

Aqueous Processing of Atmospheric Organic Particles in Cloud Water Collected via Aircraft Sampling

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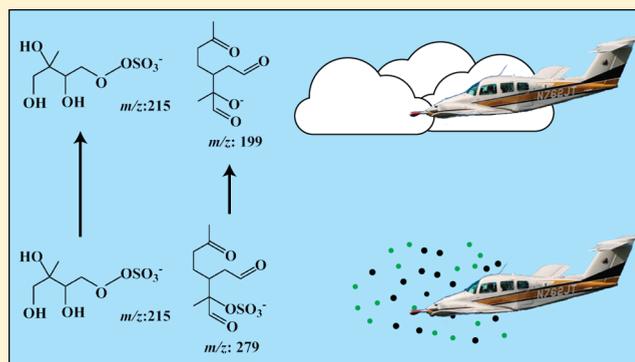
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Supporting Information

ABSTRACT: Cloudwater and below-cloud atmospheric particle samples were collected onboard a research aircraft during the Southern Oxidant and Aerosol Study (SOAS) over a forested region of Alabama in June 2013. The organic molecular composition of the samples was studied to gain insights into the aqueous-phase processing of organic compounds within cloud droplets. High resolution mass spectrometry (HRMS) with nanospray desorption electrospray ionization (nano-DESI) and direct infusion electrospray ionization (ESI) were utilized to compare the organic composition of the particle and cloudwater samples, respectively. Isoprene and monoterpene-derived organosulfates and oligomers were identified in both the particles and cloudwater, showing the significant influence of biogenic volatile organic compound oxidation above the forested region. While the average O:C ratios of the organic compounds were similar between the atmospheric particle and cloudwater samples, the chemical composition of these samples was quite different. Specifically, hydrolysis of organosulfates and formation of nitrogen-containing compounds were observed for the cloudwater when compared to the atmospheric particle samples, demonstrating that cloud processing changes the composition of organic aerosol.



INTRODUCTION

Atmospheric aerosols play a significant role in the Earth's climate system by scattering and absorbing light and impacting cloud formation.¹ By acting as cloud condensation nuclei (CCN), organic-containing particles provide a source of organic material to cloud droplets.² The composition of these cloud droplets can influence precipitation chemistry, impacting ecosystems; in addition, if droplet evaporation instead occurs, the residual particle chemical composition may impact future cloud formation.² Secondary organic aerosol (SOA), formed through the oxidation of volatile organic compounds, represents a significant mass fraction of the total submicron aerosol globally in the atmosphere, but there remain uncertainties in predictions of SOA mass concentrations.³ Underprediction of the total organic aerosol burden in the spring and summer in the midlatitudes suggests an unaccounted source of organic mass.⁴ SOA formation via aqueous reactions of dissolved organic gases and particles in

cloud droplets has been suggested as a potential candidate for the missing source of SOA in models.⁵ Indeed, inclusion of a parametrization of SOA formation in cloud droplets through aqueous reactions within a regional chemical transport model improved agreement with measurements of organic aerosol mass.⁴ However, our understanding of these processes is limited by a paucity of experimental data on the molecular characterization of organic compounds in ambient cloudwater.^{5–11}

Many laboratory studies have examined the production of high molecular weight organic compounds through reactions in aqueous solutions using atmospherically relevant species.^{5,12} These compounds are produced through a variety of pathways,

Received: March 31, 2015

Revised: June 8, 2015

Accepted: June 11, 2015

including radical reactions, inorganic–organic reactions, photochemistry, hydration, and oligomerization.¹² Aqueous oxidation reactions have been proposed to increase the overall (bulk) O:C ratio of organic compounds in cloudwater and SOA.⁵ However, the dominant reactions occurring in cloud droplets may be different from deliquesced aerosols, which are more concentrated and have longer lifetimes; these cloudwater conditions are expected to inhibit aqueous reactions leading to oligomer and organosulfate formation.⁵ Further, organosulfates, produced in deliquesced aerosol and activated as cloud droplets, could be additionally modified in cloud droplets through aqueous phase reactions such as hydrolysis.¹³ In contrast to aqueous oxidation reactions, hydrolysis reactions of organonitrates and organosulfates would reduce the O:C ratio of the resulting products.¹⁴ Aqueous-phase reactions can also create more volatile compounds through fragmentation of larger species, resulting in a net organic mass loss.¹² These are examples of the complexity and competing factors in aqueous reactions.

The southeastern United States is a unique ecosystem for studying aqueous-phase reactions within atmospheric particles and cloudwater. The combination of significant biogenic and anthropogenic emissions in the humid region has been shown to result in a cooling haze, consisting of aqueous particles.¹⁵ Previous studies demonstrated that 70–80% of water-soluble organic carbon in atmospheric particles collected near Atlanta, GA originated from biogenic emissions.¹⁶ Modeling of the spatial distribution of water-soluble volatile organic compounds and particulate liquid water content in the eastern United States indicates that anthropogenic emissions lead to higher particulate mass, which increases the amount of water condensed onto the particles.¹⁷ This may make aqueous processing a dominant SOA production mechanism in the region.¹⁷ During the 2013 Southern Oxidant and Aerosol Study (SOAS) in Alabama, samples of atmospheric particles and cloudwater were collected onboard research aircraft for later characterization of their organic constituents using high resolution mass spectrometry. Comparison of the composition of the below-cloud atmospheric particles with the cloudwater provides insights into potential aqueous-phase processing of the organic species. Several hundred unique organic compounds, many derived from biogenic precursors,⁴⁰ were identified with significant differences observed between the particle and cloudwater samples, suggesting that cloud processing plays a significant role in altering the composition of the organic compounds.

■ EXPERIMENTAL SECTION

Atmospheric particle and cloudwater samples were collected during three SOAS flights (June 10, 13, and 27, 2013) of a Beechcraft Duchess twin-engine aircraft (Purdue University Airborne Laboratory for Atmospheric Research). Sampling was conducted between ~13:00 and ~16:00 local time (central daylight time, CDT) over the region ~40 km northeast of the SOAS Centreville, AL site (32.90N, 87.25W). Atmospheric particles were collected below cloud (~1000–1200 masl) during ~30–45 min of sampling, and cloudwater was collected through the middle and upper sections (~1800–2000 masl) of developing cumulus clouds. During cloudwater and particle collection, convective available potential energy (CAPE) was measured at the Shelby County Airport in Birmingham, AL by soundings (<http://weather.uwo.edu/upperair/sounding.html>) recorded at 12:00 UTC (19:00 CDT). The CAPE values were

1069 J/kg, 1951 J/kg, and 2716 J/kg on June 10, 13, and 27, respectively. These values designate high atmospheric instability, indicating that the convective clouds were significantly influenced by the atmospheric boundary layer.

Samples of atmospheric particles were first collected during multiple passages of the aircraft below cloud using a modified rotating drum impactor.¹⁸ Particle samples in three size ranges (1.15–2.5 μm - stage A, 0.34–1.15 μm - stage B, and 0.07–0.34 μm - stage C) were collected on prebaked aluminum foil. Here, we focus on stage B samples, which had sufficient organic mass for analysis and correspond to particles that are expected to have acted as CCN to form cloud droplets. Next, the aircraft made several passages through the overlying clouds with a modified Mohnen slotted rod cloudwater collector¹⁹ extended out of the top of the aircraft; cloudwater samples (ranging from 5–15 mL each) were collected following the method of Hill et al.²⁰ Cloud droplets were collected into glass vials after impacting the collector Teflon rods, which are characterized by a 50% cutoff diameter of ~5.5 μm .²¹ After aircraft landing, particle and cloudwater samples were kept at $-40\text{ }^\circ\text{C}$ pending analysis.

High resolution negative ion mass spectra of the particle samples were obtained using a Thermo LTQ Orbitrap mass spectrometer equipped with a custom-built nanospray desorption electrospray ionization (nano-DESI) source described in detail elsewhere.^{22,23} Briefly, the nano-DESI probe is comprised of two fused silica capillaries: one supplying a solvent from a syringe pump operated at a typical flow rate of ~1 $\mu\text{L}/\text{min}$ and another capillary removing the solvent containing the extracted analyte molecules and delivering it to the mass spectrometer inlet. The resulting mixture is ionized by applying ~4 kV to the first capillary. Charged microdroplets produced at the instrument inlet are subsequently desolvated in a heated capillary operated at 250 $^\circ\text{C}$.^{22,23} In this study, the instrument was operated at a mass resolution of $m/\Delta m = 100,000$ at m/z 400 and a mass range of $m/z = 150\text{--}2000$.²³ A 70/30 (volume) mixture of acetonitrile (HPLC grade, 99.9%) and milli-q (18 MOhm) water was used as the nano-DESI solvent. The solvent droplet was drawn directly across each particle sample spot on the aluminum substrate for analysis. A background mass spectrum was acquired over the bare aluminum substrate next to the particle sample. To assist in ionization and desolvation, the cloudwater was diluted to a mixture of 70/30 (by volume) HPLC grade acetonitrile and cloudwater. The resulting solution was directly injected into the Thermo LTQ Orbitrap mass spectrometer using an ESI source operated at a typical flow rate of ~0.5 $\mu\text{L}/\text{min}$ and a high voltage of ~3.5 kV. The acquired mass range for the ESI experiment was m/z 50–2000. A field blank of ultrapure water sprayed across the cloudwater collector, prior to each cloudwater sampling period, was diluted to a 70/30 (by volume) mixture of HPLC grade acetonitrile and blank water; this was analyzed before and after each cloudwater injection.

Mass spectral peaks of over 3 times signal/noise were extracted from the raw files using the Decon2Ls program (<http://omics.pnl.gov/software/decontools-decon2ls>) developed at Pacific Northwest National Laboratory (PNNL), and features with enhancements of less than 5 times of blank intensity, as well as ^{13}C isotopes, were removed from the final list. The final peak list was grouped into homologous series using second order mass defect analysis (bases CH_2 and H_2), described in Roach et al.²⁴ Molecular formula assignment for representative peaks from each group was performed using the

Formula Calculator v 1.1 from the National High Magnetic Field Laboratory (http://www.magnet.fsu.edu/usershub/scientificdivisions/icr/icr_software.html). The parameters used for the assignment were as follows: C_{0-50} , H_{0-100} , O_{0-20} , N_{0-3} , S_{0-2} in negative mode and C_{0-50} , H_{0-100} , O_{0-20} , N_{0-3} , S_{0-1} , Na_{0-1} in positive mode. Negative ions were assumed to have formed via deprotonation exclusively, while positive ions were assumed to be formed by protonation or addition of sodium. Identification of one peak from each group enabled formula assignments for all other members of the homologous group. All peaks were assigned with a mass accuracy of ± 3 ppm, and at least 55% of the peaks and 65% of the total signal intensity were assigned molecular formulas for each sample. Because over 90% of the peaks were below m/z 400 and the increased uncertainty for assigning large masses, we focused our analysis on $m/z < 400$. For number fraction comparisons, only peaks from m/z 150–400 were considered. Bulk O:C, H:C, and N:C ratios were calculated by averaging across the individual atomic ratios of each compound assigned a formula in a given sample.²⁵ This procedure was also used to calculate average double bond equivalencies (DBE). Possible organosulfate compounds were identified with formulas having 1 sulfur atom and at least 5 oxygen atoms to account for the sulfate functionality, as well as other oxygen-containing functional groups that were likely present. Organosulfates were not expected to form within the ESI source, based on previous results from laboratory studies.⁶

RESULTS AND DISCUSSION

The mass spectral features observed in the particle and cloudwater samples indicated a diverse mixture of organic compounds with a variety of functional groups. Example negative ion mass spectra from the June 10th particle and cloudwater samples are shown in Figure 1. Mass spectra, as well

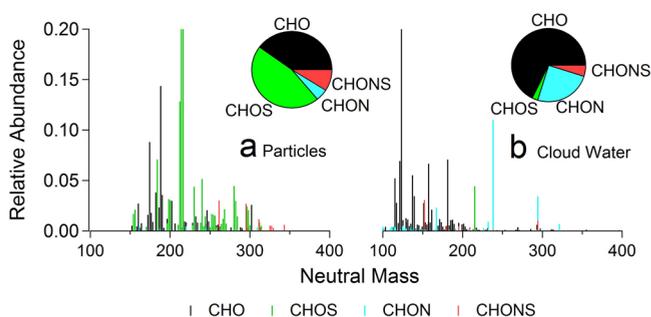


Figure 1. Negative ion mode neutral mass spectra for (a) particle and (b) cloudwater samples collected on June 10th. Assignment class is indicated by the color of the bars. Inset pie charts indicate the number fraction of each class assigned for the samples.

as a complete list of peaks and assignments, for all other samples can be found in the Supporting Information (Figures S1–S2, Tables S1–S2). CHO compounds were the most abundant by number and intensity, averaging $\sim 50\%$ of assigned peaks by number across all samples. CHOS compounds were the next most prevalent for the particle samples ($\sim 30\%$ by number on average), while CHON compounds were more numerous in the cloudwater ($\sim 20\%$ by number on average). CHONS compounds were observed in small amounts in both particle and cloud spectra, averaging $\sim 8\%$ by number across all samples. These trends are consistent with previous high resolution mass

spectrometry studies of atmospheric particles^{26,27} and cloudwater.²⁸

To gain insights into cloud processing of organic compounds, the organic molecular composition of atmospheric particles below convective cumulus clouds was compared to that of the cloudwater, with the implicit assumptions that particles acted as CCN to form the cloud droplets and that the composition of the particle samples represents the initial composition of the cloudwater before any aqueous chemical reactions occur. Following cloud droplet activation, trace gases can diffuse into cloud droplets;⁵ however, without measurement of these gases or dissolved low molecular weight species, this pathway could not be thoroughly evaluated in this work. Further reactions have been proposed to occur in evaporating cloud droplets, due to increasing solute concentrations and dehydration;^{29–31} however, since our chemical analysis was performed on whole water samples, these pathways were not investigated.

Previous studies suggested that cloud processing would likely increase the overall oxygen/carbon (O:C) ratio of organic compounds in cloudwater.⁵ However, all three pairs of cloudwater/particle samples examined in this study showed no statistically significant difference in the average O:C ratios (0.65 ± 0.35) of the organic compounds detected in the negative mode. The O:C ratios corresponding to each SOAS sample are shown in Figure 2. Previously, Nguyen et al.³² observed a similar effect in a laboratory study of aqueous isoprene SOA dissolved in water and exposed to simulated sunlight.

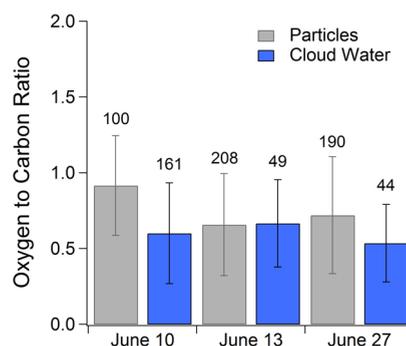


Figure 2. Average O:C ratios characteristic for organic compounds detected in negative ion mode mass spectra of particle and cloudwater samples. Error bars represent the standard error. The total number of assigned compounds in the spectra is displayed above the bars.

While the average O:C ratio of the organic material in the Nguyen et al.³² isoprene SOA study was not largely affected by the aqueous processing, photolysis of the aqueous SOA was observed to lead to oligomer fragmentation. In previous studies of isoprene oxidation and SOA formation, an inverse relationship between the number and chain length of oligomers of 2-methylglyceric acid (2-MGA) and glycolaldehyde (GLYC) and the relative humidity was observed, suggesting either fewer formation reactions within the more dilute aerosols or fragmentation due to excess water reversibly driving the likely aldol condensation reaction.^{33–36} Nonetheless, isoprene derived oligomers have been observed previously in cloudwater.⁶ Within our SOAS particle and cloudwater samples, oligomers of 2-MGA and GLYC were identified by comparison with previous laboratory studies.³³ A list of the oligomeric

compounds identified for all three flights is shown in Table S3. However, while the 2-MGA and GLYC oligomers were observed within the cloudwater, they were reduced in number when compared to the particle samples. As an example, within the range of 150–400 m/z , 16 potential 2-MGA and GLYC oligomers were found in the June 27th particle sample compared to 3 observed in the cloudwater. The June 10th sampling was the only case with a greater number of 2-MGA and GLYC oligomers identified in the cloudwater, compared to the corresponding particle sample. In addition, the June 10th and 27th particle samples contained several trimers, while the cloudwater only contained dimers and monomers, based on comparison of formulas with previous studies.³³ Evidence of possible oligomer decomposition in the cloudwater was also observed by the average number of carbons in the likely 2-MGA and GLYC oligomers across all aircraft samples decreasing from 8.1 ± 0.3 in particles to 7.4 ± 0.3 in cloudwater. This observation is in agreement with the laboratory-based study of aqueous processing of isoprene SOA by Nguyen et al.³² However, rather than indicating oligomer fragmentation, it is possible that the higher m/z values in the cloudwater could have been suppressed due to mass discrimination associated with the differences in the mass ranges scanned between the particle and cloudwater samples.

CHOS Compounds. For the SOAS flights, negative ion CHOS compounds decreased in number fraction, from an average of 29% in the particles to 6% in the cloudwater samples, as shown in Figure 3. This trend is consistent with the total

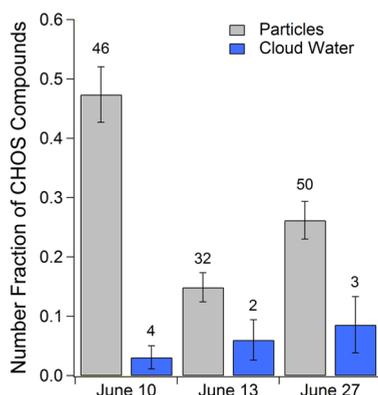


Figure 3. Number fractions of CHOS compounds, detected in the negative ion mode, present in the SOAS particle and cloudwater samples. Error bars represent the standard error of the fraction. The total number of assigned CHOS compounds in the negative spectra is displayed above the bars.

number of CHOS compounds observed as well. On average, a factor of ~ 15 more unique CHOS compounds (by number) were present in the particles compared to the cloudwater (Table S4). Modeling and experimental studies of the formation of organosulfates have shown that production is maximized in particles that are acidic and under low RH conditions.^{37,38} Thus, as expected, no new organosulfate masses were identified within the cloudwater mass spectra, compared to the corresponding particle samples. Overall, fewer than 8% of the CHOS particle-phase compounds were also observed in the cloudwater. Therefore, this trend of decreasing diversity of CHOS compounds in the cloudwater is consistent with decomposition of these compounds in the aqueous environment.

Hydrolysis of organosulfates in the cloudwater could account for the decreasing number and fraction of CHOS compounds, as discussed above. Previous laboratory kinetics studies have shown that tertiary organosulfate compounds hydrolyze in aqueous solution,¹⁵ which could be relevant during cloud events.³⁹ To investigate this process for the aircraft samples, possible hydrolysis products of particle-phase organosulfates ($\text{ROSO}_3\text{H} + \text{H}_2\text{O} \leftrightarrow \text{ROH} + \text{H}_2\text{SO}_4$) were identified by searching for compounds with a neutral mass difference of SO_3 between the particle phase organosulfates and the compounds measured in the cloudwater. Using the June 10th flight as a case study, 46 organosulfate compounds were identified in the particle sample with 30 possible corresponding hydrolysis products in the cloudwater. A neutral mass spectrum of these product mass pairs is shown in Figure 4. For the particle

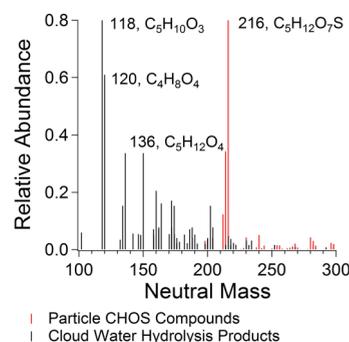


Figure 4. Neutral mass spectrum of particle-phase CHOS compounds and potential corresponding hydrolysis products, in the June 10 samples. Assignments of intense peaks are noted.

sample, 27 of the hydrolysis product masses were also identified. The presence of these CHO compounds is not unexpected since these compounds can react to form the organosulfates also found in the particle phase.¹⁴ Similarly, for the June 13th and 27th samples, 65–72% of the CHOS compounds in the particle-phase had corresponding hydrolysis product CHO formulas in the cloudwater. These organosulfates are characterized by O:C of 2.25, illustrating that they contained oxygenated functional groups beyond the sulfate group, which is expected based on previously proposed organosulfate formation pathways.⁴⁰ This full analysis, for all sampling days, is included in the Supporting Information (Table S5). This indicates that the hydrolysis reactions may dominate the chemistry of organosulfate compounds within cloudwater and can occur on cloud lifetime time scales. For the June 10th cloudwater sample, four likely organosulfates corresponded to biogenic volatile organic compound oxidation products with proposed structures from previous studies.⁴⁰ In previous laboratory studies, Darer et al.¹⁴ reported that kinetics of the hydrolysis of tertiary organosulfates under acidic conditions were relatively fast (lifetimes of minutes to hours), while at neutral pH the reaction was much slower (hours to days). Given an expected cloud pH of ~ 3 ,⁴¹ this indicates that the presence of tertiary sulfate functionality in the cloudwater samples should be rare due to hydrolysis.¹⁴ Based on this study, it is not surprising that all of the organosulfates identified in the cloudwater were proposed to have primary sulfate functionalities and were not expected to hydrolyze on the time scale of a cloud event.¹⁴ Similar trends were observed for the other two SOAS flights as well. In contrast to the low abundance of tertiary organosulfates in the cloudwater samples, 50–86% of

the identified particle-phase organosulfates, across the three SOAS flights, were characterized by tertiary functionality with hydrolysis lifetimes of ~ 20 –460 h under neutral conditions.¹⁴

Across all of the SOAS samples, the highest abundance organosulfate compounds observed were suggested to be isoprene oxidation products,⁴⁰ consistent with the high isoprene emissions in this forested region of Alabama.⁴² The peak at m/z 215 ($C_5H_{11}O_7S_1^-$) was ubiquitously abundant in all samples, as was also observed in a previous cloudwater study above the isoprene emission region of Missouri.⁶ The presence of this species across all particle and cloudwater samples suggests that it can be used as a tracer to confirm the influence of boundary layer particles on the organic composition of cloud droplets. This organosulfate is produced from isoprene epoxydiols (IEPOX) and contains a primary sulfate functional group,⁴⁰ making it stable to hydrolysis (lifetime >2500 h),³⁹ which also explains the presence of this particular organosulfate in many field aerosol samples.^{27,40,43–49} Overall, of the observed organosulfates that could be assigned possible structures, 30–50%, by number per flight, were attributed to isoprene oxidation.⁴⁰ Among the isoprene oxidation organosulfates, 2-methylglyoxal sulfate esters³⁴ were observed in all three particle samples. However, due to the tertiary functionality of the sulfate group, these compounds were not observed in the cloudwater, as expected due to their fast hydrolysis.¹⁴ In addition, many minor organosulfate compounds identified within the particles and cloudwater samples were suggested to have monoterpene precursors.

CHON Compounds. Another important difference between the particle and cloudwater samples across all three sampling days was that negative ion CHON compounds significantly increased in number fraction between the particle and cloudwater samples (Figure 5). For the SOAS samples, no

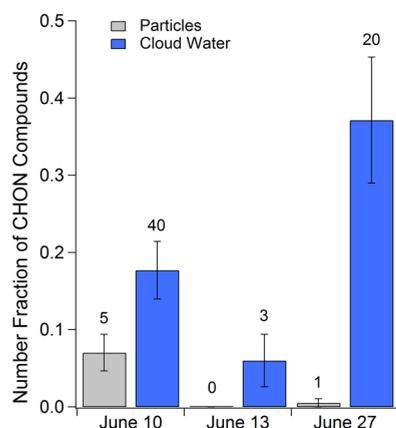


Figure 5. Number fractions of CHON compounds, detected in the negative ion mode, for the SOAS particle and cloudwater samples. Total CHON fraction error bars represent the standard error of the fraction. The total number of assigned CHON compounds in the negative spectra is displayed above the bars.

more than five CHON compounds were observed in each of the particle samples, with $\sim 4\times$ more CHON compounds detected in the cloudwater (Table S6). On average, the N:C ratio of all negative ion organic compounds increased from 0.03, for the particle-phase samples, to 0.14, for the cloudwater samples, with the cloudwater CHON class compounds having an average N:C ratio of 0.3. The overall addition of nitrogen to the organic compounds in the cloudwater could involve

reactions of organic compounds with inorganic nitrogen particulate species (e.g., ammonium, nitrate, nitrite), low molecular weight nitrogen-containing particle phase organic compounds, or water-soluble nitrogen-containing gases (e.g., HNO_3 , N_2O_5 , organic nitrates). Since the bimolecular reactions that could be generating these CHON compounds should be slower in the dilute droplet environment, it is likely that the reaction is preceded by dissolution of a soluble trace gas that serves as reactant. A few CHONS compounds were also detected in the SOAS samples, but their appearance did not show any conclusive trends between the particle and cloudwater samples.

Since most N-containing compounds preferentially form positive ions, previous studies have examined CHON compound formation in the aqueous phase using positive ion mode detection.^{29,30,37} Therefore, positive mode data for the CHON compounds were examined to assess whether the same trends observed in the negative mode were also found in the positive mode. The number of assigned compounds in the positive spectra was too small for a robust statistical analysis. However, despite this, some trends can be gleaned from the raw number of CHON compounds assigned in the positive ion mode. In two of the three SOAS flights, an increase in the number of assigned CHON compounds was observed for the cloudwater samples compared to the particle samples, suggesting CHON compound formation in cloud droplets. A list of assigned positive mode CHON compounds is shown in Table S2. With an average N:C ratio of 0.24, the positive mode CHON compounds detected in the cloudwater display a similar N:C ratio as the negative mode CHON compounds. However, the negative mode CHON compounds detected in the SOAS cloudwater samples were markedly different from the positive mode in other characteristics. Overall, the H:C ratio of the negative mode compounds was lower than the positive mode (Figure S3), indicating less saturated compounds in the negative mode. In addition, 46% of the negative mode CHON compounds were calculated to have an aromaticity index⁵⁰ (AE) above 0.67, indicating that many of these compounds likely have aromatic structures. In contrast, only 8% of the positive mode compounds had AE values above 0.67, indicating many of these compounds likely did not contain aromatic structures, in line with the observation of generally saturated formulas.

The formation of CHON compounds in aqueous organic mixtures has been studied previously using bulk solutions in the laboratory.^{29,30} De Haan et al.²⁹ and Lee et al.³⁰ both observed CHON compounds in aerosols following bulk solution atomization and suggested that evaporation increases the rates of reactions of organic compounds with amines and ammonium ions by increasingly concentrating the solution, with sulfate promoting the reactions. The observation of CHON formation within the SOAS cloud droplets suggests that droplet evaporation may not be a unique process generating N-containing compounds. In the aqueous isoprene SOA study of Nguyen et al.³² multinitrogen-containing compounds were observed to form following illumination of the aqueous solution, and a decrease in the number of single nitrogen-containing compounds in the aqueous solution was also observed. This observation was attributed to photolytic reaction involving organonitrates³² and could also be explained by the expected fast hydrolysis of tertiary organonitrates.¹⁴ However, for the SOAS cloudwater samples, 75% of the negative mode CHON compounds and most of the positive

mode CHON compounds correspond to formulas (Tables S1 and S2) with multiple nitrogen atoms and/or too few oxygen atoms to be assigned as organonitrates. Therefore, while there could be nitrate functionalities present in some of the compounds, it is more likely that the CHON species have other N-containing heteroatom moieties. The positive mode CHON compounds observed in the SOAS cloudwater were characterized by an average O:C ratio of 0.44 which is within the range of bulk O:C ratios (0.3–0.7) measured by De Haan et al.²⁹ Including both positive and negative mode data, these compounds are generally in line with the products observed in all three previous aqueous-phase CHON formation studies.^{29,30,32} However, none of the assigned formulas in the current study were found to exactly correspond to any of the compounds reported in the previous laboratory studies.^{29,30,32} Further laboratory studies are needed to elucidate the chemical mechanisms that result in the formation of these CHON compounds within cloud droplets. Previously, aromatic N-containing compounds have been found to act as chromophores in brown carbon aerosol, changing the optical properties of the particles and their climate impacts.^{29,32,37}

Overall, the majority of the compounds observed in the SOAS particle and cloudwater samples corresponded to oxidation products of isoprene and monoterpenes, as anticipated due to the significant biogenic volatile organic compound emissions from the local forested region. While the average properties (e.g., O:C ratios) of high molecular weight compounds in the measured particles and cloudwater did not differ significantly, aqueous-phase cloud processing was observed to lead to organosulfate hydrolysis and CHON compound formation. This indicates that cloud processing of organic aerosol could play a significant role in changing the chemical properties of the aerosol following cloud evaporation. The aqueous-phase formation of nitrogen-containing organic compounds, which may have light absorbing properties,^{30,32,34,37} could affect the radiative forcing budget in environments influenced by both biogenic and anthropogenic emissions, and future laboratory studies should focus on identification of the mechanisms responsible for this type of chemistry. Future modeling studies which add reaction pathways which hydrolyze tertiary organosulfates and generate nitrogen-containing organics through aqueous processing should improve estimations of cloud and aerosol chemistry.

■ ASSOCIATED CONTENT

● Supporting Information

Negative ion mass spectra and tables of assigned compounds, including identified oligomers and organosulfates. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01639.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Funding for SOAS sampling was provided by NSF (AGS-1228496) and EPA (R835409). High-resolution mass spectrometry analyses were performed at the Environmental Molecular Sciences Laboratory (EMSL), a national scientific

user facility located at the Pacific Northwest National Laboratory (PNNL) and sponsored by the Office of Biological and Environmental Research of the U.S. Department of Energy (DOE). PNNL is operated for DOE by Battelle Memorial Institute under Contract No. DE-AC06-76RL0 1830. Travel funds to PNNL were provided by the University of Michigan College of Literature, Science, and the Arts and Department of Chemistry.

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