Nontargeted Tandem Mass Spectrometry Analysis Reveals Diversity and Variability in Aerosol Functional Groups across Multiple Sites, Seasons, and Times of Day

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ABSTRACT: Organic aerosol (OA) is a complex mixture of compounds with diverse elemental and structural features, and its composition affects its health and environmental impacts. A detailed speciation of the functional group distribution in OA is important for constraining atmospheric reaction pathways and products, evaluating chemical mechanisms and models, and understanding OA impacts. We used high-resolution tandem mass spectrometry to perform a nontargeted analysis of OA functional groups from three diverse ambient sites across times of day and seasons. We observed a range of oxygen-, nitrogen-, and/or sulfur-containing functional groups, including oxygenates such as hydroxyls (29−69%) and carboxylic acids (19−59%), that dominated the functional group distribution and that may participate in hydrogen bonding and thus impact the chemical and physical properties of OA (percentages indicate average

ion abundance contributions across campaigns). We also observed esters (7−39%) and ethers (13−42%) that suggest the importance of oligomerization. On average, organonitrates represented only 12% of identified nitrogen-containing groups and organosulfates represented 21% of identified sulfur-containing groups, while we observed many other nitrogen- and/or sulfur-containing structures that were important contributors to OA composition (e.g., amines, imines, nitrophenols, and sulfides). Most compounds (81%) were multifunctional and likely multigenerational oxidation products, which typically contained two to five functional groups in total.
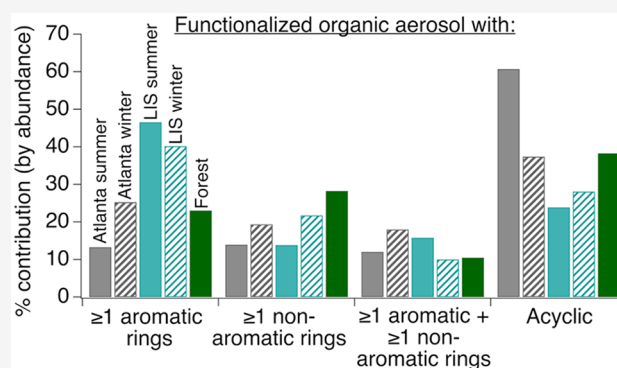
INTRODUCTION

Atmospheric particulate matter is known to have significant effects on human health and on global climate forcing.[1−3] Organic aerosol (OA) represents 20−90% of atmospheric particulate matter[1] and consists of a complex mixture of tens of thousands of compounds.[4] The elemental and structural composition of these organic compounds drives their health and environmental impacts. For example, functional groups like organic peroxides are suspected to form reactive oxygen species in the body that may cause cellular oxidative stress.[5] Functional groups that increase a compound's hygroscopicity (e.g., hydroxyl and carboxylic acid) may increase a particle's propensity to act as a cloud condensation nucleus.[5]

Characterizing the functional group distribution of OA can help in constraining reaction pathways and products in the atmosphere,[6,7] evaluating models, and ultimately improving our understanding of the impacts of OA. Several methods are used to measure functional groups in atmospheric samples, including Fourier transform infrared spectroscopy (FTIR),[6,8−10] nuclear magnetic resonance (NMR),[11−13] spectrophotometric methods,[14] and tandem mass spectrometry (MS/MS).[7,15,16]

FTIR and NMR are widely used. FTIR has low time resolution and cannot provide compound-specific information for components of a complex mixture.[3,16] However, it is capable of analyzing ∼80% of OA mass and accurately quantifying several of the most atmospherically relevant functional groups (e.g., hydroxyl and carbonyl).[3] NMR's strengths are similar to FTIR's, but there are challenges associated with high detection limits and identifying functional groups in complex mixtures.[5,7,15]

Several studies use MS/MS, often with derivatization to improve compound detection. This limits these studies to functional groups that can be derivatized in a specific and reliable manner (e.g., hydroxyl, carbonyl, and carboxylic acid), without causing unwanted side reactions.[5] Many past studies that used MS/MS have sought to discern oxidation pathways

and products linked to a targeted set of precursors or functional groups.[17−23]

Here, we perform a nontargeted analysis of OA functional groups across three ambient sites using liquid chromatography with electrospray ionization and high-resolution quadrupole time-of-flight tandem mass spectrometry (LC-ESI-Q-TOF) without prior derivatization. The objectives of this work are (1) to evaluate the distribution of oxygen-, nitrogen-, and sulfur-containing functional groups in OA collected at three diverse field sites (urban inland, urban coastal, and forested), (2) to compare the functional group distribution across times of day, seasons, and locations, and (3) to compare our results to the current understanding of primary and secondary sources of these functional groups. The broader goal of this study's molecular-level data and OA composition analysis is to inform laboratory, ambient, and modeling research that aims to study the evolution of complex OA mixtures.

MATERIALS AND METHODS

OA samples were collected at three ambient sites. Summer 24 h $PM_{2.5}$ samples were collected in a northern Michigan forest (henceforth "forest"). Daytime and nighttime summer and winter PM_{10} samples were collected near downtown Atlanta, GA, and on the Long Island Sound coast of Connecticut (henceforth "LIS") following previously described procedures.[24] Additional details are provided as Supporting Information (Supporting Information S1), including a discussion of solvent selection for filter extraction and analysis (Supporting Information S2).

All samples were analyzed by LC-ESI-Q-TOF, in both MS mode (TOF only) and MS/MS mode (tandem MS mode). MS mode instrument conditions, data processing, and quality control have been previously described.[24] Ions detected in MS mode that passed all stringent blank subtraction and peak and formula QC/QA criteria[24] were exclusively targeted for MS/MS using their m/z and retention time, in both positive and negative ionization mode. Both positive and negative mode data are shown here; when a compound was ionized in both modes, its abundance in each mode was averaged and it was included in the functional group tally only once. For detailed speciation of these complex mixtures, we used an equivalent ionization efficiency across compounds (Supporting Information S3). The filter extraction and sample ionization methods used here were tailored for functionalized compounds; thus, analyses were focused on functionalized primary organic aerosol (POA) and secondary organic aerosol (SOA).[24]

MS/MS spectra were imported to SIRIUS with CSI:Finger-ID for molecular structure prediction. We selected this software because of its strong performance at small-molecule identification in past studies[25−27] and in our evaluation with reference standards and known structures (discussed in detail in Supporting Information S4).

In SIRIUS, we limited ionization adducts to $[M + H]^+$, $[M + Na]^+$, and $[M − H]^−$, elemental composition to $C_{3−60}H_{4−122}O_{0−20}N_{0−3}S_{0−1}$, and mass tolerance to 7 ppm (Supporting Information S4).[24] Finally, we compiled the top-scoring candidate structure for each compound and used the APRL Substructure Search Program (developed by Ruggeri and Takahama) to enumerate atmospherically relevant functional groups (Figure S1) for which SMARTS patterns existed and performed accurately and reliably when tested with known structures.[28] In our analyses, the top-scoring structure was included in the functional group tally. However, we observed that the software generally produced a consistent functional group distribution across top-scoring hits, typically with only functional group position varying between the top candidates (i.e., the top candidates tended to be positional isomers, which are very challenging to distinguish with automated structural identification techniques[25]). See Figure S2 for a summary of methods and Table S14 for a summary of sampling campaigns.

The goal of this work was not to predict exact structures (which is not possible for large complex mixtures in a nontargeted analysis without additional information). Instead, we relied on quality-controlled accurate ion masses from high-resolution MS analysis for MS/MS data acquisition and focused on functional group identification (Supporting Information S4).

This multicampaign study complements past FTIR and NMR studies; while in some respects, these results are less quantitative than those of past FTIR and NMR studies due to challenges with predicting exact ionization efficiency for individual multifunctional compounds, they leverage the chemical detail from MS/MS analysis to provide molecular-level functional group composition data for a broad set of oxygen-, nitrogen-, and sulfur-containing features across compounds in complex OA mixtures. These methods are synergistic, and a combination of them used across ambient and laboratory platforms provides a powerful tool for improving our understanding of OA structural composition.

RESULTS AND DISCUSSION

We observed a diverse range of oxygen-, nitrogen-, and/or sulfur-containing functionalities (Figure 1) and carbon backbone structures (abstract graphic). Many of these functional groups have been discussed in smaller subsets in past studies (referenced below). Here, we analyzed the relative prevalence of 30 key functional groups together, using molecular-level MS/MS data to evaluate changes in functional group distribution across times of day, seasons, and sites (Figure 2). These OA functional groups were formed by gas-phase chemistry with subsequent aerosol uptake, by aqueous-phase chemistry (given the prevalence of aerosol liquid water in the Eastern United States),[29] and/or potentially by other condensed-phase chemistry. Unless otherwise specified, results discussed here are weighted by ion abundance.

Oxygenated Hydrogen-Bonding Groups Dominate the Functional Group Distribution. Figure 1 includes many oxygen- and nitrogen-containing functional groups that are intermolecular hydrogen bond donors and/or acceptors (e.g., hydroxyls, carbonyls, carboxylic acids, esters, amines, imines, and amides). Here, we observed the dominance of hydroxyls and carboxylic acids across sites, which may participate in hydrogen bonding and thus impact aerosol viscosity (and phase state)[32] and thermodynamic mixing behavior.[33]

Hydroxyl Groups. Hydroxyl groups were prominent across all campaigns, consistent with important known oxidation pathways (e.g., C=C OH[•] addition, isomerization, autoxidation, and $RO_2^{•}$ + $RO_2^{•}$ reactions).[3] In addition, hydrolysis reactions at sites with high aerosol liquid water concentrations may increase hydroxyl group prevalence (e.g., via hydrolysis of carbonyls[9−41] or organonitrates[34] to yield the corresponding alcohol). Variance in hydroxyl group contribution occurred between sites. At the LIS site, hydroxyl groups ranged from 53% to 69% relative prevalence (Figure 1B), while they remained below 40% at the Atlanta and forested sites (Figure 1A,C) with the exception of Atlanta winter daytime results.
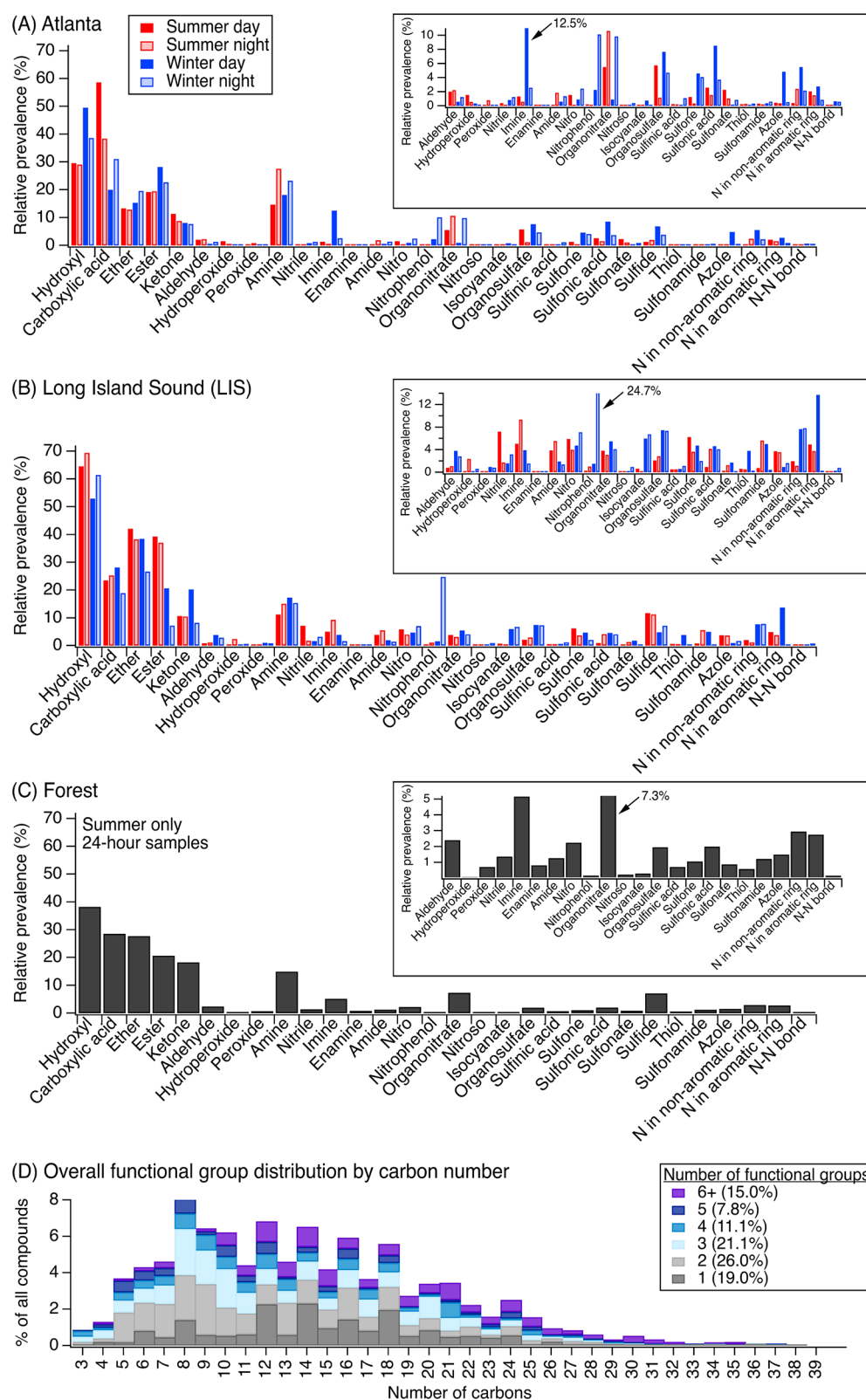
Figure 1. Relative abundance of organic aerosol functional groups across times of day, seasons, and sites, where the percentage of observed compounds containing one or more of each functional group is shown weighted by ion abundance. Campaign averages are shown for (A) the Atlanta summer and winter campaigns (PM$_{10}$), (B) the LIS summer and winter campaigns (PM$_{10}$), and (C) the forest campaign (PM$_{2.5}$). Insets provide a magnified view of less prevalent functional groups. These are the results of a nontargeted MS/MS analysis, in which we did not explicitly target any particular known or suspected oxidation products. Tables S1−S4 show associated relative prevalence data. For comparison, results tabulated by functional group occurrence (i.e., unweighted by ion abundance) are shown in Figure S3. On average, differences in the relative prevalence of groups between occurrence and abundance-weighted approaches were small (2 ± 3%), and most abundance-weighted results were slightly lower than the corresponding results by occurrence (i.e., 63%, 31%, and 6% of abundance-weighted results were lower than, higher than, or equal to those by occurrence, respectively). Results for peroxides, hydroperoxides, and highly reactive functional groups are lower limits due to

Figure 1. continued

possible degradation or transformation on the filter surface during sampling, during filter storage or extraction, or during MS analysis.[30] (D) Eighty-one percent of compounds observed across all campaigns were multifunctional and contained two to five functional groups. This figure shows the average distribution of functional group occurrence by carbon number; results for each individual campaign are shown in Figures S4−S6. Past work modeling aged urban and biogenic OA shows a similar range of carbon numbers and degree of functionalization, though in our ambient data we observe a fairly even degree of functionalization across carbon numbers, while modeled data show a larger contribution from more functionalized compounds with fewer carbon atoms.[31]

The LIS site was meters from the ocean; the increased prevalence of hydroxyl groups may suggest the influence of primary carbohydrates from dissolved organic carbon in seawater (from bubble bursting at the surface, which could result in hydroxyl and ether groups)[6] or chemical processing that favors hydroxylation during overwater transport to the site. Polyols were important across sites; they contributed on average $27 \pm 14\%$ and as much as 50−51% at the LIS site in the summer.

Carbonyls and Carboxylic Acids. While ketones and aldehydes are formed by chemical pathways similar to those of alcohols,[3] they combined to total only 9−24% here, perhaps due to an increased importance of isomerization,[3,35] aqueous-phase hydrolysis (see Hydroxyl Groups),[36−38] and/or the relative importance of OH• and $NO_3^•$ oxidation (which may produce carbonyls)[3,39] versus ozonolysis (which tends to produce carboxylic acids).[3,40] Carboxylic acids were prominent at the Atlanta site in the summer, where they contributed more during the day (59%) than at night (39%). Two prominent formation pathways include gas-phase ozonolysis and aqueous-phase OH•-initiated oxidation under high-NO_x conditions.[38] Ozone may also be an important oxidant at the LIS site, where ozone concentrations are high in the summer due to precursor transport from New York City and land−sea interactions.[41] Lower carboxylic acid prevalence at the LIS site (19−28%) compared to that in Atlanta (Figure 2E and Figure S7E) may be related to oligomerization at the LIS site (see Evidence for Oligomerization Processes).

Prevalence of Nitrogen- and Sulfur-Containing Functional Groups beyond Organonitrates and Organo-sulfates. While organonitrates and organosulfates are prominent in OA, we observed 88% of nitrogen and 79% of sulfur to exist in other functional groups (Figure S18). This highlights the diversity in sources and chemistry of nitrogen- and/or sulfur-containing compounds and underlines the need to consider the breadth of heteroatom-containing compounds and their formation pathways in future studies.

Organonitrates. Organonitrates are ubiquitous in the atmosphere.[39] These are formed by $NO_3^•$ oxidation at night or by reaction with OH• and then NO during the day (i.e., $RO_2^• + NO$).[39,42−44] Past measurements of organonitrates in the southeast United States reported 3−12% organonitrate prevalence in PM_1 OA during the summer and ≤25% in winter.[39,45,46] Consistent with past results,[45−47] we observed a nighttime PM_{10} contribution of 10−11% in Atlanta, versus 1−6% during the day.

At the LIS site across seasons, the relative prevalence of organonitrates was 3−6% and generally slightly greater during the day. While this diel trend is opposite to that commonly observed in the southeast United States, NO_x concentrations at the LIS site in the summer and winter were low ($\sim 1 \pm 2$ and 4 ± 6 ppb, respectively, versus ∼15 and ∼50 ppb, respectively, near Atlanta[45]), which could increase the importance of daytime $RO_2^• + NO$ pathways versus nighttime $NO_3^•$ pathways at the LIS site.

Organonitrates at the forested site represented 7% of $PM_{2.5}$ abundance, similar to past estimates of 9% of PM_1 OA at a Colorado forested site (BEACHON-RoMBAS).[39] While NO_x concentrations in the forest were low (median daytime [NO] of ≈23 ppt[48]), BVOCs like isoprene and monoterpenes are known to be major contributors to particulate organonitrates via $RO_2^• + NO$ or $NO_3^•$ pathways.[39,42,43,49]

Our reported contributions of organonitrates may be underestimated due to hydrolysis on filters during sampling. Primary/secondary organonitrates are relatively stable against hydrolysis, in contrast with tertiary organonitrates that hydrolyze in minutes to hours depending on pH (filter samples were collected over 8 or 23 h).[34,39,50−56] In addition, the fraction of organonitrates that can undergo hydrolysis varies and is larger for OH•-derived than for $NO_3^•$-derived organonitrates.[55] As mentioned in Hydroxyl Groups, organo-nitrate hydrolysis may slightly increase the hydroxyl group contribution.

Amines. Amines were important across all campaigns, similar to previously reported contributions of ∼5−20% at a range of ambient sites.[6,8,12,57−60] Mechanisms have been proposed for amine formation via reaction with atmospheric ammonia[61] and for the reaction of monoterpene-derived oxidation products with small gas-phase amines to yield a variety of nitrogen- and oxygen-containing products (where the amine replaces a carbonyl or acid on the existing oxidation product and is reported to occur with other carbonyl/acid groups on multifunctional compounds).[62] Here, we observed $23 \pm 8\%$ of amines paired with carboxylic acids and $5 \pm 3\%$ paired with carbonyls (Figures S8−S10 and Tables S5−S13). Amine contributions were notable at each site (11−28%), while carbonyl contributions remained relatively low (9−24%). Together, this could suggest amine replacement of carbonyls to yield nitrogen-containing (and potentially oxygen-containing) structures in the ambient atmosphere.[61,62]

We observed an increased amine contribution at night in Atlanta and in the summer LIS data compared to during the day (Figures 1A,B and 2A,B); this may be driven by a buildup of primary emissions in the nocturnal boundary layer and/or by chemical reactions that depleted daytime amine concentrations (e.g., via photolysis, reaction with OH• in the presence of NO_x,[63] reaction with O_3,[64] reaction with organic acids to form amides,[65,66] reactions with carbonyls to form imines and enamines,[62,67−69] and multistep ozonolysis pathways that may yield organonitrites and organonitrates[69,70]).

Other Nitrogen-Containing Groups. Across all sites, we observed contributions of imines (1−13%) and amides (0.1−6%), which may form when amines/ammonia react with carbonyls or acids, respectively (see Amines). Nitro/nitro-phenol groups were observed at multiple sites and can be formed chemically by aqueous-phase nighttime nitration of catechols by HNO_2[71] and by gas-phase reactions of aromatics
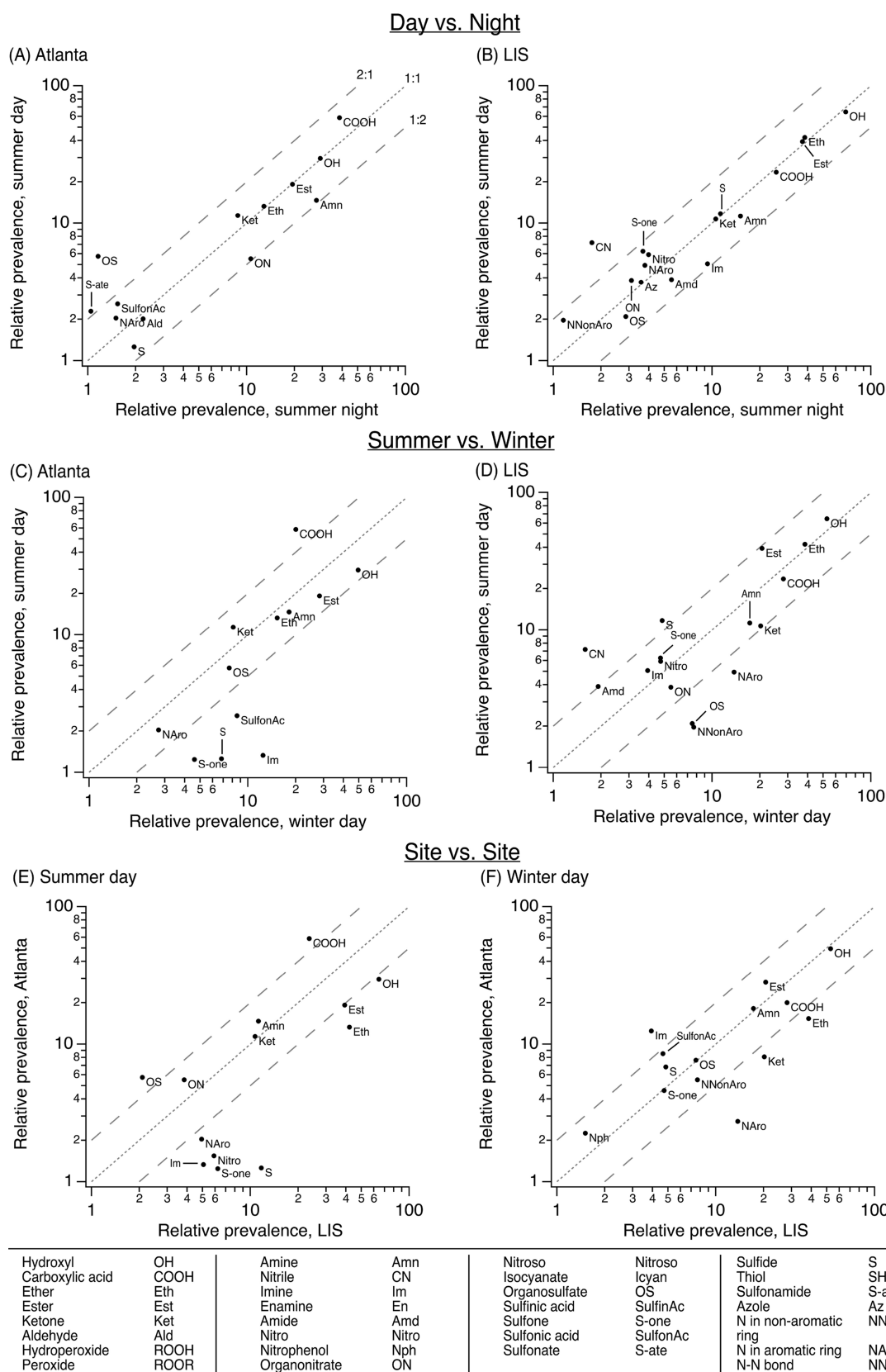
Figure 2. Select comparisons of times of day, seasons, and sites, showing the percent relative prevalence of frequently occurring functional groups (with >1% relative prevalence, weighted by abundance). These data are average relative prevalence values across each campaign, weighted by ion abundance. Points above the 1:1 line indicate a greater prevalence during the sampling period described on the *y*-axis, while points below the 1:1 line indicate a greater prevalence during the sampling period described on the *x*-axis. Prominent diel variations existed for some functional groups but were subtle for others, while greater differences existed seasonally and geographically. Additional relative prevalence visual comparisons are shown in Figure S7.

with OH$^{\bullet}$ and subsequent NO$_2$ addition (whose products peak at night and partition to the particle phase at low temperatures).[72,73] While we observed minimal nitro/nitrophenol group contributions in the forest where NO$_x$ concentrations were low, we observed notable contributions in Atlanta and especially LIS winter nighttime samples, perhaps due to a combination of NO$_x$ emissions with aqueous- and/or gas-phase chemistry (along with low temperatures and thus increased partitioning of gas-phase products to the particle phase). Nitrophenols can then undergo heterogeneous oxidation by OH$^{\bullet}$ and photolysis during the day, decreasing their daytime prevalence.[72–75] Nitro/nitrophenol groups may also be directly emitted in diesel exhaust, from wood combustion, and from consumer product solvents;[7,76] however, their prevalence here in urban air/outflow warrants further study of their ambient formation under dark, wet conditions given that nitrophenols have well-known health and environmental impacts.[73]

Organosulfates and Other Sulfur-Containing Groups. We observed an organosulfate prevalence of 1–8% of PM abundance across sites. In the southeast United States, organosulfates have been reported at 15.5% of PM$_{2.5}$ organic carbon in Atlanta (in 2015) and 7.3% at one rural forested location (in 2013).[77] Our results are similar to National Park IMPROVE estimates of an upper bound contribution of 5–10% organosulfates to total organic mass, with a range of values across sites and seasons.[78] Contributions at the LIS site, where SO$_2$ concentrations were low (<1 ppb), increased from summer (2–3%) to winter (7–8%). This may be driven by a slight increase in SO$_2$ concentration and thus the concentration of the organosulfate precursor H$_2$SO$_4$ in winter.[79] On average, organosulfates represented 21% of all sulfur-containing groups; the remaining 79% included sulfones, sulfonates,[77,80–82] sulfonic acids,[82,83] sulfonamides, sulfides, and sulfinic acids.[83]

Evidence for Oligomerization Processes. While esters and ethers have diverse direct sources, their presence may suggest that oligomerization processes are important at these sites, particularly at the LIS site (7–39% esters and 27–42% ethers).[20,84–88] Aged OA sampled downwind of urban areas (e.g., New York City) may be enriched with esters and thus correspondingly depleted of carboxylic acids (and possibly hydroxyls, if the combining compounds do not contain additional hydroxyls, which is unlikely on the basis of polyol prominence).[6] Also, past work has linked increased prevalence of ethers along with hydroxyls to oligomerization reactions in wet aerosol (both prominent at the LIS site (Figure 1)).[87]

These esters and ethers tended to occur in multifunctional compounds (Figures S8–S10) with low or extremely low volatility (Figure S12) and a molecular weight consistent with the mass range of terpene-derived SOA dimers (315 and 336 amu, respectively (Figure S11)),[89] supporting the case that these functional groups occurred due to oligomerization (versus direct emissions).

Multifunctional Compounds Highlight a Significant Degree of Chemical Processing. Across all campaigns, an average of 81% of compounds were multifunctional (Figure 1D and Figure S13); the fraction of compounds at all sites with one (19 ± 7%) or two (26 ± 7%) functional groups suggests that only a subset of functionalized OA could be the result of one or two generations of oxidation. This highlights the degree to which this OA is aged and was particularly notable for the LIS summertime samples (89% multifunctional (Figure S13)).

Compounds containing oxygen, nitrogen, and sulfur functionalities (CHONS) are of note, as their presence has been previously reported,[24,90–95] though little is known about this compound class. While we observed a few functional groups that contained both nitrogen and sulfur (e.g., sulfonamides (0.2–6%), some azoles (0.1–3%)), CHONS compounds tended to be multifunctional with a combination of oxygen-, nitrogen-, and/or sulfur-containing features (Figures S8–S10). An analysis of survival yield to evaluate parent ion stability[96–98] showed that in general, multifunctional compounds tended to fragment more readily than monofunctional compounds (Figures S14–S16).

In summary, we characterized the diversity of multifunctional compounds at three ambient sites; we observed the dominance of hydroxyl and carboxylic acid groups, notable contributions from esters and ethers that suggest the importance of oligomerization, functional groups that suggest the prominence of aqueous processing (e.g., nitrophenol, prominence of hydroxyl groups relative to carbonyls), and a variety of nitrogen- and sulfur-containing groups beyond organonitrates and organosulfates. These molecular-level measurements enable a detailed investigation of the chemical structures in ambient complex OA mixtures, including an analysis of co-occurring functional groups (e.g., Figures S8–S10). These results and data will help inform future studies across ambient, laboratory, and modeling platforms, will help constrain chemical oxidation pathways and resulting OA properties (e.g., phase state[99,100]) in the atmosphere, and will provide additional bases for evaluating chemical models that aim to simulate OA composition across multiple generations of oxidation.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.9b00702.

> Details of supplemental methods, functional group structures, method summary flowchart, functional group distribution tallied by occurrence, distribution of functional group count by carbon number for each site, additional visualizations of relative prevalence comparisons across times of day, seasons, and sites, functional group pairing analysis, molecular weight distributions, volatility distributions, prevalence of monofunctional compounds, and survival yield analysis (PDF)

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Author Contributions

J.C.D. and D.R.G. designed the study and led analyses. J.C.D. collected samples at the LIS site. T.J. and N.L.N. collected samples at the Atlanta site. J.H.S. and P.B.S. collected samples at the forested site. J.C.D. analyzed all data and compiled results. J.C.D. and D.R.G. wrote the paper, and all authors contributed to refining the manuscript.

Notes

■ ACKNOWLEDGMENTS

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