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Measurements of Isoprene-Derived Organosulfates in Ambient Aerosols by Aerosol Time-of-Flight Mass Spectrometry—Part 2: Temporal Variability and Formation Mechanisms

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Ⓢ *Supporting Information*

ABSTRACT: Organosulfate species have recently gained attention for their potentially significant contribution to secondary organic aerosol (SOA); however, their temporal behavior in the ambient atmosphere has not been probed in detail. In this work, organosulfates derived from isoprene were observed in single particle mass spectra in Atlanta, GA during the 2002 Aerosol Nucleation and Characterization Experiment (ANARChE) and the 2008 August Mini-Intensive Gas and Aerosol Study (AMIGAS). Real-time measurements revealed that the highest organosulfate concentrations occurred at night under a stable boundary layer, suggesting gas-to-particle partitioning and subsequent aqueous-phase processing of the organic precursors played key roles in their formation. Further analysis of the diurnal profile suggests possible contributions from multiple production mechanisms, including acid-catalysis and radical-initiation. This work highlights the potential for additional SOA formation pathways in biogenically influenced urban regions to enhance the organic aerosol burden.
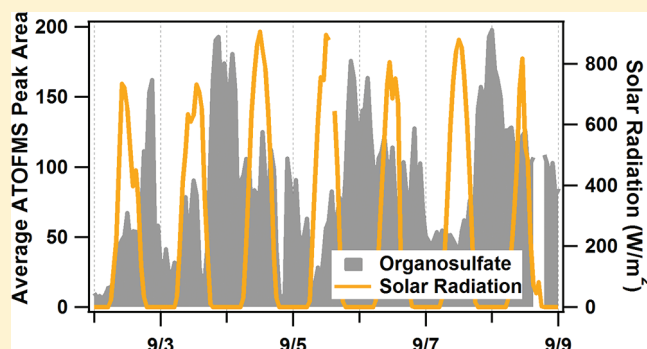
1. INTRODUCTION

Organic species can significantly influence the health and climate impacts of atmospheric particulate matter due to their potential toxicity and effect on hygroscopicity.[1] Organic aerosols can arise from both primary (directly emitted) and secondary (formed in the atmosphere) sources.[2] Despite extensive research in recent years,[2] models often under-predict the contribution of secondary organic species to aerosol mass[3] as a result of the remaining low scientific understanding of organic aerosol formation pathways.

Biogenic volatile organic compounds (BVOCs) can play a significant role in the formation of secondary organic aerosols (SOA) due to their high reactivity toward atmospheric oxidants. Indeed, radiocarbon dating has attributed a dominant fraction (~65%) of SOA to biogenic sources in heavily forested regions.[4] Isoprene (2-methyl-1,3-butadiene, C_5H_8) is the most abundant BVOC and has been implicated in SOA formation (ref 5 and references therein). Further, in urban environments,

BVOCs can interact with anthropogenic pollutants resulting in an enhancement of the organic aerosol mass.[6,7] Anthropogenic emissions can influence biogenic SOA in a number of ways,[8] including by introducing new chemical pathways to produce unique, low-volatility chemical species. Herein, we focus on a specific class of compounds, organosulfates, which have been demonstrated to form via reaction between BVOCs and particulate sulfate derived predominantly from industrial SO_2 emissions.[9]

Several mechanisms have been proposed from laboratory investigations to explain the formation of organosulfate compounds, including acid-catalyzed alcohol sulfate-esterification,[10] reaction with sulfate radicals ($SO_4^-\cdot$, $HSO_4\cdot$),[11−13] or acid-catalyzed
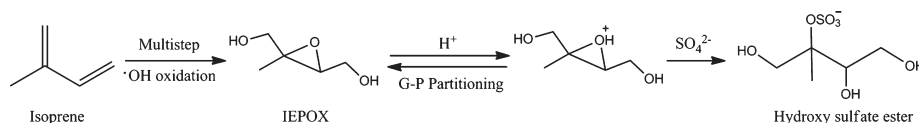
Scheme 1. Organosulfate Formation via IEPOX Intermediate (adapted from ref 14)

epoxide hydrolysis.[14,15] The esterification mechanism has been shown to be kinetically limited and not likely to occur in the ambient atmosphere.[16] Radical-initiated formation has been proposed following the observation of organosulfate production in smog chamber reactions under irradiated conditions, which ceased in the dark.[11,17] Several studies have implicated the role of epoxide intermediates in leading to SOA compounds,[18−20] and in particular to organosulfate species.[14,21] The atmospheric fate of the isoprene-derived epoxide (IEPOX) largely depends on aerosol pH and liquid water content,[22] but has been shown to produce 2-methyltetrols and, in the presence of acidic sulfate aerosol, organosulfate species, as shown in Scheme 1.

In Part 1 of this study, we described observations of the size-resolved mixing state of organosulfates during the 2002 Aerosol Nucleation and Characterization Experiment (ANARChE) and the 2008 August Mini-Intensive Gas and Aerosol Study (AMIGAS) in Atlanta, GA.[23] The online mass spectrometry analysis employed in these studies provided the high time resolution necessary to monitor rapid changes in aerosol composition. Herein, we describe the temporal trends of organosulfate species and the resulting insights into the possible formation mechanisms occurring in the ambient atmosphere. To our knowledge, this is the first study to investigate in real-time the temporal variability of ambient particle-phase organosulfate species.

2. EXPERIMENTAL SECTION

2.1. Field Measurements. Aerosol sampling was performed during two field studies at the Jefferson Street Southeastern Aerosol Research and Characterization (SEARCH) Network site (33.8° N, 84.4° W), a mixed residential−industrial location about 4 km northwest of metro Atlanta.[24] Data are presented in Eastern Standard Time.

Real-time ATOFMS measurements were made of single particles during ANARChE from August 4−11, 2002 and during AMIGAS from August 22-September 10, 2008. Additional details of ATOFMS data collection and analysis are provided elsewhere.[23,25] Briefly, ATOFMS detected the size and chemical composition of individual particles from 50−350 nm during ANARChE and 200−3000 nm during AMIGAS. ATOFMS collects both positive and negative spectra for each particle; for the data sets considered here, some negative spectra displayed incorrect mass calibration in the mass range of interest (>100 m/z) due to instability in the mass spectrometer voltages. The manual correction method applied to the data is described in the Supporting Information. Further, as described by Hatch et al.,[23] organosulfates were predominantly detected in submicrometer particles; therefore, only the submicrometer particles (0.2−1 μm) with dual-polarity spectra collected during AMIGAS are included in the detailed analysis herein. All particles with dual-polarity spectra were included from ANARChE since these measurements were restricted to particles <350 nm.

Co-located instrumentation monitored meteorology (wind speed/direction, precipitation, temperature, relative humidity, solar radiation), and gas-phase pollutant levels (NO_x, CO, O_3, SO_2, HNO_3).[24] Continuous $PM_{2.5}$ samplers also monitored total carbon levels.[26] During AMIGAS, gas-phase water-soluble organic carbon (WSOC) measurements were obtained by a mist-chamber.[27]

3. RESULTS AND DISCUSSION

As discussed by Hatch et al.,[23] ATOFMS detected isoprene-derived organosulfates at m/z −139, −153, −155, −199, and −215 during both ANARChE and AMIGAS. Identification of these species was verified through ATOFMS analysis of chemical standards and comparison of ambient ATOFMS data to accurate mass analysis obtained from co-located filter samples analyzed off-line by high resolution mass spectrometry.[23] For brevity, this manuscript focuses on the marker at m/z −215 since it was the most abundant isoprene-derived organosulfate compound observed in the ATOFMS data by a significant margin (~4×) and the other markers displayed similar temporal profiles, as shown in the Supporting Information for the AMIGAS campaign. While the formation mechanism of m/z −215 will be explored below, for simplicity, it will be referred to as the IEPOX-derived organosulfate since both IEPOX and the corresponding organosulfate were detected in Atlanta during AMIGAS.[28]

3.1. Temporal Trends of Organosulfate Species. Because both ANARChE and AMIGAS were conducted during summer, comparison of the data sets serves to provide verification of observations and improved understanding of the general behavior of organosulfate species. However, it should be noted at the outset that this work focuses on the qualitative trends of organosulfates during these Atlanta field campaigns. The ATOFMS mass spectral data have not been scaled to correct for potential instrumental differences (e.g., MS tuning) that could influence the absolute peak intensity measured during each campaign. Therefore, only the relative trends in organosulfate mass spectral peak area observed in the two data sets will be compared herein (e.g., similarities in diurnal cycle); differences in the peak magnitude should not be used to infer differences in organosulfate concentrations between the two studies.

Using the high time resolution of real-time, single-particle data, the peak area of the IEPOX-derived organosulfate at m/z −215 was shown to fluctuate significantly throughout the ANARChE and AMIGAS campaigns (Figure 1). Much of this variation can be attributed to changes in meteorology. Both study periods exhibited several days characteristic of a diurnal cycle, as evidenced by regular patterns in meteorological (e.g., temperature, relative humidity) and gas-phase pollutant data (e.g., ozone) (ANARChE: 8/4−8/5/02, 8/8−8/11/02; AMIGAS: 8/29−8/31/08, 9/3/08, 9/6−9/10/08). Additionally, during AMIGAS, two tropical cyclones (TCs; Gustav, 8/24−9/4/08[29] and Hannah, 8/26−9/7/08[30]) influenced the southeastern United States. The time periods that TCs directly impacted
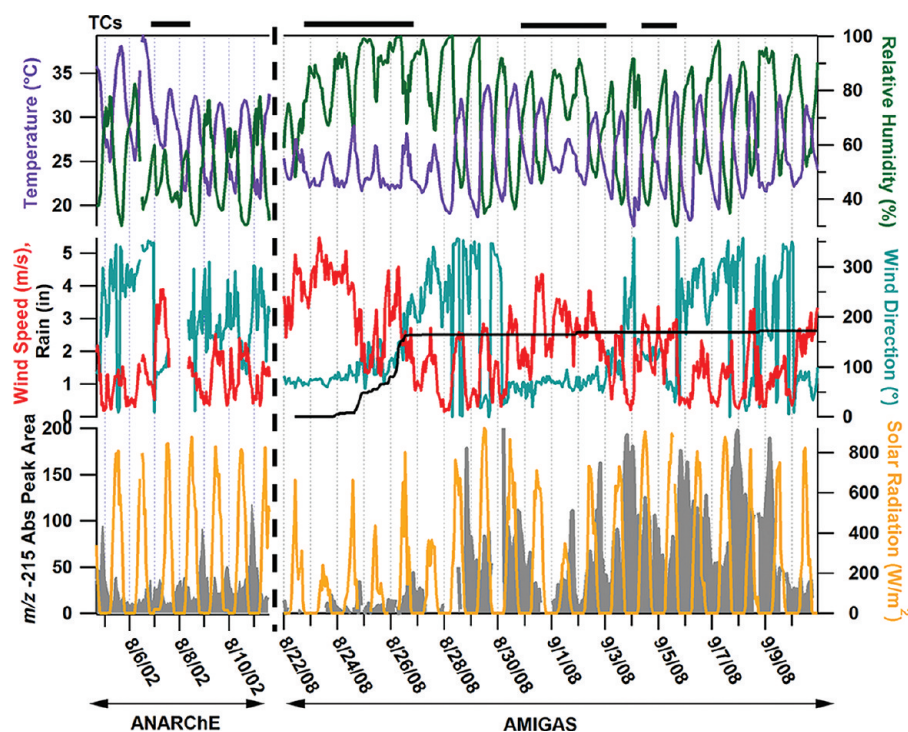
Figure 1. Hourly averaged temporal variation in the absolute area of m/z -215, solar radiation, wind speed and direction, precipitation, temperature, and relative humidity. Black bars indicate time periods influenced by tropical cyclones (TCs). Data from both ANARChE and AMIGAS are included, separated by the dashed line.

the Atlanta region are inferred from the prevailing southeasterly winds and fast wind speeds (i.e., 8/23−8/27/08, 8/31−9/2/08, 9/4−9/5/08; Figure 1), and included a rain episode from 8/24−8/26/08. Tropical storm Bertha was also present in the Gulf of Mexico during ANARChE (8/4−8/9/02)[31] and may have slightly influenced the Atlanta region, as indicated by a shift in meteorology on 8/6−8/8/02 (Figure 1). The high temporal resolution of ATOFMS measurements provided unique observations of the behavior of organosulfate species during both the calm days and the meteorological events, as described below.

3.1.1. Diurnal Trends. The non-TC days during ANARChE (8/4−8/5/02, 8/8−8/11/02) and AMIGAS (8/29−8/31/08, 9/3/08, 9/6−9/10/08) provided insight into the typical diurnal cycle of organosulfate species in Atlanta. Consistently during both campaigns, the highest abundance of organosulfate species occurred at night during periods with low wind speeds (Figure 1). The stagnant wind conditions and buildup of NO_x and CO (Figure 2) indicate that a stable boundary layer was present overnight. Radiosonde data were obtained from the NOAA Integrated Global Radiosonde Archive[32] to investigate the boundary layer stability; vertical temperature profiles are included in Figure 3. These soundings were taken at 12Z (7am EST), but are expected to be representative of the nocturnal temperature profile since breakup of inversions in Atlanta has been observed to occur after 9 am.[33] The radiosonde data confirmed the presence of nocturnal temperature inversions during these periods (Figure 3) yielding a very shallow mixed layer and increased pollutant levels (e.g., NO_x and CO; Figure 2). The nights characterized by the strongest inversions, as indicated by the temperature difference between the top and bottom of the inversion layer, are associated with the highest levels of organosulfates (e.g., 9/6/08, 9/8/08, Figures 1 and 3). Also of note, an

inversion was not present on 9/10/08 (Figure 3), which could explain the lower abundance of organosulfates observed on this night during AMIGAS (Figure 1). These soundings and the diurnal trends observed by ATOFMS provide strong evidence for the role of a stable boundary layer in the formation of organosulfates in Atlanta.

The night-time meteorology also displayed a characteristic decrease in temperature and increase in relative humidity (RH), providing favorable conditions for condensation of water and semivolatile species. While IEPOX is not expected to partition appreciably to the organic phase,[28] Eddingsaas et al.[22] predicted an increase in IEPOX uptake with increasing aerosol water content, as would be expected under the high nocturnal RH conditions. It should also be noted that the presence of water can influence the ionization of species from a particle in the ATOFMS, and in particular has been shown to suppress negative ion formation.[34] Since organosulfate species were detected as negative ions and in higher abundance at night (higher RH and therefore higher aerosol water content), it is believed that the observed diurnal trend is not a measurement artifact, but rather, perhaps represents a lower bound on the nighttime organosulfate abundance relative to other species in the particles.

The peak area of m/z -215 strongly tracks NO_x ($NO_2 + NO$) concentration during both ANARChE and AMIGAS (Figure 2). Interestingly, IEPOX has been shown to form under low-NO_x conditions,[14] making the correlation between the IEPOX-derived organosulfate and NO_x somewhat unexpected. Several possible explanations exist for this relationship: (1) Particulate organosulfate species and NO_x may have increased overnight independently of each other, driven predominantly by the lowering of the boundary layer. In this scenario, the organosulfate precursors may have formed during the day under low-NO_x
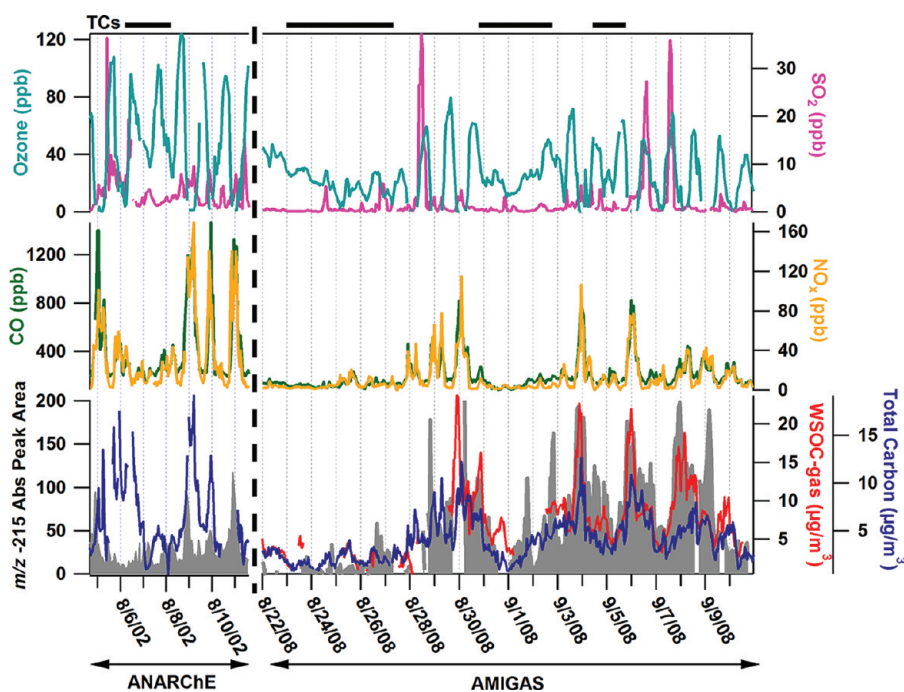
Figure 2. Hourly averaged temporal variation in the m/z -215 absolute peak area, gas-phase water-soluble organic carbon (WSOC), total PM$_{2.5}$ carbon mass concentration (Total Carbon), NO$_x$, CO, O$_3$, and SO$_2$. Black bars indicate time periods influenced by tropical cyclones (TCs). Data from both ANARChE and AMIGAS are included in the figure, separated by the dashed line.

conditions, followed by condensation of the semivolatile oxidized VOCs and organosulfate formation overnight. The overnight increase in NO$_x$ would then be largely uninvolved in the organosulfate mechanism. (2) It is also possible that nocturnal nitrogen oxide chemistry played a role in the formation of organosulfates by raising aerosol acidity, an important parameter in the formation of organosulfates.[35] Overnight, NO$_2$ reacts with ozone to produce NO$_3\cdot$, which can subsequently react with NO$_2$ to form N$_2$O$_5$; heterogeneous hydrolysis of N$_2$O$_5$ yields HNO$_{3(aq)}$ (ref 36 and references therein). Figure 4 shows the temporal trends of NO$_2$, HNO$_{3(g)}$, particulate nitrate, and m/z -215. The rise in NO$_2$ concentration overnight closely tracks the ATOFMS nitrate signal (m/z -62), indicating the possible conversion of NO$_x$ into HNO$_3$ by the reaction outlined above. Further, Brown et al. have demonstrated an increase in N$_2$O$_5$ uptake to aerosols with high sulfate content,[37] as is typical of Atlanta aerosol. While measurements of NO$_3\cdot$ and N$_2$O$_5$ were not available for these studies, previous work has shown that N$_2$O$_5$ is the dominant species under high NO$_2$ conditions,[36] as observed overnight in Atlanta (Figure 4). In addition, we note that gas-phase nitric acid decreases as night falls (Figure 4), consistent with the partitioning of HNO$_3$ to the aerosol phase. Since the condensation of nitric acid and increase in particulate nitrate coincide with the rise in organosulfate abundance, it is possible that the reactive nitrogen species played a role in the formation of organosulfate by raising the aerosol acidity and thus enhancing the reactive uptake of organosulfate precursors. Although, on the basis of these measurements, we cannot definitively establish a causal link between reactive nitrogen chemistry and organosulfate formation versus a dominant role of the nocturnal boundary layer, we note that both scenarios (1) and (2) involve partitioning/reactive uptake of the organosulfate precursors overnight. (3) A third possible explanation for the correlation between organosulfates

and NO$_x$ involves the indirect formation of organosulfates via an organonitrate intermediate. Organonitrates can arise from reaction of isoprene with OH under high-NO$_x$ conditions during the day[19] or at night with nitrate radical;[38] particulate nitrate can also act as a nucleophile toward epoxides similar to sulfate in Scheme 1.[39] Tertiary organonitrates have been found to undergo rapid substitution by water or sulfate, leading to the formation of polyols and organosulfates.[39] Indeed, nitrooxy-organosulfate species derived from isoprene have been previously observed in Atlanta by Surratt et al.,[40] wherein one or two nitrate groups are in the place of hydroxyl groups in the product compound of Scheme 1. The hydrolysis of such compounds would produce the same m/z -215 ion described herein. In summary, the apparent correlation between organosulfates and reactive nitrogen species could be driven by a combination of effects (1)−(3), or by some other mechanism, warranting further exploration.

By peaking mostly at night, organosulfate species are largely anticorrelated with O$_3$, which forms by photochemical processes during the day. However, the highest night-time concentrations of organosulfates generally follow days with high O$_3$ levels (e.g., 8/8−8/9/02 and 9/3−9/4/08; Figure 2). This relationship indicates that there was likely a high degree of photochemical isoprene oxidation contributing to the enhanced O$_3$ levels[41] and leading to the daytime formation of the organosulfate precursors, which then became concentrated under the low nocturnal boundary layer. These observations are supported by the water-soluble organic carbon (WSOC) measurements from AMIGAS (Figure 2). Gas-phase WSOC levels increased overnight, consistent with a low mixing height concentrating these species (likely including the organosulfate precursors) in the atmosphere, which likely enhanced the gas-to-particle partitioning.

Somewhat surprisingly, a clear trend between organosulfates and SO$_2$ was not observed: the large SO$_2$ spikes did not appear
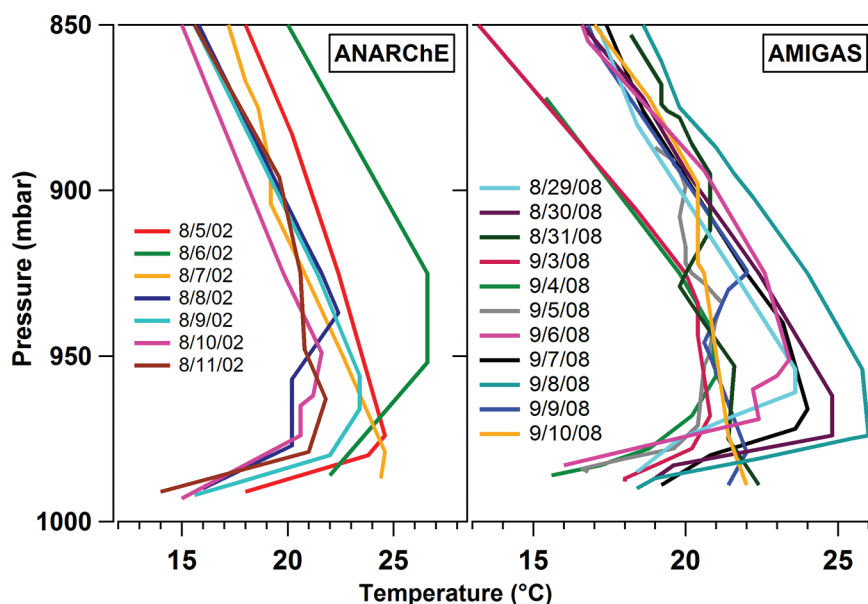
Figure 3. Vertical temperature profiles during ANARChE (left) and AMIGAS (right) obtained from the NOAA Integrated Global Radiosonde Archive.[32] Only non-TC days are shown for AMIGAS to avoid graph clutter.
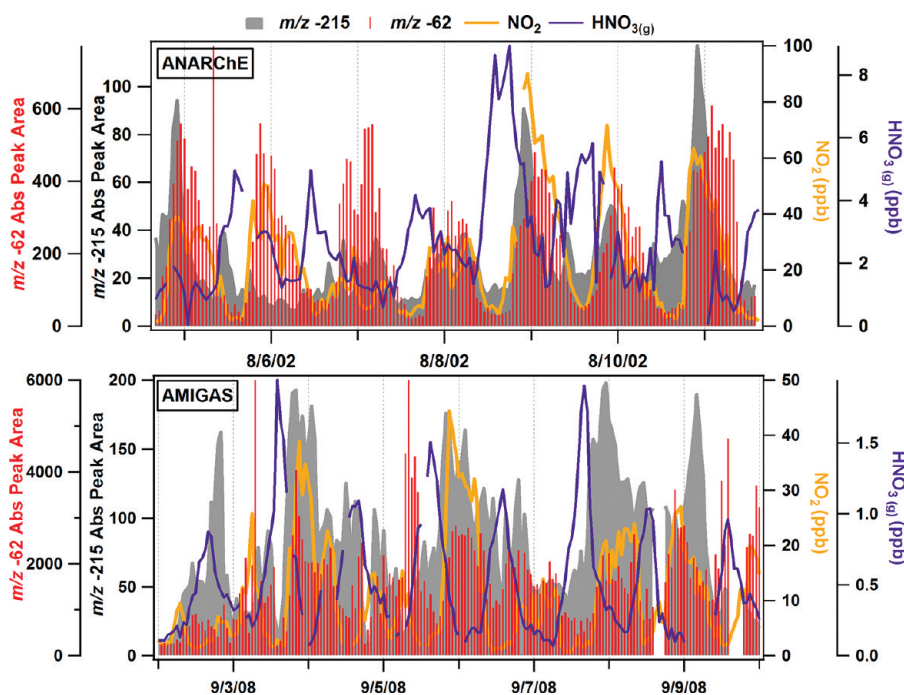
Figure 4. Hourly averaged temporal trends in the absolute peak areas of m/z −215 and m/z −62 (NO_3^-), $HNO_{3(g)}$, and NO_2 during ANARChE (top) and AMIGAS (bottom). For graph clarity, only the period with highest organosulfate abundance (9/2−9/10/08) is shown for AMIGAS.

to significantly enhance the levels of organosulfates. However, a small afternoon increase in organosulfate abundance is noted on the afternoon of 8/5/02 during an SO_2 plume. Similarly, during AMIGAS, an SO_2 spike on the afternoon of 9/6/08 led to one of the only days with higher organosulfate levels during the day than the following night.[23] It is possible that the semivolatile nature of IEPOX prevented extensive partitioning during the day, even if there was an increase in aerosol acidity induced by SO_2 emissions.

The correlations of organosulfates with meteorological and gas-phase pollutant data described above suggest that gas-to-particle partitioning may be the key step in determining the concentration of particle-phase organosulfate species. As the boundary layer height and temperature decrease and RH increases at night, there is likely enhanced partitioning of the isoprene oxidation products (i.e., IEPOX in the case of the m/z −215 marker) followed by particle-phase reactions resulting in organosulfate formation. The relatively long gas-phase IEPOX
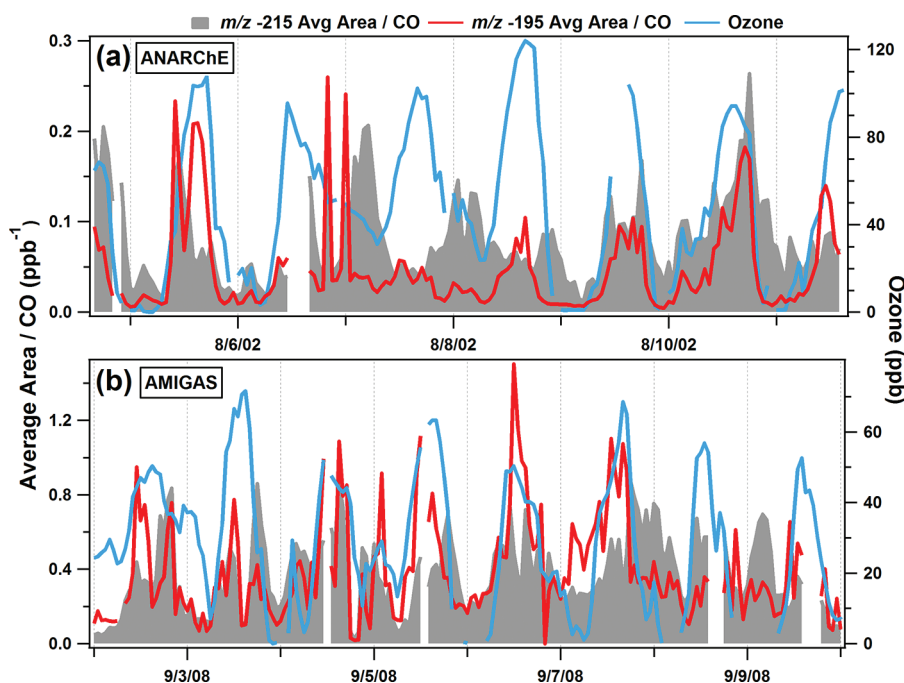
Figure 5. Hourly averaged temporal trends of m/z −215 and −195 absolute peak areas normalized by CO concentration during ANARChE (top) and AMIGAS (bottom). For graph clarity, only the period with highest organosulfate abundance (9/2−9/10/08) is shown for AMIGAS. The ozone traces are overlaid to highlight the correlation with photochemical activity.

lifetime of 18−22 h[42] is consistent with this proposed delay between afternoon photochemical production of IEPOX and the nighttime formation of organosulfates. We note that IEPOX and other organosulfate precursors could have formed locally or advected from other locations during the day; indeed it is likely that the organosulfate precursors form regionally, given the similarities between the IEPOX concentration in Atlanta versus a rural Georgia site.[28]

3.1.2. Tropical Cyclone Influence. The lowest abundance of m/z −215 occurred during the rainy, TC-influenced period of AMIGAS (8/24−8/27/08) when the aerosols and pollutants were scavenged by precipitation or advected from the area, as evidenced by the low levels of gas-phase pollutants and total particulate carbon (Figure 2). This period and the additional TC periods (9/1−9/2/08, 9/4−9/5/08) were characterized by high wind speeds and predominantly southeasterly winds. During these storms, solar radiation and O_3 concentration decreased (Figures 1 and 2), consistent with a decrease in photochemical activity, resulting in reduced formation of isoprene oxidation products, and therefore lower organosulfate abundance.

During ANARChE, the levels of organosulfates were lowest from 8/6−8/8/02. A shift in meteorology is clear from the wind speed and relative humidity data (Figure 1); a decrease in barometric pressure was also observed on 8/6/02 (not shown). As mentioned above, TC Bertha present in the Gulf of Mexico may have induced the shift in meteorological patterns, though its potential influence on Atlanta has not been verified. Additionally, a deeper temperature inversion was present on 8/6/02 and a negligible one existed on 8/7/02 (Figure 3); this change in boundary layer height could have also contributed to the lower organosulfate abundance on these nights.

3.2. Possible Formation Mechanisms of Organosulfates. Since boundary layer stability appears to play a strong role in

the absolute levels of particulate organosulfate species in Atlanta, the possible chemical mechanisms were further investigated by normalizing the organosulfate peak area by CO concentration. CO has been used as an inert chemical tracer to separate the effects of vertical mixing and chemical reactions on pollutant concentrations.[43] The CO-normalized temporal profiles are shown in Figure 5. During the ANARChE campaign, the normalized IEPOX-derived organosulfate levels exhibited a maximum in the afternoon on the days not influenced by a TC (8/4−8/5/02, 8/9−8/11/02), coinciding with high ozone concentrations indicative of high photochemical activity. The concurrent increase in the ATOFMS sulfuric acid marker (m/z −195, $HSO_4 \cdot H_2SO_4^-$)[44] is consistent with photochemical production from SO_2 and possibly indicates the importance of particle acidity in the formation of organosulfates. However, previous studies have also proposed a radical-initiated organosulfate formation mechanism via reaction between isoprene and sulfate/bisulfate radical giving rise to the m/z −215 organosulfate.[11,17] As these radical reactions occur under irradiated conditions, potential contribution of this mechanism to the daytime organosulfate concentration cannot be ruled out. It is noteworthy that organosulfate compounds have been observed with the same molecular formulas via both the radical-initiated and acid-catalyzed mechanisms[10,11] and thus these ATOFMS measurements cannot differentiate the afternoon contributions from these two potential pathways. It is therefore possible that the afternoon increase in organosulfate levels is due to either the radical formation mechanism or acid-catalyzed reactive uptake (or both).

As described above, the highest absolute levels of organosulfates were detected overnight, primarily driven by the low boundary layer height. While the precursors may have formed elsewhere, it is likely that the organosulfates formed locally, as

opposed to advection of organosulfate-containing particles to Atlanta, given the very low wind speed (<0.5 m/s) during these periods. The radical-initiated mechanism cannot explain the production of organosulfates overnight due to the lack of solar radiation required to form the sulfate radicals. Therefore, nocturnal organosulfate formation can likely be attributed to acid-catalyzed reactive uptake of the precursors. During AMIGAS both the particle size and temporal trends (Figures S2 and S3 of the Supporting Information) demonstrate a relationship of increasing IEPOX-derived organosulfate with increasing m/z −195, an indicator of acidity. While the trends from ANARChE and AMIGAS are not in full agreement on the correlation between organosulfates and sulfuric acid (discussed in the Supporting Information), it is important to note that nitric acid possibly contributed to the nocturnal aerosol acidity, as described above, with consistent trends during both studies (Figure 4). Further, particulate IEPOX was detected during AMIGAS, including night-time samples,[28] and its role in forming organosulfate species has been confirmed by smog chamber studies,[14] thus providing additional support for the hypothesized reactive-uptake of IEPOX in leading to the overnight formation of organosulfates.

In summary, the results from ANARChE and AMIGAS indicate that several formation mechanisms can contribute to the production of particulate organosulfate species in Atlanta. While further studies are necessary to better elucidate the conditions that favor a given formation pathway in the ambient atmosphere, the ATOFMS observations suggest that organosulfates form by the following atmospheric processes: During the daytime, isoprene is photochemically oxidized to IEPOX, with moderate organosulfate production from either a radical-initiated mechanism or acid-catalyzed reactive uptake. Since IEPOX is semivolatile and reactive uptake increases with aerosol water content,[22] it likely partitions to the aerosol phase to a greater extent as the RH increases and the temperature and boundary layer height decrease at night. Upon condensation, the acid-catalyzed mechanism likely dominates with subsequent particle-phase formation of organosulfate species. These results highlight the important roles of aqueous-phase processing and boundary layer stability in SOA formation.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Additional information regarding the data correction method, temporal profiles of other organosulfate markers (Figure S1), and discussion of the correlation between aerosol acidity and organosulfate formation (Figures S2−S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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