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Article

Seasonal Contribution of Isoprene-Derived Organosulfates to Total Water-Soluble Fine Particulate Organic Sulfur in the United States

Yuzhi Chen, Tracy Dombek,* Jenny Hand, Zhenfa Zhang, Avram Gold, Andrew P. Ault, Keith E. Levine, and Jason D. Surratt*

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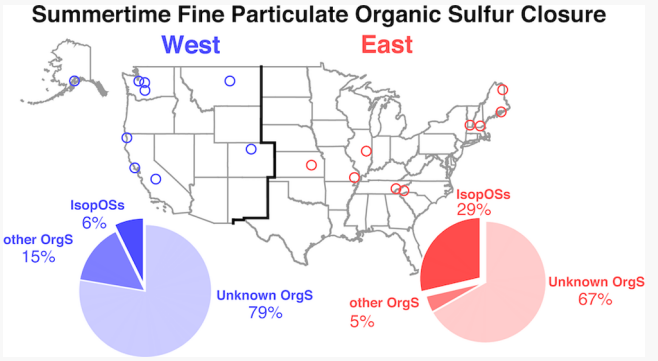
ABSTRACT: Organosulfates (OSs) are the most abundant class of organosulfur (OrgS) compounds in atmospheric fine particulate matter ($PM_{2.5}$). Globally, isoprene-derived OSs (iOSs) are the most abundantly reported OSs; however, total sulfur mass closure in $PM_{2.5}$ has not been conducted at the molecular level in order to understand how iOS contributions vary by season and by location in the United States (U.S.). In this work, iOSs were quantitively characterized in $PM_{2.5}$ collected from 20 ground sites within the Interagency Monitoring of Protected Visual Environments (IMPROVE) network during the 2016 summer and winter seasons. Total water-soluble sulfur (TWS-S) and sulfur from inorganic sulfate (S_{inorg}) were also chemically determined, with the imbalance between TWS-S and S_{inorg} used as an upper-bound estimate of water-soluble OrgS concentrations. Significantly higher fine particulate OrgS concentrations (~20% of TWS-S) were observed at most sites only in summer, coincident with elevated iOS concentrations in the eastern U.S. On average, iOSs (130 ng m^{-3}) explained 29 and 4% by mass of OrgS and of organic matter (OM), respectively, in the eastern U.S. In the western U.S., iOSs (11 ng m^{-3}, on average) accounted for 6 and 0.5% by mass of OrgS and OM, respectively. In winter, iOSs were hardly detected, consistent with reduced isoprene emissions. Our study shows that ~70 and 80% of OrgS mass in the eastern U.S. and western U.S., respectively, remain unexplained at the molecular level. This study provides critical insights into the abundance, prevalence, and spatial variability of fine particulate iOSs across the U.S.



KEYWORDS: *IMPROVE network, biogenic, sulfate, fine particulate matter, secondary organic aerosol*

INTRODUCTION

Inorganic sulfate ($Sulf_{inorg} = SO_4^{2-} + HSO_4^-$) is a significant component of atmospheric fine particulate matter ($PM_{2.5}$, aerosol particles ≤2.5 μm in aerodynamic diameter).[1] $Sulf_{inorg}$ is assumed to be the primary form of S(VI) in $PM_{2.5}$, with the capacity to impact atmospheric chemistry, air quality, and climate because of its predicted impacts on aerosol acidity and hygroscopicity as well as on visibility and cloud nucleation.[2] Organosulfur (OrgS) compounds, such as organosulfates (OSs), have been widely identified in ambient $PM_{2.5}$ samples.[3−18] OSs can contribute substantially to organic carbon (OC) (1−17%)[19−21] and organic matter (OM) (5−30%)[5,22−24] in $PM_{2.5}$ and are associated with the formation of secondary organic aerosol (SOA) involving atmospheric oxidation of both anthropogenic volatile organic compounds[25−27] and biogenic volatile organic compounds (BVOCs).[5,28−32] Formation of fine particulate OSs has been demonstrated to occur through various pathways: acid-catalyzed reactive uptake of epoxides onto acidic $Sulf_{inorg}$ aerosol,[3,5,8,26,28,32−36] heterogeneous reaction between sulfur dioxide (SO_2) and aerosol-phase organic peroxides,[37,38] nucleophilic substitution of organic nitrates by $Sulf_{inorg}$,[39,40] sulfoxy radical-initiated oxidation of unsaturated compounds,[41−44] and acid-catalyzed perhydrolysis of organic hydroperoxides.[45]

Studies have reported discrepancies between the concentrations of total particulate S measured by X-ray fluorescence spectroscopy, inductively coupled plasma (ICP) interfaced to either optical emission spectroscopy (ICP−OES) or mass spectrometry, and those of inorganic sulfate sulfur (S_{inorg}) measured by ion chromatography (IC), specifically, a statistically significant $[S]/[S_{inorg}]$ ratio > 1 that could not be explained by the combined uncertainties in sampling and analytical techniques.[20−22,46] The total S and S_{inorg} imbalance is indicative of the presence of S in non-S_{inorg} forms and

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approximates an upper bound estimate for the abundance of fine particulate OrgS. Liquid chromatography interfaced to electrospray ionization high-resolution tandem mass spectrometry methods operated in the negative ion mode have been used to characterize fine particulate OSs at the molecular level because of their low volatility and chemical instability in analytical protocols requiring heating and prior derivatization (e.g., gas chromatography interfaced to mass spectrometry).[28,47−50] An approach that combines analytical techniques for measuring total S, $Sulf_{inorg}$, and OrgS compounds at the molecular level has recently been employed to investigate fine particulate S mass closure for Centerville, AL, during the 2013 Southern Oxidation and Aerosol Study campaign.[31] In that study by Riva et al.,[31] total OrgS compounds quantified by reverse-phase liquid chromatography interfaced to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry were estimated to contribute 50−60% of particulate OrgS determined from the difference between total S measured by isotope ratio−inductively coupled plasma-mass spectrometry and S_{inorg} measured by IC.

BVOC-derived OSs serve as molecular tracers for the capability of anthropogenic S emissions to enhance SOA formation from biogenic emissions.[51] Through laboratory studies, gas-phase isoprene epoxydiols (IEPOX), which are abundant atmospheric oxidation products of isoprene under low-nitric oxide (NO) conditions,[52] have been demonstrated to undergo acid-catalyzed multiphase chemistry with acidic $Sulf_{inorg}$ aerosols and thus are key to explaining the formation of methyltetrol sulfates (MTSs, referred to as IEPOX OS monomers in past studies) and their substantial contribution to IEPOX-derived SOA.[31,34,36,53−55] In field measurements, MTSs make significant contributions to total particulate S (up to 19%),[56] OC (up to 13%),[19,55] and organic aerosols (up to 15%).[24,55,56] Our laboratory has reported that diastereomers of 2-methyltetrol sulfates (2-MTSs), the predominant MTS isomers,[55] can be transformed to highly functionalized and oxygenated OSs through heterogeneous oxidation by the hydroxyl radical ($^{\bullet}OH$).[57] In other words, the class of IEPOX-derived OSs encompasses a considerable number of OSs beyond those directly formed via reactive uptake of IEPOX onto $Sulf_{inorg}$ aerosols. Nonetheless, concentrations of known IEPOX-derived OSs (including those OSs recently demonstrated to form from heterogeneous $^{\bullet}OH$ oxidation of particulate 2-MTSs) and their contributions to ambient fine particulate OrgS have yet to be fully assessed.

In this study, a complete characterization of water-soluble fine particulate S is conducted by using highly sensitive analytical techniques on ambient $PM_{2.5}$ filter extracts collected from the Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring program.[58] The aqueous filter extracts were analyzed for total S by ICP−OES and S_{inorg} by IC. The difference between the two independent measurements was then used to determine the upper bound of total fine particulate OrgS mass. Using the same aqueous filter extracts, fine particulate OSs were characterized and quantified at the molecular level using hydrophilic interaction liquid chromatography interfaced to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (HILIC/ESI−HR-QTOFMS). This work provides a comprehensive understanding of the seasonal and spatial variability of isoprene-derived OSs (iOSs) and their contributions to fine particulate OrgS in the United States (U.S.).

2. MATERIALS AND METHODS

2.1. $PM_{2.5}$ Filter Samples from IMPROVE. The data presented in this work were obtained from ambient $PM_{2.5}$ filter samples collected for the IMPROVE network from 19 sites in winter (January/February) 2016 and from 20 sites in summer (July/August) 2016 (Table S1). It should be noted that the selected $PM_{2.5}$ filter samples were from the established collection schedule of the IMPROVE network and not additional filters collected for this specific study. In addition, summer and winter seasons were solely selected in order to have the largest differences in emissions. Most sites are in the rural/remote locations with the exception of two urban sites: Fresno, CA (FRES1) and Puget Sound, WA (PUSO1). The IMPROVE sampling system consists of four independent sampling modules (modules A−D), each of which collects one 24 h sample every 3 days.[58] Nylon filters utilized in module B are typically analyzed by IC for water-soluble particulate $Sulf_{inorg}$. As previously described by Malm et al.,[58] a carbonate denuder is placed in the module B inlet to remove gaseous nitric acid (HNO_3) and SO_2 that may create artifacts upon interaction with the aerosol particles collected onto the filters.[59] The 24 h nylon filters were extracted individually in deionized water and submitted for total S determination by ICP−OES and S_{inorg} determination by IC at RTI following published protocols.[60] Differences between total S and S_{inorg} serve as upper bound mass estimates of total OrgS for comparison with OrgS compounds characterized and quantified by HILIC/ESI−HR-QTOFMS.

2.2. HILIC/ESI−HR-QTOFMS Analysis of OrgS Compounds. While total S and S_{inorg} determinations were based on individual 24 h nylon filter extracts, they were composited seasonally to increase the detection limit for HILIC/ESI−HR-QTOFMS analysis of OrgS compounds. A 1 mL aliquot was drawn from four 24 h nylon filter extracts [eight for the site at Shining Rock, NC (SHRO1) in summer] to create a 4 mL seasonal composite sample representative of either the summer or the winter season for each site (Table S1). Seasonal composite samples were frozen in conical vials in a freezer maintained below 0 °C. A Virtis 5 L freeze dryer was used to sublimate samples in a chamber under vacuum held near −55 °C for 24−48 h. Dried extracts of composite samples were reconstituted in 0.3 mL of 95:5 (v/v) acetonitrile (ACN, HPLC grade, Fisher Chemical): Milli-Q water (H_2O) prior to HILIC/ESI−HR-QTOFMS analysis. Calibrations of synthetic standards (Table S2) prepared in the same solvent mix (95:5 ACN/H_2O) were performed to quantify OrgS compounds identified from the IMPROVE $PM_{2.5}$ samples. The preparation of the synthetic standards is summarized in Section S1. HILIC/ESI−HR-QTOFMS analysis was carried out on an Agilent 6500 Series UPLC system equipped with an ESI source interfaced with an Agilent 6250 Series accurate mass quadrupole time-of-flight mass spectrometer operated in negative ion mode. A 5 μL aliquot of standards and samples was injected onto a Waters ACQUITY UPLC ethylene-bridged hybrid amide (BEH amide) column (2.1 × 100 mm, 1.7 μm particle size, Waters) at a flow rate of 0.3 mL min^{-1}. Detailed operating procedures (gradient elution program, mass calibration, tuning, voltages, etc.) of the HILIC/ESI−HR-QTOFMS system have been previously described.[31,55,57]

2.3. IMPROVE OC and OM Data. OC and OM concentrations ($\mu g\ m^{-3}$) were retrieved from the publicly available IMPROVE database (http://views.cira.colostate.edu/

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fed/QueryWizard/Default.aspx) for individual 24 h samples on the same dates as listed in Table S1. While daily OM concentrations were also available, IMPROVE calculates OM from OC by applying a constant multiplier (OM/OC ratio, f_{OC}) of 1.8 by default.[61] In reality, f_{OC} is dependent on the form of OC, and therefore varies seasonally and spatially, with lowest values typically observed at urban sites in winter and highest values in rural/suburban sites in summer.[62−66] Recently, Hand et al.[63] performed multiple linear regression analysis using the daily IMPROVE site data for the contiguous U.S. and reported seasonal regression median OC coefficients between 2011 and 2016 for the four study regions (i.e., Northwest [NW], Northeast [NE], Southwest [SW], and Southeast [SE]) separated at 40° N and −100° W. The reported median OC coefficients during 2011−2016 for NW, NE, SW, and SE regions are 1.60, 1.79, 1.38, and 1.75, respectively, in winter and 2.01, 2.13, 1.98, and 2.21, respectively, in summer. Following the same region definition, we applied the season- and region-specific median OC coefficients reported by Hand et al.[63] as f_{OC} to the daily samples and recalculated OM as $f_{OC} \times$ OC. The f_{OC} assignment by site and season is listed in Table S1. For direct comparison with the OrgS compound concentrations determined for the seasonal composite samples, the OM concentrations were averaged over the same period as the seasonal composite sample for each site.

3. RESULTS AND DISCUSSION

3.1. Total Sulfur (S), Inorganic Sulfate Sulfur (S_{inorg}), and Organic Sulfur (OrgS). Total fine particulate S measured by ICP−OES was directly compared to S_{inorg} measured by IC (Figure S1). If total S was composed entirely of S_{inorg}, the ratio of S/S_{inorg} should be unity. A positive deviation from unity indicates the possible presence of fine particulate OrgS, especially in the form of OSs, which are typically the most abundant class of OrgS compounds.[22] Overall, a statistically significant discrepancy ($S/S_{inorg} > 1$) has been observed for summer samples but not for winter samples (as demonstrated in Figure S1), consistent with previous investigations using the IMPROVE samples.[60] To determine whether the observed deviations of S/S_{inorg} from unity at individual sites were caused by analytical uncertainties associated with measurements by ICP−OES and IC, we calculated the relative S imbalance (OrgS/S) using eq 1 and the uncertainty (δ(OrgS/S)) for each composite sample.

$$\mathrm{OrgS}/S = \frac{S - S_{inorg}}{S} \quad (1)$$

The uncertainty was derived from the propagation of errors associated with each of the two analytical techniques (Section S2). A calculated OrgS/S greater than δOrgS/S is considered significant. Based on this criterion of significance, two sites — Hawaii, HI (HAVO1) and Organ Pipe Cactus National Monument, AZ (ORPI1)—were excluded from summer sites, while only four winter sites—FRES1, Great Smoky Mountain National Park, NC (GRSM1), PUSO1, and UL Bend, MT (ULBE1)—met this criterion and were considered for further S mass closure analysis using the HILIC/ESI−HR-QTOFMS data.

Figures S2A, S3A, and S4 show a clear statistical difference (p-value ∼ 0.018) between the western (including the KPBO1 site in Alaska) and eastern U.S. in terms of absolute OrgS abundance. The summertime composite-averaged OrgS concentrations were determined to be 0.3 (±0.2) μg m^{-3} for the western U.S. and 0.5 (±0.2) μg m^{-3} for the eastern U.S. However, the mean fractional contributions of OrgS to total S are similar [i.e., 0.16 (±0.03] for western U.S. and 0.17 (±0.05) for eastern U.S.].

On the other hand, significant deviations of S/S_{inorg} from unity were rarely observed for most sites in winter (Table S1, and Figure S3C,D). Exceptions were found for FRES1, GRSM1, PUSO1, and ULBE1, where appreciable amounts of fine particulate OrgS were observed. Hence, the four winter sites along with all summer sites were subjected to further HILIC/ESI−HR-QTOFMS analyses for characterization of molecular OrgS compounds as discussed in the following section.

3.2. Molecular-Level Identification and Quantification of OrgS Compounds. Tables S3 (summer) and S4 (winter) summarize OrgS compounds identified in IMPROVE samples by HILIC/ESI−HR-QTOFMS, and Table S2 gives the standards used for quantification. The structural assignments of the measured ions were based on the comparison of their elemental compositions and retention times (RTs) with available authentic standards and compounds identified in published HILIC/ESI−HR-MS/MS separations.[19,55,67] Except for methyl sulfates, hydroxyacetone sulfates (HASs), MTSs, lactic acid sulfates (LASs), glycolic acid sulfates (GASs), and methane sulfonic acid (MSA), OSs were quantified by the surrogate standards having the closest RT. During HILIC separation, the hydrophilic layer formed from adsorption of water on the stationary phase allows improved separation of polar compounds. The BEH amide column used in this study has been demonstrated to further improve the retention of OSs, carboxylic acids, polyols, and other compounds with hydroxy functional groups.[55,57,68] In the gradient elution program, the aqueous fraction of the mobile phase increases with time, resulting in longer RTs of compounds with stronger interactions with the hydrophilic layer of the stationary phase, especially through electrostatic interactions and hydrogen bonding.[68] A log-linear correlation was observed between the response factors of the OS calibrants and their RTs (Figure S5). Increasing ESI droplet surface tension with decreasing organic fraction in the mobile phase promotes ESI ionization,[69] which could be one contributor to this phenomenon. However, mobile phase composition is not the sole factor that determines ESI ionization and response factors of analytes. Staudt et al. have demonstrated that ESI response factors of structurally similar aromatic OS isomers did not monotonically increase with increasing organic fraction of the mobile phase.[70] Considering the limited number of OS calibrants currently available to our community and that were used in the present study, we could not rule out the possibility that some OSs fall out of this trend. Further investigations with inclusion of a greater number and variety of OS standards are needed to establish a robust trend.

To assess the possible instability of OSs, especially tertiary sulfates, during sample preparation steps, including filter extraction in water and freeze−drying, quality control (QC) tests were conducted and are discussed in Section S4. In short, we quantified the recoveries of OrgS standards from extractions of nylon filters in water and during the freeze−drying process. The QC results showed high recoveries for all six OS standards (>80%). However, the mean recovery for the only sulfonate standard, MSA, was only 46% with a large

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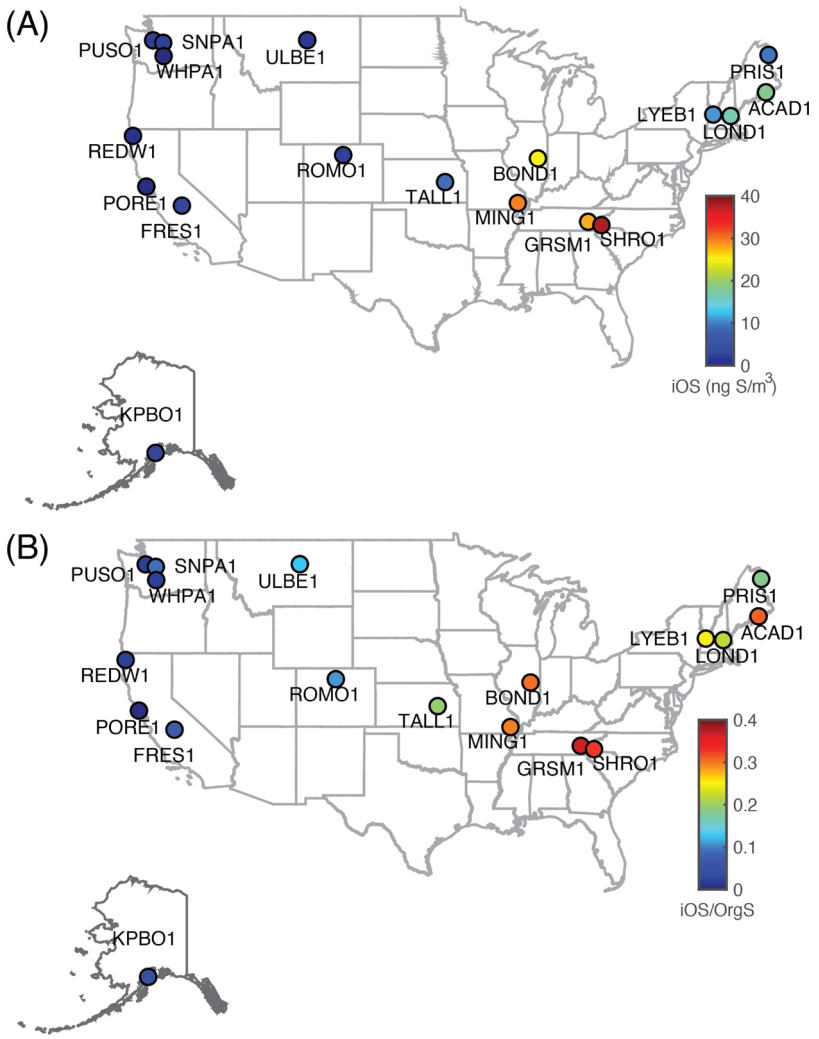

Figure 1. 2016 Summertime (July–August) composite averaged (A) iOS concentrations in ng S m^{-3} and (B) mass fractions of iOSs to total OrgS. iOSs accounted for in this figure include 2-MTS, 2-MGS, GASs, LASs, HASs, OS 139, OS 185, OS 211, OS 213, OS 227, OS229, OS 231, OS 171, OS 169, OS 197, OS 183, and NOS 260. The break-down concentrations and contributions to OrgS and OM are shown in Figures 2 and S9, respectively.

variability (1σ = 33%). Given the reasonably high recovery rates measured for standard OSs, we did not apply the recovery correction to OS concentrations measured in the IMPROVE samples. MSA concentrations were not corrected because of the high variability of recovery rates measured in the QC test. Overall, the OS concentrations reported below should be regarded as lower-bound (conservative) estimates.

3.2.1. iOSs in Summer 2016. iOSs, on average, are the most abundant identified class of water-soluble OSs detected across the U.S. during summer conditions (Table S3). The compounds classified as iOSs refer to those that have been confirmed to form from oxidation of isoprene during both laboratory studies and field measurements. The deprotonated $C_5H_{11}O_7S^-$ ions, with nominal mass-to-charge ratios (m/z) of 215, are identified as MTS isomers (IEPOX OS in past studies) and were the most abundant [24 (±29) ng m^{-3}] iOSs as well as water-soluble OrgS compounds, detected during summer conditions over the entire U.S. Four major peaks eluting at 2.1, 2.5, 4.3, and 5.6 min (Figure S6) were assigned based on published studies.[55,57] The two earliest-eluting peaks were assigned as the secondary MTS diastereomers [(2*R*,3*S*)/(2*S*,3*R*)- and (2*S*,3*S*)/(2*R*,3*R*)-1,3,4-trihydroxy-3-methylbutan-2-yl sulfates], and the two later-eluting peaks were assigned as the tertiary MTS diastereomers [(2*R*,3*S*)/(2*S*,3*R*)- and (2*S*,3*S*)/(2*R*,3*R*)-1,3,4-trihydroxy-2-methylbutan-2-yl sulfates, 2-MTSs]. 2-MTSs are the most abundant MTS isomers measured in the Southeastern U.S. (SE U.S.) and Amazonia regions[55,57] and are attributed principally to the reactive uptake of β-IEPOX, which represents 97% of the atmospheric isomeric pool of IEPOX.[53,55] Interestingly, the secondary and the tertiary MTS isomers were observed with comparable ion intensities (Figure S6) at Shining Rock, NC (SHRO1). The tertiary MTS diastereomers were even less abundant than the secondary MTS diastereomers at some locations. A recent bulk reaction study suggests that yield of 3-MTS diastereomers (corresponding to the first two peaks of m/z 215 EIC in Figure S6) from β-IEPOX is only slightly enhanced under high pH conditions, and tertiary 2-MTS diastereomers should still be favored under most atmospheric conditions.[71] Therefore, we suspect that additional chemical pathways favoring the yield of the secondary MTS isomers may exist to explain the observed ratios of secondary to tertiary MTS isomers in the ambient $PM_{2.5}$ samples. Note that quartz filters were extracted in methanol in the referenced studies, while nylon filters were

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extracted in water in the present study. The differences in filter medium and extraction medium may impact the final recovered isomer distribution, which warrants further examination for more equivalent comparisons across different studies. In the present work, the highest concentrations of MTSs were measured at the GRSM1 (composite concentration = 69 ng m^{-3}) and SHRO1 (composite concentration = 100 ng m^{-3}) sites during the summer season (Figure 1). Note that the concentrations reported in this work were from composites of a limited number of 24 h samples, only representative of half-month averages during the summer season. Therefore, they are not directly comparable to values reported for the SE U.S. region by prior studies (~160 ng m^{-3} to ~2.3 μg m^{-3}) which either spanned a longer sampling period during summer or purposefully selected samples collected during intense isoprene SOA formation events.[19,31,55,72,73]

Following MTSs, 2-methylglyceric acid sulfate (2-MGS) was the second most abundant OrgS compound [13 (±29) ng m^{-3}] in summer 2016. 2-MGS has been proposed to form from multiphase reaction of particulate $Sulf_{inorg}$ with methacrylic acid epoxide or hydroxymethylmethyl-α-lactone, both of which are produced from the $^{\bullet}$OH-initiated oxidation of isoprene under high-NO_x conditions.[74,75] In addition, sulfate radical-initiated oxidations of methacrolein (MACR) and methyl vinyl ketone (MVK) have been demonstrated to form 2-MGS in laboratory studies.[41,42] MACR and MVK are known major isoprene oxidation products in the presence of NO_x.[76−78] Sulfate radical-initiated oxidation of MACR and MVK also produce GAS, HAS and LAS, which were detected in abundance as well. In fact, the abundance of GAS [12 (±12) ng m^{-3}] was on par with 2-MGS in summer 2016. Laboratory investigations suggest that GAS formation is associated with aqueous processing/oxidation of glyoxal[79] and glycolic acid in the presence of acidic sulfate,[12] with the latter being a more efficient route of GAS formation. Although glyoxal and glycolic acid have both biogenic and anthropogenic origins, isoprene is a globally important precursor for glycolaldehyde[80,81] whose gas-phase oxidation yields glyoxal[82] and aqueous-phase oxidation yields both glyoxal and glycolic acid.[83] Most recently, heterogeneous $^{\bullet}$OH oxidation of particulate MTSs was demonstrated as an alternative pathway to form 2-MGS and GAS.[57] This pathway also forms OS ions at m/z at 213 ($C_5H_7O_7S^-$), 211 ($C_5H_7O_7S^-$), 229 ($C_5H_9O_8S^-$), 231 ($C_5H_{11}O_8S^-$), 227 ($C_5H_7O_8S^-$), 185 ($C_5H_9O_7S^-$), 171 ($C_3H_7O_6S^-$), and 169 ($C_3H_5O_6S^-$, which is not LAS), and 139 ($C_2H_3O_5S^-$). These heterogeneous $^{\bullet}$OH oxidation products of fine particulate MTSs have been resolved by the HILIC/ESI−HR−QTOFMS method in the present study and are consistent with the RTs measured during recent laboratory[57] and field studies,[19,55,67,68] supporting the identifications proposed in Table S3. In addition, moderate-to-strong correlations (r^2 = 0.40−0.98) were found between MTSs and most of these OSs (Figure S8), supporting atmospheric aging of particulate MTSs through heterogeneous $^{\bullet}$OH oxidation as an important and likely source of these OSs. One exception was found for m/z 171 ($C_3H_7O_6S^-$), which has a relatively low Pearson correlation with MTSs (r^2 = 0.25), indicating either a strong non-linear correlation or potential sources other than MTSs.

Consequently, we attributed all the particulate OSs above, along with OS ions at m/z 183 ($C_4H_7O_6S^-$),[42,45,84] 197 ($C_5H_9O_6S^-$),[5] and 260 ($C_5H_{10}NO_9S^-$)[28] to the category of iOSs. Summing up these OSs provides a rough estimate of iOSs for each site. The spatial variability of iOS concentrations and their contributions to total OrgS during summer 2016 is shown in Figure 1. A distinct difference between the western and eastern U.S. was observed. Average concentrations of iOSs were 130 (±60) ng m^{-3} corresponding to 20 (±10) ng S m^{-3} in the eastern U.S. region and 11 (±6) ng m^{-3} corresponding to 2 (±1) ng S m^{-3} in the western U.S region. The average contribution of iOSs to total OrgS (iOS/OrgS) is 29% (±7%) in the eastern U.S. and 6% (±5%) in the western U.S. The average concentrations of iOSs accounted for 4% (±2%) of fine particulate OM in the eastern U.S. and 0.5% (±0.3%) of fine particulate OM in the western U.S. The highest iOS concentrations and contributions to total particulate OrgS were observed at two sites in the Appalachia region, GRSM1 and SHRO1, where high isoprene and sulfur dioxide (SO_2) emissions and environmental conditions are conducive to isoprene oxidation chemistry leading to SOA formation.[85,86] The composite-averaged iOS concentration was 176 ng m^{-3} at the GRSM1 site, accounting for 39% of the OrgS and 7% of the OM. At the SHRO1 site, composite-averaged iOSs totaled 237 ng m^{-3}, corresponding to 34% of the OrgS and 5% of the OM. These observations are consistent with the previous ground-based and aircraft measurements that have reported some of the highest iOSs and IEPOX SOA concentrations in the SE U.S.[12,19,67,72,87−91]

Substantial iOS concentrations and high iOS/OrgS were also observed at the two midwestern U.S. (MW U.S.) sites: Mingo National Wildlife Refuge, MO (MING1), and Bondville, IL (BOND1). Rarely have OS measurements been conducted and reported for the MW U.S. region. However, Hughes and Stone[23] have measured OSs in $PM_{2.5}$ collected in Iowa City, IA, in September 2017, where the most abundant OS compounds quantified were in the class of iOSs defined here. In another recent field study, Hughes et al.[24] reported that the measured fine particulate iOSs contributed up to 15% of the total OM in $PM_{2.5}$ collected at Zion, IL, a location strongly impacted by southerly winds originating from forested areas in Missouri as well as industrial activities to the south of the Great Lakes region. Elevated isoprene mixing ratios and particulate $Sulf_{inorg}$ concentrations due to the prevailing winds promote the formation of iOSs. The BOND1 site is south of the Zion, IL site, and is rich in iOSs likely for the same reason. It is worth mentioning that the contribution of iOSs to OM at BOND1 site (Figures S9 and S10) was the highest (6.2%) of all the sites in summer 2016. The MING site was more likely to be influenced by isoprene emissions from the broadleaf forests of the Missouri Ozarks due to the geographical proximity.[92,93] We note that the highest IEPOX SOA concentrations were coincident with highest $Sulf_{inorg}$ concentrations, sampled by AMS on flights around the MW U.S. during the SEAC4RS aircraft field campaign in summer 2013.[94]

Moderate abundance of iOSs (64−118 ng m^{-3}) was observed at the four northeastern U.S. (NE U.S.) sites in the New England region during summer, Presque Isle, ME (PRIS1), Acadia National Park, ME (ACAD1), Lye Brook Wilderness Areas, VT (LYEB1), and Londonderry, NH (LOND1). To the authors' knowledge, no previous measurements of fine particulate OSs have been made in this region. Isoprene is an abundant and reactive BVOC in this region, with large sources from the forested areas in New Hampshire and Maine.[95,96] According to previous backward trajectory

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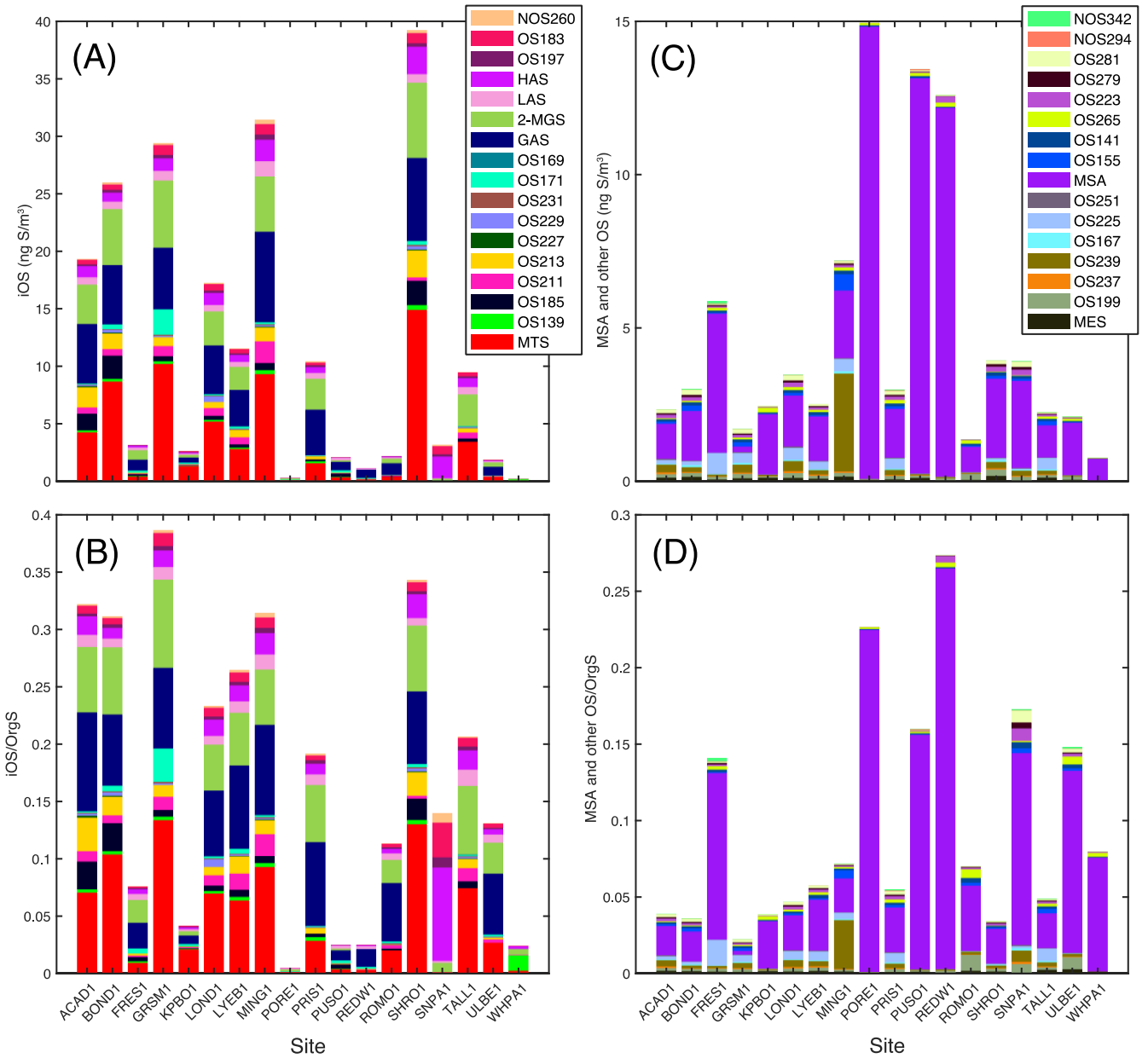

Figure 2. 2016 Summertime (July–August) composite-averaged speciated OrgS concentrations (ng S m^{-3}) and their fractional contributions to total OrgS mass. (A) iOS mass; (B) iOS/OrgS; (C) MSA and other quantified OS mass; (D) MSA and other quantified OS/OrgS. Detailed information including elemental compositions and proposed structures can be found in Table S3.

analyses, fine particulate $Sulf_{inorg}$ concentrations and aerosol acidity in New England were associated with air masses from MW U.S. and Northeast megalopolis.[97] These factors likely explain the iOSs observed at those sites in the New England region.

3.2.2. OSs/Sulfonates Derived from Other Precursor VOCs in Summer 2016. From the above analysis, the summation of iOSs, even for the SE U.S. sites, contributes only up to 39% of the total OrgS mass (maximum observed at the GRSM1 site), indicating that the total S mass closure from known sources of isoprene origin is far from complete and other sources of OrgS compounds remain to be identified to achieve S mass balance. MSA, the only non-OS OrgS compound characterized in this work, was ubiquitously detected. MSA concentration ranks 4th among all quantified OrgS compounds during summer 2016 across the U.S. The average concentrations of MSA were determined to be 17 (±17) and 4 (±2) ng m^{-3}, corresponding to 13% (±8%) and 2.1% (±0.8%) of OrgS mass in the western and eastern U.S., respectively. In particular, MSA contributes substantially to OrgS mass at the western U.S. sites, including the FRES1, Kenai Peninsula Borough, AK (KPBO1), Snoqualmie Pass, WA (SNPA1), and ULBE1 sites; it was the dominant OrgS species at the Point Reyes National Seashore, CA (PORE1), PUSO1, Redwood National Park, CA (REDW1), and White Pass, WA (WHPA1) sites, as shown in Figure 2. MSA, which forms largely from the oxidation of dimethylsulfide (DMS) emitted by oceanic phytoplankton, is a ubiquitous component of marine aerosols.[98−100] A reconstruction of DMS climatological concentration in 1999 based on the global surface ocean DMS database has shown that highest DMS sea concentrations and ocean-to-atmosphere flux occurred in June and July for the California current

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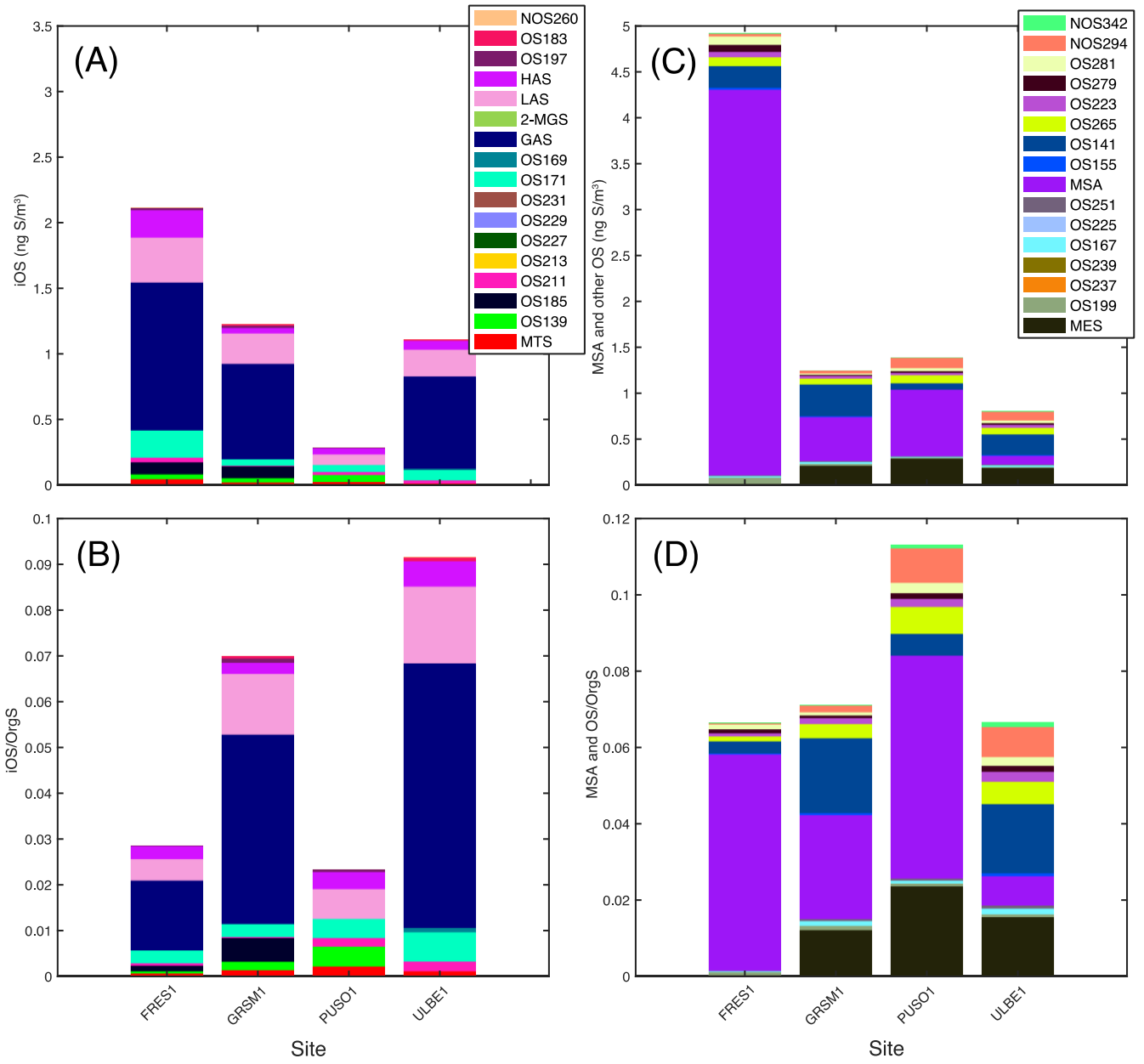

Figure 3. 2016 Wintertime (January–February) composite-averaged speciated OrgS concentrations (ng S m^{-3}) and their fractional contributions to OrgS. (A) iOS mass; (B) iOS/OrgS; (C) MSA and other quantified OS mass; (D) MSA + other quantified OS/OrgS. Detailed information including elemental compositions and proposed structures can be found in Table S4.

biogeochemical province along the west coast, while relatively lower values occurred over the gulf of Maine during the same months.[101] Although the data from this study are not representative of 2016, they imply that elevated DMS concentrations along with increased photochemical activity in summer may account for higher particulate MSA concentrations detected at the west coast sites and relatively lower particulate MSA concentrations detected at the NE U.S. sites reported in this work. Detection of particulate MSA at inland sites is not unprecedented.[31,102] Since DMS, as the source of MSA, has been exclusively attributed to oceanic emissions hitherto, regional transport may play an important role here, which requires validation in the future.

The remaining fine particulate OSs characterized by targeted MS analyses based on the literature are summarized in Table S3. Their VOC precursors include MACR, MVK, green leaf volatiles, monoterpenes, alkanes, alkenes, and unknown sources. Some OS species have multiple-reported precursors, including isoprene. However, it is impossible to identify the sources without additional collocated measurements for individual sites, which is beyond the scope of this study. Site-specific concentrations, fractional mass contributions to total OrgS, and fractional mass contributions to fine particulate OM attributed to non-iOSs are shown in Figures 2 and S9. Non-iOSs species average < 0.5 ng S m^{-3} and contributed to <1% of total water-soluble OrgS mass during summer 2016 in the U.S.

3.2.3. OSs in 2016 Winter Samples. As indicated by total S and S_{inorg} analyses above, differentiable S imbalance during winter was observed only at the FRES1, GRSM1, PUSO1, and ULBE1 sites. The largest S imbalance (i.e., OrgS concentration) was observed at the FRES1 site (Figure S3), and MSA

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alone explained almost 60% of the S and 42% of mass out of total quantified OrgS compounds by HILIC/ESI−HR-QTOFMS (Figures 3 and S11). As expected, most iOSs, including MTS diastereomers, were not abundantly detected in winter at FRES1. OS 171 ($C_3H_7O_6S^-$), a reported heterogeneous $^{\bullet}$OH oxidation product of particulate MTSs, was more abundant than its likely precursor MTSs. GAS, HAS, and LAS, whose formation was strongly associated with isoprene oxidation in the summer, are also more important contributors to wintertime OrgS than IEPOX-derived OSs. Therefore, sources other than isoprene likely dominate the production of these OSs in winter. Parent ions with OSs at m/z 141 ($C_2H_5O_5S^-$) and m/z 265 ($C_{12}H_{25}O_4S^-$) were measured at higher concentrations in winter relative to summer at all four sites. The RTs of OS 141 and OS 265 are consistent with previous reports of 2-hydroxyethyl sulfate and dodecyl sulfate, respectively, which are attributed to anthropogenic sources.[23,67] Quantitative results for all OSs and their contributions to total OrgS and OM are shown in Figures 3 and S11, respectively, and mean concentrations for the four sites are summarized in Table S4. Overall, the quantified OrgS compounds explained only 13% (10−16%) of OrgS mass in winter for the four sites, with the major fraction of OrgS mass still unaccounted for. The quantified OrgS compounds only explained 0.7% (0.3−1.1%) of the OM mass.

3.3. Atmospheric Implications. The present study utilized the combination of ICP−OES and IC to estimate the total water-soluble OrgS mass and HILIC/ESI−HR-QTOFMS to identify and quantify OrgS compounds at the molecular level in $PM_{2.5}$ samples collected from the IMPROVE network in 2016, providing the most comprehensive picture of iOS concentrations and their contributions to total fine particulate S mass closure in the U.S. to date. The iOSs quantified in this work reflect an up-to-date mechanistic understanding of the iOS formation chemistry. The highest concentrations of iOSs were observed at sites in the SE and MW U.S. in the July/August IMPROVE samples, followed by NE U.S. The HILIC/ESI−HR-QTOFMS protocol employed was sensitive enough to measure non-zero levels of iOSs in the western U.S., although their mass concentrations were the lowest of all U.S. regions. The ground-level filter-based observations reported here on the prominent spatial differences of iOS concentrations between the western and eastern U.S. agree with previous aircraft measurements using real-time single-particle mass spectrometry.[12,16] Our attempts to close the fine particulate S mass budget demonstrated that iOSs explained, on average, ∼30% of total fine particulate OrgS mass in the eastern U.S. and ∼6% in the western U.S. in summer 2016. Even when certain significant non-isoprene-derived OrgS mass contributors, including GAS, LAS, and HAS, were excluded, the remaining iOSs still explained 19% of the total OrgS mass in the eastern U.S. Not surprisingly, IEPOX-derived particulate MTSs along with their oxidation products are the largest sources of summertime particulate OrgS in the eastern U.S., contributing on average 11% of OrgS mass. In terms of OM mass closure, the average iOS concentrations totaled 130 (±60) ng m^{-3}, equivalent to 4% (±2%) of OM in the eastern U.S.

However, 67% of OrgS mass in the eastern U.S. and 79% in the western U.S. remained unaccounted for during summer 2016. The losses of OrgS compounds associated with sample preparation procedures might help to close the OrgS mass budget (especially at sites where MSA levels were appreciative), but as demonstrated by the QC tests, analytical procedures do not appear to be the determining factor for losses of iOS compounds. As mentioned in Section 3.2, surrogate standards were used due to the lack of authentic standards, which could bias the quantitative results of individual analytes. This highlights the continuing need for the development of synthetic routes for many OSs. Synthesis of authentic standards will facilitate more accurate quantification of OSs and verify whether the log-linear relation between OS ionization efficiency and RT holds (Section 3.1 and Figure S5) for the employed HILIC separation method, warranting future research efforts. The HILIC method utilized in this study was designed for polar OSs with carboxyl and/or hydroxyl groups, favoring the separation and quantification of isoprene-derived OSs; this HILIC method may underrepresent hydrophobic OSs, such as those derived from long-chain alkanes and polycyclic aromatic hydrocarbons.[25,26] Reverse-phase liquid chromatography methods[5,8,9,31,56] can be used to accompany HILIC methods in order to quantitatively characterize both the hydrophobic and hydrophilic, respectively, OSs at the molecular level. Furthermore, OrgS compounds identified in the present study (Tables S3 and S4) are likely far from complete. As yet unidentified S-containing compounds will probably be necessary to account for the missing fine particulate S mass reported in this study. A broader pool of OrgS species such as sulfonates, sulfides, thiols, polycyclic aromatic sulfur heterocycles, dialkylsulfates, and so on, is poorly understood in the context of atmospheric aerosols, requiring future investigations.[25,51,103,104] Finally, the difference between TWS-S and S_{inorg} being used as an upper bound estimate of total OrgS could contribute to a low bias of the OrgS mass fraction attributed to iOSs and other characterized OrgS species and a high bias of the unidentified OrgS fraction.

Many studies on fine particulate S conducted to date have focused principally on iOSs and source apportionment at single sampling locations within the SE region,[5,28,31,67,68,72,73,105] while such studies are generally lacking in the NE and western U.S. Our results show that during summer, iOSs are likely to be substantial contributors to the total OrgS and OM masses in the NE U.S. as well as in the SE and MW U.S. Future field measurements and targeted modeling investigations in the western U.S. as well as additional locations in the NE U.S. are necessary to understand the sources and factors that govern the formation of iOSs and other OSs on a national scale. OrgS compounds are known to alter aerosol physicochemical properties including acidity, morphology, and phase state as well as activity as cloud condensation nuclei and ice nuclei.[31,106−111] From a total S mass closure perspective, ∼80% of fine particulate water-soluble S was in the form of $Sulf_{inorg}$ in both western and eastern U.S. during summer 2016 (Figure S13). As $Sulf_{inorg}$ continues to decrease due to air quality control measures imposed on anthropogenic SO_2 emissions, the fractional contribution of iOSs to particulate S and total particulate mass may continue to rise.[31] This is particularly important for aerosol acidity and liquid water content predictions as current chemical transport models only account for inorganic sulfate during thermodynamic calculations.[112,113] The biased predictions of aerosol acidity and liquid water content can further influence model predictions of other atmospheric processes (e.g., multiphase chemistry of IEPOX).[34,106,114−116] Hence, our results provide a basis to update and improve predictability

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of fine particulate OrgS compounds in regional- and global-scale atmospheric chemistry models. Accurate prediction of fine particulate S composition and corresponding aerosol physicochemical properties is crucial to assess the impact of fine particulate S on air quality and climate now and in the future.[31,41,110,111,117−121]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.1c00102.

> Preparation of synthetic standards used in quantifications of molecular OrgS compounds; uncertainty associated with ICP−OES, IC, and HILIC/ESI−HR−QTOFMS; procedures and results of quality control test for estimating the recovery rates of OSs during filter extraction and drying; comparison of sulfur imbalance between summer and winter seasons; relation between HILIC/ESI−HR−QTOFMS response factors and retention times of molecular OrgS standards; spatial and seasonal distributions of total OrgS mass concentrations; detailed information on molecular OrgS compounds identified in $PM_{2.5}$ samples collected from the IMPROVE network; speciated OrgS concentrations and contributions to OM at individual IMPROVE sites; EICs of identified OrgS compounds; spatial distribution of iOS concentrations and contribution to OM; and comparison of total water-soluble sulfur mass closures between western and eastern U.S. (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Tracy Dombek − *Analytical Sciences, RTI International, Research Triangle Park 27709 North Carolina, United States*; Email: tdombek@rti.org

Jason D. Surratt − *Department of Environmental Sciences and Engineering, Gillings School of Global Public Health and Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill 27599 North Carolina, United States*; orcid.org/0000-0002-6833-1450; Email: surratt@unc.edu

Authors

Yuzhi Chen − *Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, University of North Carolina at Chapel Hill, Chapel Hill 27599 North Carolina, United States*; Present Address: Y.C.—Atmospheric Sciences and Global Change Division, Pacific Northwest National Laboratory, Richland, Washington 99352, United States

Jenny Hand − *Cooperative Institute for Research in the Atmosphere, Colorado State University, Fort Collins 80523 Colorado, United States*; orcid.org/0000-0002-4644-2459

Zhenfa Zhang − *Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, University of North Carolina at Chapel Hill, Chapel Hill 27599 North Carolina, United States*

Avram Gold − *Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, University of North Carolina at Chapel Hill, Chapel Hill 27599 North Carolina, United States*

Andrew P. Ault − *Department of Chemistry, University of Michigan, Ann Arbor 48109 Michigan, United States*; orcid.org/0000-0002-7313-8559

Keith E. Levine − *Analytical Sciences, RTI International, Research Triangle Park 27709 North Carolina, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsearthspacechem.1c00102

Author Contributions

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Notes

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