

Measurements of Isoprene-Derived Organosulfates in Ambient Aerosols by Aerosol Time-of-Flight Mass Spectrometry - Part 1: Single Particle Atmospheric Observations in Atlanta

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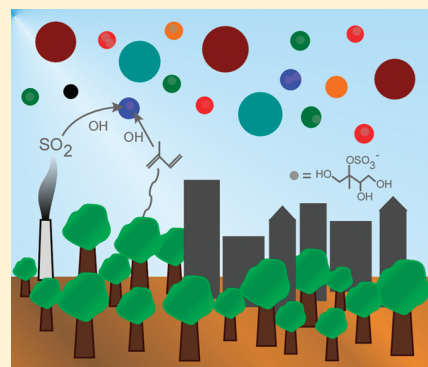
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S Supporting Information

ABSTRACT: Organosulfate species have recently been identified as a potentially significant class of secondary organic aerosol (SOA) species, yet little is known about their behavior in the atmosphere. In this work, organosulfates were observed in individual ambient aerosols using single particle mass spectrometry in Atlanta, GA during the 2002 Aerosol Nucleation and Characterization Experiment (ANARChE) and the 2008 August Mini-Intensive Gas and Aerosol Study (AMIGAS). Organosulfates derived from biogenically produced isoprene were detected as deprotonated molecular ions in negative-ion spectra measured by aerosol time-of-flight mass spectrometry; comparison to high-resolution mass spectrometry data obtained from filter samples corroborated the peak assignments. The size-resolved chemical composition measurements revealed that organosulfate species were mostly detected in submicrometer aerosols and across a range of aerosols from different sources, consistent with secondary reaction products. Detection of organosulfates in a large fraction of negative-ion ambient spectra — ca. 90–95% during ANARChE and ~65% of submicrometer particles in AMIGAS — highlights the ubiquity of organosulfate species in the ambient aerosols of biogenically influenced urban environments.



1. INTRODUCTION

Secondary organic aerosol (SOA) can contribute substantially to atmospheric aerosol mass and arises from both biogenic and anthropogenic emissions of volatile organic compounds (VOCs). In heavily forested regions, the biogenic contribution to SOA can be substantial due to high emissions of VOCs from vegetation.¹ Isoprene (2-methyl-1,3-butadiene, C₅H₈) is an abundant biogenic VOC and has recently emerged as a potentially significant source of SOA.^{2,3} The two double bonds of isoprene are highly reactive toward atmospheric oxidants and are therefore susceptible to oxidation, ultimately forming semivolatile compounds such as 2-methyltetrols and 2-methylglyceric acid (ref 2 and refs therein). Subsequent gas-to-particle partitioning can result in further particle-phase reactions yielding high-mass oligomers and organosulfate compounds (ROSO₃H).² In this manuscript, we investigate the isoprene-derived organosulfate species, a class of low-volatility oxidation products that could potentially contribute significantly to organic aerosol mass, and further, due to their high polarity and water solubility, could enhance the cloud condensation nuclei (CCN) activity of organic aerosols.⁴

Particulate organosulfate species have been previously measured in filter samples of ambient aerosols using a variety of off-line analytical methods. Surratt et al.⁵ detected both isoprene- and monoterpene-derived organosulfates in the southeastern United States utilizing high-performance liquid chromatography coupled to electrospray ionization mass spectrometry (ESI-MS); a similar method was used to characterize organosulfates in aerosols collected from K-puszt, Hungary,⁶ and Bavaria, Germany.⁷ Altieri et al.⁸ measured similar organosulfate species in New Jersey rainwater samples using Fourier-transform ion-cyclotron resonance mass spectrometry (FT-ICRMS). Additionally, organosulfates were detected by ESI-FT-ICRMS in atmospheric fog samples.⁹ Organosulfate functional groups have also been detected in a marine environment with continental influence by Fourier-transform infrared spectroscopy,¹⁰ and in a remote marine environment impacted only by oceanic biological sources (e.g. algal blooms) using ESI-MS.¹¹ These studies have provided

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valuable insight into the important contribution of organosulfate species to ambient aerosols in diverse environments. However, nearly all previous studies relied on off-line sample collection and analysis, which provides limited information on the average bulk aerosol composition.

Online mass spectrometric-based measurements are capable of providing real-time information on the evolving aerosol population. Currently, there are two widely used methods of online aerosol mass spectrometry: single-particle mass spectrometry (SPMS- e.g. aerosol time-of-flight mass spectrometry; ATOFMS¹²), which uses laser desorption/ionization (LDI) for aerosol analysis, and the aerosol mass spectrometer (AMS)¹³ that uses thermal desorption with subsequent electron-impact ionization. Recently, Farmer et al.¹⁴ demonstrated a high degree of fragmentation during the measurement of organosulfate compounds by the AMS; organosulfates were shown to decompose almost completely into inorganic sulfate and organic fragments. Because ambient aerosols are often internal mixtures of organic carbon and inorganic sulfate,¹⁵ extensive fragmentation makes it nearly impossible for the AMS to detect organosulfate species within the complex ambient aerosol matrix.

Recently, an SPMS technique was utilized for aircraft observations of isoprene-derived organosulfates. Measurements by the particle ablation by laser mass spectrometry (PALMS) instrument displayed high levels of organosulfate species in the tropical free troposphere and southeastern United States.¹⁶ Although this study provided unique quantitative characterization of organosulfates from SPMS, several features of ATOFMS provide additional information. PALMS uses a higher energy laser for particle ablation than ATOFMS ($\lambda = 193$ vs 266 nm), which can induce greater fragmentation of organic species and thereby limits the detection of organosulfates unless the instrument is operated in a lower laser power mode, as described in ref 16. Further, whereas the TOF mass analyzer of PALMS is restricted to single-polarity measurements, ATOFMS measures both positive and negative spectra for single particles, which yield more detailed information on the mixing state (i.e. sources and aging) of ambient aerosols.

In this study, single-particle ATOFMS measurements were made during the 2002 Aerosol Nucleation and Characterization Experiment (ANARChE) and the 2008 August Mini-Intensive Gas and Aerosol Study (AMIGAS) in Atlanta, GA. The southeastern United States is characterized by high concentrations of both isoprene¹⁷ and anthropogenic SO₂ from coal-burning power plants and industrial emissions.¹⁸ The atmospheric oxidation of both isoprene and SO₂ via reaction with hydroxyl radical forms the organic and sulfate precursors necessary for organosulfate formation, and therefore the Atlanta region provides an ideal location to characterize these compounds in ambient aerosols. Initial observations of organosulfates in individual ambient aerosols obtained through online measurements are discussed herein. Detailed discussions of the temporal variability and possible formation mechanisms of organosulfate compounds are included in a companion paper (Hatch et al. "Measurements of isoprene-derived organosulfates in ambient aerosols by aerosol time-of-flight mass spectrometry- Part 2: Temporal variability and formation mechanisms", ES&T, 2011. Hereafter referred to as Hatch, 2011).

2. EXPERIMENTAL SECTION

Field Measurements. Aerosol sampling was performed during two field studies at the Jefferson Street (JST) 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.¹⁹ Real-time ATOFMS measurements were made of single particles during ANARChE from August 4–11, 2002 and AMIGAS from August 22 to September 11, 2008. Because these studies were conducted during the same time of year, they provide a good opportunity to compare and verify the observed trends. Time is given in local time.

ATOFMS has been described in detail previously;¹² a brief summary is provided here. Aerosols enter the instrument via an inlet and are accelerated to a size-dependent terminal velocity. Two different ATOFMS instruments were utilized during these studies, differing mainly in the aerosol inlet and detectable particle size range. During ANARChE, an aerodynamic lens inlet was used²⁰ with a size-cut upstream provided by stages of a micro-orifice uniform deposit impactor (MOUDI);²¹ aerosols with aerodynamic diameters of 50–350 nm were analyzed. During AMIGAS, a converging nozzle inlet was used to detect aerosols in the 200–3000 nm range. Following the inlet, the ATOFMS instruments are nominally the same. In the particle sizing region, aerosols traverse two 532 nm continuous wave lasers yielding the particle velocity. A size calibration was performed using polystyrene latex spheres of known diameter to convert velocity to vacuum aerodynamic diameter. Aerosols were then desorbed and ionized at 266 nm using a Q-switched Nd:YAG laser. During ANARChE, the laser was operated at 2.0 mJ and during AMIGAS, the laser power was 1.1 mJ from August 22–29 and 1.4–1.5 mJ thereafter.

Data analysis was performed by importing single-particle mass spectra into Matlab (The MathWorks, Inc.) using the YAADA toolkit.²² Particles were clustered based on similarities in mass spectral peak identities and intensities using the ART-2a adaptive resonance theory method²³ with a vigilance factor of 0.8 (ANARChE) and 0.75 (AMIGAS), learning rate of 0.05, and 20 iterations. During AMIGAS, only a fraction of particles (32% of submicrometer, 80% of supermicrometer) yielded negative spectra, whereas 99% of particles during ANARChE contained dual-polarity spectra. This disparity is largely attributed to the evaporation of water in the aerodynamic lens inlet used during ANARChE;²⁴ the presence of water has been shown to suppress negative ion formation.²⁵ Data analysis was restricted to the subset of particles containing dual-polarity spectra since the organosulfate content could not be assessed for particles with only positive spectra; no corrections have been applied to account for the low fraction of negative spectra obtained during AMIGAS.

During AMIGAS, undenuded high-volume filter samples were also collected in segregated day (10 a.m. to 6 p.m.) and night (10 p.m. to 6 a.m.) periods and were analyzed by ultraperformance liquid chromatography coupled to ESI-high-resolution time-of-flight mass spectrometry (UPLC/ESI-HR-TOFMS). The filter sampling and analysis protocols are described elsewhere.²⁶

Organosulfate Standard Analysis. To test the detection capabilities of ATOFMS toward organosulfates and identify common marker ions for ambient aerosol apportionment, a synthesized standard of the organosulfate derivative of 2, 3-epoxy-1,4-butanediol (BEPOX) was analyzed as a proxy for the isoprene epoxydiol (IEPOX)-derived organosulfate.²⁷ The standard solution was a mixture of sodium sulfate, sulfuric acid, and the BEPOX-derived organosulfate. Because pure sulfate salts

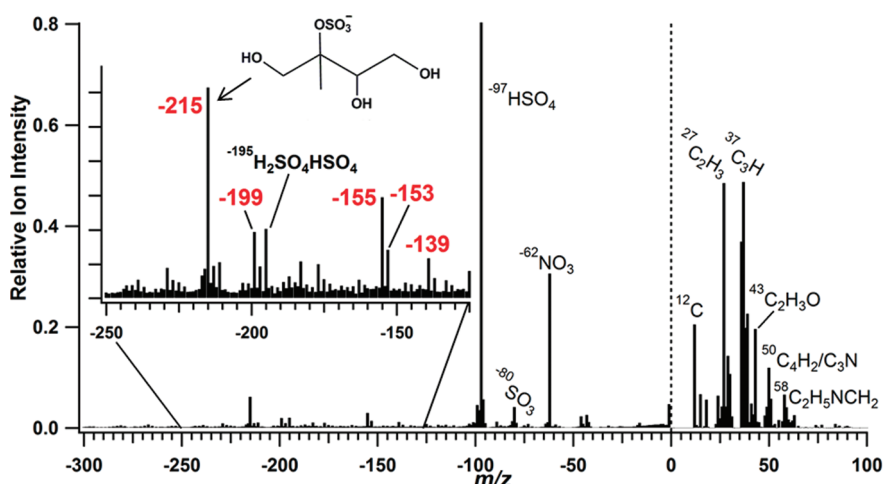


Figure 1. Average positive and negative-ion mass spectra of organic carbon-type particles measured during ANARChE. The spectra represent the average of $\sim 41\,000$ particles. The inset molecule represents the IEPOX-derived organosulfate species ($m/z -215$).

have been shown to poorly absorb the laser pulse at 266 nm,²⁸ dihydroxybenzoic acid (DHB) was added to the sample matrix as a chromophore to facilitate desorption and ionization of the standard particles and to better approximate the composition of ambient aerosols. The standard solution was analyzed by aerosolizing an aqueous solution with a Collison atomizer, drying the resulting aerosol with two diffusion driers, and introducing the particles directly into the ATOFMS.

3. RESULTS AND DISCUSSION

Identification of Organosulfate Species. High mass species at $m/z -139$, -153 , -155 , -199 , and -215 were observed in multiyear ATOFMS measurements conducted in Atlanta during the ANARChE and AMIGAS campaigns. The example spectrum shown in Figure 1 represents the average of an organic carbon particle cluster observed during ANARChE ($\sim 41\,000$ particles). The aforementioned peaks are hypothesized to be organosulfate species derived from isoprene oxidation products based on previous work by Surratt and co-workers who identified these compounds in chamber studies⁵ and filter samples of ambient aerosols collected at the JST site.²⁶ These compounds have been identified as organosulfates derived from the following isoprene oxidation products: glycoaldehyde⁵ ($m/z -139$), hydroxyacetone⁵ ($m/z -153$), glyoxal⁵ or glycolic acid²⁹ ($m/z -155$), 2-methylglyceric acid⁵ ($m/z -199$), and the IEPOX²⁷ ($m/z -215$). In those studies, organosulfates were detected as deprotonated molecular ions via ESI-MS. Because the LDI method used in ATOFMS is considered a harder ionization technique than ESI, a BEPOX-derived organosulfate standard (Figure S1 of the Supporting Information) was aerosolized and analyzed by ATOFMS to confirm that it is capable of measuring intact organosulfate compounds. The synthetic standard is analogous to the compound attributed to the organosulfates of 2-methyltetrols formed through acid-catalyzed reactive uptake of IEPOX (structure included in Figure 1).^{27,30} However, it lacks a methyl group (Figure S1 of the Supporting Information), and thus appears 14 m/z units lower ($m/z -201$) than the IEPOX-derived compound ($m/z -215$). In the average ATOFMS spectrum (Figure S1 of the Supporting Information), the predominant peak arising from the BEPOX-organosulfate standard is, in fact, the pseudomolecular ion at $m/z -201$. Additionally, ATOFMS

analysis of a synthesized standard of the glycolic acid-derived organosulfate ($m/z -155$) was also dominated by the deprotonated ion (results not shown). These results indicate that the pseudomolecular ion is the dominant species observed for organosulfate compounds under LDI at 266 nm and supports the assignment of the aforementioned ambient peaks to organosulfate species.

Comparison between ATOFMS and Filter Samples during AMIGAS. Given the limitation of nominal mass resolution in the ATOFMS mass spectra, there remains the possibility that other isobaric species could yield these m/z values. To rule this out, ATOFMS results were compared with the chromatographic peak areas obtained by the UPLC/ESI-HR-TOFMS analysis of filter samples collected during the AMIGAS campaign (Figure 2). Only submicrometer particles measured by ATOFMS were included in this comparison, as the organosulfates were primarily detected on particles in this size range (discussed below). The ATOFMS and UPLC/ESI-HR-TOFMS methods show good agreement for the $m/z -215$ marker ($R^2 = 0.53$), further confirming that the peaks observed by ATOFMS can be attributed to the isoprene-derived organosulfates.

There are several possible explanations for the significant, yet moderate correlation ($R^2 = 0.53$) between the ATOFMS $m/z -215$ peak area and the chromatographic peak area from the UPLC/ESI-HR-TOFMS analysis of the filter extracts. For example, positive artifacts could have influenced the filter sampling through increased uptake of organosulfate precursors from the gas phase to a filter substrate with a pre-existing sulfate-rich aerosol loading and subsequent condensed-phase processing to nonvolatile organosulfates. Minor contributions from matrix effects or other artifacts associated with laser/desorption ionization³¹ during ATOFMS analysis were also possible. However, matrix effect are likely most significant when examining relatively pure particles, a condition that is rarely observed in atmospheric aerosols from a polluted region. Therefore, we expect that matrix effects played, at most, a minor role in the detection of organosulfates in Atlanta. A combination of factors likely played a role in the moderate correlation between the analysis methods and further studies are necessary to characterize the artifacts associated with each measurement technique. However, the correlation observed in the present study is sufficient to support

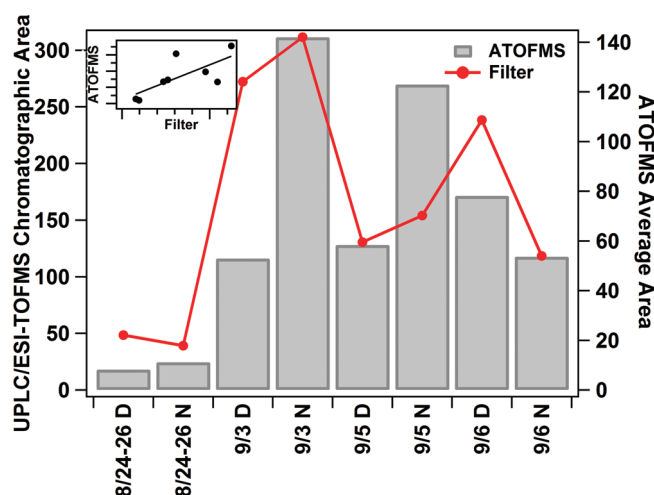


Figure 2. Comparison of m/z -215 abundance measured in single particles by ATOFMS with day/night filter samples analyzed by ultra-performance liquid chromatography (UPLC). For this comparison, the uncalibrated chromatographic peak area from the filter extracts was used; the ATOFMS absolute peak area of m/z -215 was averaged over the corresponding filter time periods; only submicrometer particles were included in the comparison. D = 10 a.m. to 6 p.m.; N = 10 p.m. to 6 a.m. The inset shows the correlation plot between the two measurements ($R^2 = 0.53$).

the qualitative ATOFMS observations presented here and in the forthcoming Hatch, 2011.

Isoprene-Derived Organosulfate Markers. Whereas standards from the other organosulfate markers (-139 , -153 , & -199) have not been analyzed by ATOFMS, the correlations between most of the markers and m/z -215 (Figure S2 of the Supporting Information) show good correlations during both ANARChE (m/z -139, $R^2 = 0.08$; m/z -153, $R^2 = 0.64$; m/z -155, $R^2 = 0.69$; and m/z -199, $R^2 = 0.50$) and AMIGAS (m/z -139, $R^2 = 0.23$; m/z -153, $R^2 = 0.54$; m/z -155, $R^2 = 0.51$; and m/z -199, $R^2 = 0.62$). These correlations indicate that these species arise from similar formation mechanisms and further corroborate the assignment of these peaks to organosulfate species. The poor correlations between m/z -139 and m/z -215 are attributed to the lower peak area of m/z -139, and thus the reduced signal-to-noise ratio associated with this peak. Whereas different correlations were observed between the minor organosulfate markers and m/z -215, they arise from different isoprene oxidation products, as described above, and display different product yields under different reaction conditions.⁵ Therefore, a perfect correlation between the organosulfate markers is not necessarily expected.

Assuming the different isoprene-derived organosulfate markers exhibit similar ionization efficiency and degree of fragmentation under LDI, the peak areas can be used to indicate relative abundances. The same trends were observed during both ANARChE and AMIGAS with the marker at m/z -215 being the most abundant organosulfate, displaying $\sim 4\times$ higher peak area than the other species, followed by m/z -155 > -199 > -153 > -139. There are several potential explanations for the higher concentration of m/z -215 including differences in precursor concentrations or in organosulfate product yield/formation kinetics, but these effects could not be resolved in this study. However, additional characterization studies

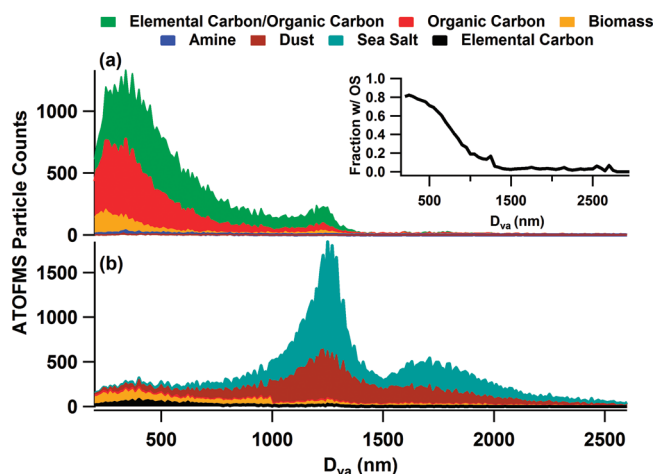


Figure 3. Size-dependent mixing state comparison of particles with dual-polarity spectra that contained (a) and did not contain (b) organosulfate species during AMIGAS. The y axis represents particle counts measured by ATOFMS per 10 nm size bin, given in vacuum aerodynamic diameter. The inset shows the fraction of particles in each size bin that contained organosulfate species.

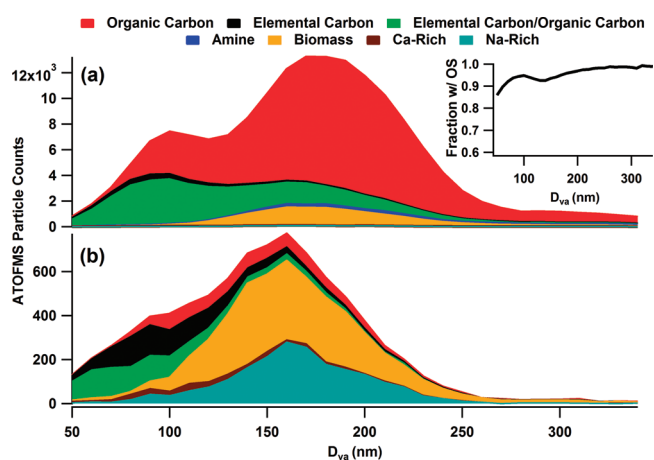


Figure 4. Size-dependent mixing state comparison of particles with dual-polarity spectra that contained (a) and did not contain (b) organosulfate species in 10 nm size bins during ANARChE. Note the difference in y axis scales between (a) and (b). The inset shows the fraction of particles in each size bin that contained organosulfate species.

should also be performed to investigate the detection efficiency of various organosulfate compounds. In particular, it should be noted that clear ion signals from monoterpene-derived organosulfates were not observed in these ATOFMS data sets, despite their previous detection in Atlanta.²⁶ A discussion of the possible reasons for the absence of monoterpene-derived organosulfates is provided in the Supporting Information.

Size Dependence & Mixing State of Organosulfate Species. Measurements from both ANARChE and AMIGAS provide information on aerosols over a broad size range (50–3000 nm) to assess the possible size-dependence of organosulfates. The particle size distributions measured by ATOFMS are included in Figures 3 (AMIGAS) and 4 (ANARChE), separated by the presence or absence of organosulfate species and categorized by particle type. It is clear from the AMIGAS data that organosulfates were overwhelmingly concentrated in submicrometer aerosols,

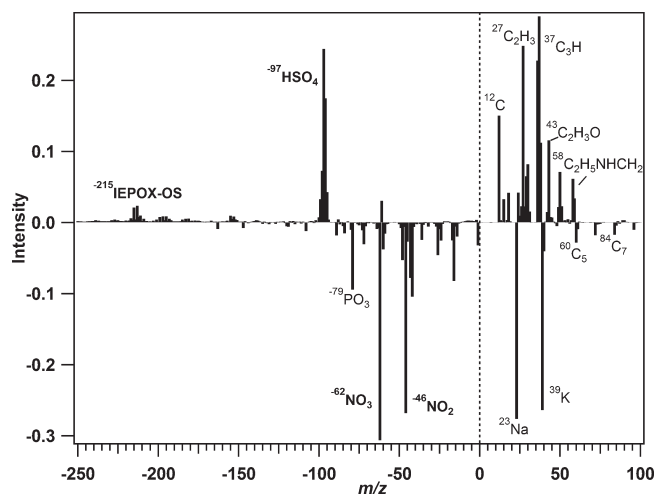


Figure 5. Difference spectra between particles (from all particle types) measured during ANARChE that contain organosulfate species (170 005) and those without (7991). The organosulfate-rich particles are strongly enriched in sulfate (m/z -97).

with only minor contribution to supermicrometer particles. This trend is likely due to the secondary nature of these compounds: since particles a few hundred nanometers in diameter dominate the aerosol surface-area distribution,³² they provide greater opportunity for collisions and subsequent uptake of gas-phase species. These findings are in general agreement with those of Lukács et al.,³³ who detected the largest organosulfate mass concentrations in accumulation mode particles collected on impactor stages in K-puszt, Hungary. The ANARChE data provides additional insights into the organosulfate content of ultrafine particles. Because Lukács et al.³³ did not observe significant organosulfate mass in the smallest impactor stage (~ 100 nm), it is noted that organosulfates were detected on nearly all (~ 85 – 95%) of the ultrafine particles (50 – 100 nm) detected during ANARChE (Figure 4). However, the mass concentration of organosulfate species was not quantified from the ATOFMS data and therefore the overall mass contribution from these ultrafine particles could not be assessed for direct comparison to Lukács et al.³³

The size distribution of organosulfate-containing particles observed during ANARChE is shifted to slightly larger sizes than those lacking organosulfates (Figure 4). This observation indicates that the organosulfate-containing particles had possibly undergone a higher degree of atmospheric processing (aging) thereby acquiring a thicker coating of secondary species. The relationship between particle aging and organosulfate content was further explored using the ability of ATOFMS to determine the mixing state of individual particles. Difference spectra between all particles containing and lacking organosulfates during ANARChE are included in Figure 5. It is clear that the particles containing organosulfates (positive intensity) are strongly enriched in sulfate, relative to the particles lacking organosulfates (negative intensity), and indicating they had undergone a high degree of aging. However, simple aging is not sufficient to explain organosulfate formation as the organosulfate-deficient particles appear to be slightly aged as well, indicated by the presence of secondary nitrate (m/z -46, NO_2^- and -62, NO_3^-). Rather, atmospheric processing leading to particles rich in sulfate, a necessary precursor to organosulfate formation is important, though the effect of sulfate – by either simply acting as a reactant or

influencing aerosol acidity – cannot be determined from these studies. However, the trend of higher sulfate content in the organosulfate containing particles is true across the different particle types and also holds for AMIGAS, as shown by the mass spectra for individual particle types provided in Figures S3 and S4 of the Supporting Information. While not surprising, these observations demonstrate that a particle's sulfate content is likely a key parameter influencing organosulfate formation, consistent with the work of Minerath et al.,³⁴ who observed an increase in organosulfate yield with increasing sulfate concentration.

From this analysis, it appears that the predominant characteristics influencing organosulfate levels are particle size (i.e. surface area-to-volume ratio) and sulfate concentration, highlighting the role of atmospheric processing in leading to particulate organosulfate species. However, further research is necessary to better understand the role of particle aging and mixing state on the partitioning/formation of organosulfate species. The additional observation that organosulfates were primarily detected on carbonaceous particle types (e.g. organic carbon, elemental carbon/organic carbon) is described in the Supporting Information. Part 2 of this work (Hatch, 2011) will explore possible organosulfate formation mechanisms in more detail.

Atmospheric Significance. Organosulfate species were detected on ~ 90 – 95% of particles containing dual-polarity spectra during ANARChE and $\sim 65\%$ of submicrometer particles during the AMIGAS campaign. Whereas the mass contribution of these organosulfate compounds to individual particles was not determined for this study, it is clear that they have the potential to influence a great number of particles. Given the high polarity and water solubility of these isoprene-derived organosulfate compounds, they may play a significant role in increasing the hygroscopicity and CCN activity of carbonaceous aerosols in regions influenced by biogenic and anthropogenic pollutants.

ATOFMS has been demonstrated to be an effective technique for measuring organosulfate compounds in real-time within individual atmospheric particles. Data from several past field campaigns have been reexamined for the presence of organosulfates derived from isoprene. Markers comparable to those measured during ANARChE and AMIGAS were also detected in other isoprene-rich locations, including New York, NY (2002); Boston, MA (2003); Chapel Hill, NC (2003); and the Sacramento, CA area (2010). Multiyear observations of organosulfate species in Atlanta, as well as their detection in other regions of the United States, highlight the significant contribution of these compounds to organic aerosols. It is also noteworthy that the IEPOX-derived organosulfate discussed herein has not been measured in Riverside, CA, a region that has been extensively monitored by ATOFMS^{35–37} and is generally characterized by lower emissions of isoprene and SO_2 . These observations point to the regional nature of SOA processing and the strong influence of biogenic emissions in the southeastern United States.

■ ASSOCIATED CONTENT

S Supporting Information. Results and discussion, mass spectra, and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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