MEGAN, BEIS, and their impacts on air quality predictions. *Environ. Sci. Technol.* **2011**, *45* (10), 4438−4445.

(70) Carlton, A. G.; Turpin, B. J.; Altieri, K. E.; Seitzinger, S. P.; Mathur, R.; Roselle, S. J.; Weber, R. J. CMAQ model performance enhanced when in-cloud secondary organic aerosol is included: Comparisons of organic carbon predictions with measurements. *Environ. Sci. Technol.* **2008**, *42* (23), 8798−8802.

(71) Carlton, A. G.; Pinder, R. W.; Bhave, P. V.; Pouliot, G. A. To what extent can biogenic SOA be controlled? *Environ. Sci. Technol.* **2010**, *44* (9), 3376−3380.

(72) Fraser, M. P.; Grosjean, D.; Grosjean, E.; Rasmussen, R. A.; Cass, G. R. Air quality model evaluation data for organics. 1. Bulk chemical composition and gas/particle distribution factors. *Environ. Sci. Technol.* **1996**, *30* (5), 1731−1743.

(73) Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T.; Rasmussen, R. A. Air quality model evaluation data for organics. 4. C2−C36 Non-aromatic hydrocarbons. *Environ. Sci. Technol.* **1997**, *31* (8), 2356−2367.

(74) Nguyen, T. K. V.; Petters, M. D.; Suda, S. R.; Guo, H.; Weber, R. J.; Carlton, A. G. Trends in particle-phase liquid water during the Southern Oxidant and Aerosol Study. *Atmos. Chem. Phys.* **2014**, *14* (20), 10911−10930.

(75) Nenes, A.; Pandis, S.; Pilinis, C. ISORROPIA: A New Thermodynamic Equilibrium Model for Multiphase Multicomponent Inorganic Aerosols. *Aquat. Geochem.* **1998**, *4* (1), 123−152.

(76) Fountoukis, C.; Nenes, A.; ISORROPIA, I. I. a computationally efficient thermodynamic equilibrium model for $K^+-Ca^{2+}-Mg^{2+}-NH4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O$ aerosols. *Atmos. Chem. Phys.* **2007**, *7* (17), 4639−4659.

(77) Nguyen, T. K. V.; Capps, S. L.; Carlton, A. G. Decreasing aerosol water is consistent with OC trends in the southeast U.S. *Environ. Sci. Technol.* **2015**, *49* (13), 7843−7850.

(78) Hatch, L. E.; Creamean, J. M.; Ault, A. P.; Surratt, J. D.; Chan, M. N.; Seinfeld, J. H.; Edgerton, E. S.; Su, Y.; Prather, K. A. Measurements of isoprene-derived organosulfates in ambient aerosols by Aerosol Time-of-Flight Mass Spectrometry - Part 1: Single particle atmospheric observations in Atlanta. *Environ. Sci. Technol.* **2011**, *45* (12), 5105−5111.

(79) Nguyen, T. B.; Crounse, J. D.; Teng, A. P.; St. Clair, J. M.; Paulot, F.; Wolfe, G. M.; Wennberg, P. O. Rapid deposition of oxidized biogenic compounds to a temperate forest. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (5), E392−E401.

(80) Setschenow, J. Über die konstitution der salzlösungen auf grund ihres verhaltens zu kohlensäure. *Z. Phys. Chem.* **1889**, *4*, 117−125.

(81) Schwarzenbach, P. M.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; John Wiley & Sons: New York, 1993.

(82) Donaldson, D. J.; Vaida, V. The influence of organic films at the air−aqueous boundary on atmospheric processes. *Chem. Rev.* **2006**, *106* (4), 1445−1461.

(83) Gordon, J. E.; Thorne, R. L. Salt effects on the activity coefficient of naphthalene in mixed aqueous electrolyte solutions. I. Mixtures of two salts. *J. Phys. Chem.* **1967**, *71* (13), 4390−4399.

(84) Gordon, J. E.; Thorne, R. L. Salt effects on non-electrolyte activity coefficients in mixed aqueous electrolyte solutions—II. Artificial and natural sea waters. *Geochim. Cosmochim. Acta* **1967**, *31* (12), 2433−2443.