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Article

Chemical Signatures of Seasonally Unique Anthropogenic Influences on Organic Aerosol Composition in the Central Amazon

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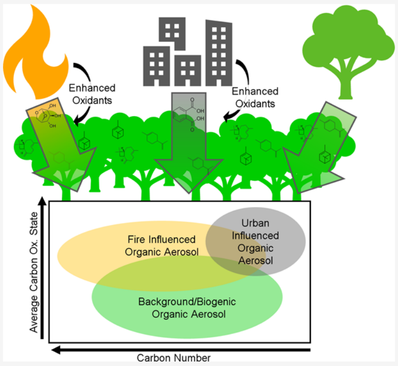
ABSTRACT: Urbanization and fires perturb the quantities and composition of fine organic aerosol in the central Amazon, with ramifications for radiative forcing and public health. These disturbances include not only direct emissions of particulates and secondary organic aerosol (SOA) precursors but also changes in the pathways through which biogenic precursors form SOA. The composition of ambient organic aerosol is complex and incompletely characterized, encompassing millions of potential structures relatively few of which have been synthesized and characterized. Through analysis of submicron aerosol samples from the Green Ocean Amazon (GoAmazon2014/5) field campaign by two-dimensional gas chromatography coupled with machine learning, ~1300 unique compounds were traced and characterized over two seasons. Fires and urban emissions produced chemically and interseasonally distinct impacts on product signatures, with only ~50% of compounds observed in both seasons. Seasonally unique populations point to the importance of aqueous processing in Amazonian aerosol aging, but further mechanistic insights are impeded by limited product identity knowledge. Less than 10% of compounds were identifiable at an isomer-specific level. Overall, the findings (i) provide compositional characterization of anthropogenic influence on submicron organic aerosol in the Amazon, (ii) identify key season-to-season differences in chemical signatures, and (iii) highlight high-priority knowledge gaps in current speciated knowledge.



KEYWORDS: *secondary organic aerosol, air pollution, urbanization, biomass burning, cheminformatics*

INTRODUCTION

Anthropogenic activities influence the composition and properties of ambient fine aerosol material under a broad array of conditions, with effects that are heavily dependent upon both the location and types of disturbances caused by humans and the composition and quantities of local natural emission sources. In the central Amazon, two broad classes of human activities have been shown to perturb the quantities and characteristics of fine aerosols: urbanization, and biomass burning.[1−4] These perturbations are important because both have been demonstrated to significantly influence aerosol radiative forcing.[1,5,6] Biomass burning during the Amazonian dry season causes $PM_{2.5}$ levels to frequently exceed World Health Organization guidelines and has been associated with adverse public health outcomes for residents of the central Amazon.[7,8] In the central Amazon, fires are nearly entirely anthropogenic in nature. The high humidity and frequent rainfall make natural sources of fires extremely infrequent and unlikely, and fires are set to clear land for soybean cultivation and cattle farming.[7,9,10] Burning activity is most intense during the dry season, which lasts from approximately August to October in the central Amazon.[1,3] In addition to experiencing elevated biomass burning emissions, atmospheric residence times during the dry season are longer. These factors together contribute to dry season aerosol concentrations that are approximately an order of magnitude higher than the wet season, with a more oxidized bulk composition.[2,3,11]

The Amazonian wet season, which typically lasts from late January to mid-April in the central Amazon, is characterized by frequent rain, less significant biomass burning activity, and low particle number and mass concentrations.[2,12] Because of the reduced influence of fires, perturbations from the more interseasonally consistent source of urban areas become more important during the wet season. In regions downwind of cities, urban emissions produce substantial changes in the composition

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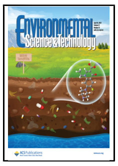

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and quantities of organic aerosol.[2] The enhancement of organic material in Amazonian regions downwind of cities, specifically the city of Manaus, has been studied through varying combinations of models and observations.[2,4,11,13−19] While some of the increases can be attributed to primary organic emissions from the city and formation of secondary aerosol material from anthropogenic organics,[18] the formation of SOA from biogenic volatile organic compounds (BVOCs) is also found to increase under influence from the urban plume and thereby contributes to elevated aerosol formation. The mechanisms driving these enhancements are incompletely characterized, and recent efforts to reproduce the enhancements using explicit molecular-based models were not able to reproduce observed enhancements, although parameterized approaches have been more successful.[4,16] This indicates that our current understanding of how urban emissions impact biogenic SOA formation at the compound-specific level does not adequately capture real ambient dynamics.

The organic composition of the atmosphere is extremely complex, with the number of potential secondary and tertiary products that can theoretically be produced from well-characterized reactive gas-phase precursors extending into the millions.[20,21] This complexity makes identifying key reaction pathways highly challenging, such as those pathways that produce urban influenced biogenic SOA enhancement in the Amazon. Controlled laboratory experiments provide opportunities to better understand the complexity of ambient conditions by simplifying systems down to individual components which can enable the identification of key tracers of influence from a given precursor, but these controlled experiments are often conducted under conditions that are extremely dissimilar from reality. As reported in Porter et al., 2021, the vast majority of chamber oxidation experiments are carried out under conditions that are far drier and more concentrated and have higher NO_x than the environments in which the vast majority of Earth's SOA is formed, including the central Amazon.[22] Aqueous processing, which occurs when water-soluble organics partition into droplets and undergo aqueous-phase chemical reactions, is a potentially important mechanism controlling the composition of secondary organic material, particularly under humid conditions.[23−25] However, the mechanisms by which aqueous processing alters the chemical fate of important precursors and the effects under ambient conditions in the Amazon remain incompletely characterized.

Given its global importance, organic aerosol from the Amazon rainforest has been analyzed for isomer-specific composition with varying foci and degrees of complexity. Previous targeted approaches include speciation of four tracers of specific aerosol source groups,[26] as well as broader approaches investigating high-molecular-weight compounds including alkanes, alkanoic acids, PAHs, and alcohols,[27] and water-soluble organic carbon in smoke.[28] These approaches are summarized in Martin et al.[29] The number of compounds reported in the latter two works are in the mid-10's, and challenges related to the large fractions of organic mass that cannot be attributed to identifiable compounds are referenced.[30] Analysis of aerosol organic bulk composition by methods including aerosol mass spectrometry (AMS) has been utilized to great effect to identify sources and characteristics of Amazonian organic aerosols,[2,3,18,31] but these measurements do not yield the same insights into mechanisms and unique sources as structure-specific techniques. In this work, the combination of high-resolution chromatography-mass spectrometry and machine learning enables enhanced characterization of over 1300 unique compounds, a significant step forward building on these previous analyses.

The present study investigates the organic composition of submicron aerosol at a speciated isomer-specific level to achieve the following goals: First, to identify the compositional fingerprints of anthropogenic influence on aerosol composition and compare these influences across seasons. Second, to identify critical knowledge gaps between compounds catalogued in mass spectral databases and real ambient aerosol organic material produced under unique conditions, and isolate key novel compound populations that provide insights into the mechanics of anthropogenic perturbations of biogenic secondary aerosol formation.

■ METHODS

Collection of Submicron Aerosol Samples at GoAmazon2014/5. During the GoAmazon2014/5 field campaign, submicron aerosol samples were collected on quartz filters at the T3 semiremote site in the central Amazon. Samples were collected using a sequential sampler described in Yee et al., 2019,[32] and filters were stored frozen at −20 °C prior to analysis. Wet season samples were collected with 12 h resolution and dry season samples were collected with 4 h resolution. 54 wet season samples spanning 27 days of measurements between 8 February and 20 March 2014 were selected for analysis from the wet season, while 129 samples (equating to 21.5 days of analysis) from between 8 September and 11 October were selected from the dry season. A full description of sampling infrastructure is provided in Supporting Information SI.1.1.

TD-GCxGC-EI-ToF-MS Analysis. Filter samples were analyzed by thermal desorption two-dimensional gas chromatography coupled with electron ionization time-of-flight mass spectrometry (TD-GCxGC-EI-ToF-MS). This analytical technique is described in detail in Supporting Information SI.1.2. Briefly, aliquots of filter material are introduced into the thermal desorption unit of the instrument (Gerstel), where they are gradually heated under a continuous carrier gas flow of helium enriched with the derivatization agent *n*-methyl-*N*-trimethylsilyl trifluoroacetamide to thermally desorb organic constituents from the filter material. This method enhances the recovery of polar organics and minimizes the thermal decomposition of labile molecules.[33] The potential for artifacts is discussed in greater detail in SI.1.2. Desorbed analytes are separated by two-dimensional gas chromatography (Agilent and Zoex), and separated organics are ionized by 70 eV EI and detected using HR-ToF-MS (Tofwerk, m/Δm = 4000). An example TD-GCxGC-EI-ToF-MS chromatogram is illustrated in Figure S1.

Data Analysis and Chemical Properties Modeling. From 11 samples representing a range of conditions across both seasons (Table S1), a library of 1325 unique organic compounds were compiled. Artifacts including thermal decomposition products can occur in analysis methods involving heat, but the characterization of such artifacts is very much limited by the availability/existence of authentic standards of thermally labile compounds that can be tested for this phenomenon, and as such remains a very active area of research. That said, the possibility that some of the analytes observed here are decomposition products rather than the compounds present in the atmosphere cannot be entirely ruled out. Still, these observed compounds can be useful indicators of chemical sources and pathways. This limitation and prior work characterizing thermal decomposition in GC-MS methods is discussed in greater depth in SI.1.2. The

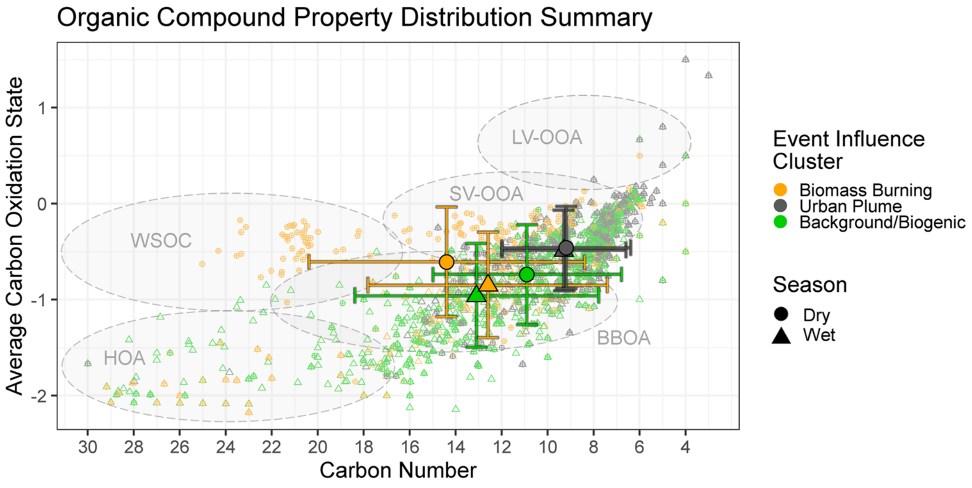

Figure 1. Summary of chemical properties of organic compounds speciated and traced over the wet and dry seasons of the GoAmazon field campaign. Small markers indicate individual observed organics, with shape and color indicating season and assigned influence group. Carbon numbers of not identifiable compounds are predicted on a continuous scale, and predicted carbon numbers are therefore not restricted to integer values. Large marker positions indicate the unweighted average properties of each population of compounds in $\overline{\mathrm{OS}}_{\mathrm{c}} - n_{\mathrm{c}}$ space, and error bars indicate the standard deviation of each property for each grouping. Compounds are assigned to influence clusters of biomass burning (orange), urban plume influenced (dark gray), and background/biogenic (green). Light gray text and outlines indicate regions of ambient organic aerosol classes reported in Kroll et al.,[34] with BBOA indicating biomass burning organic aerosol, WSOC indicating water-soluble organic carbon, and SV-OOA indicating semivolatile oxidized organic aerosol, LV-OOA indicating low-volatility oxidized organic aerosol, and HOA indicating hydrocarbon-like organic aerosol.

compounds were traced across all samples from both seasons. Compounds were grouped into clusters of similar temporal variability using dynamic time warping hierarchical clustering, and these clusters were identified as urban influenced, biomass burning influenced, or background based on comparisons to supporting measurements, in particular previously published aerosol mass spectrometer organic composition factorization,[2,3] and literature review of identifiable constituents in each cluster. Where possible, compounds were identified through comparisons to authentic standards analyzed on the GCxGC instrument and comparisons between mass spectra of observed compounds and entries in the NIST14 mass spectral database. For identifiable compounds, carbon number and average carbon oxidation state were directly calculated from the chemical formula. For not identifiable compounds, chemical properties were predicted using a machine learning-based model, Ch3MS-RF, which predicts chemical properties (vapor pressure, carbon number, average carbon oxidation state, and oxygen-to-carbon ratio) and quantification factors from mass spectra and retention indices. Additional information on data analysis and properties modeling is provided in Supporting Information SI.1.2.

■ RESULTS AND DISCUSSION

Anthropogenic Perturbations of Aerosol Chemical Property Distributions. Biomass burning influenced, urban influenced, and background/biogenic compounds occupy different though overlapping areas of chemical properties space. Each influence source cluster contains a diverse group of species and the chemical property spaces of each population overlap, as indicated by the overlapping standard deviation bars in Figure 1. However, differences between property distributions of each population of compounds (both interseasonally and between influence source groups in each season) are statistically significant (t-test p-values <.05), with the following exceptions. The wet and dry season urban influenced clusters are not significantly different in either dimension, and the average carbon numbers of wet season burning influenced and background/biogenic compounds are not significantly different.

As illustrated in Figure 1, urban influenced organics inhabit consistently lower carbon number and more oxidized regions of $\overline{\mathrm{OS}}_{\mathrm{c}} - n_{\mathrm{c}}$ space compared to the other influence categories, with an average carbon number of 9.3 and average carbon oxidation state of −0.49 in the wet season and an average carbon number of 9.2 and average carbon oxidation state of −0.46 in the dry season. The urban influenced clusters are also most tightly grouped with respect to carbon number, with carbon number standard deviations of 2.7 and 2.8 (wet and dry seasons, respectively), compared to standard deviations consistently >4 for all other groupings. This phenomenon is illustrated in the example sample distribution mappings provided in Panel B of Figures S2 and S3. Given the general description of precursor oligomerization, fragmentation, and functionalization outlined in Kroll et al., 2011,[34] this is likely indicative of higher degrees of fragmentation in the secondary aerosol formation pathways forming these products. Different precursors could also contribute to the differing distributions, but the fraction of urban influenced SOA coming from biogenic precursors[4] would share the precursors of the background cluster, rendering comparisons between the background/biogenic and urban clusters particularly informative. Higher degrees of fragmentation relative to functionalization and oligomerization could at least partially contribute to the phenomenon reported in Shilling et al., 2018,[11] which found less organic aerosol mass enhancement from secondary aerosol formation than expected in the GoAmazon urban plume.

The position of the average chemical properties of both sets of urban attributed measurements, comparisons between urban influenced compounds and those produced in chamber oxidation studies, and the temporal dynamics of specific well-characterized tracers of monoterpene oxidation chemistry all point to likely contributions of alterations in monoterpene oxidation chemistry to aerosol enhancement under urban influenced conditions. These findings provide observational

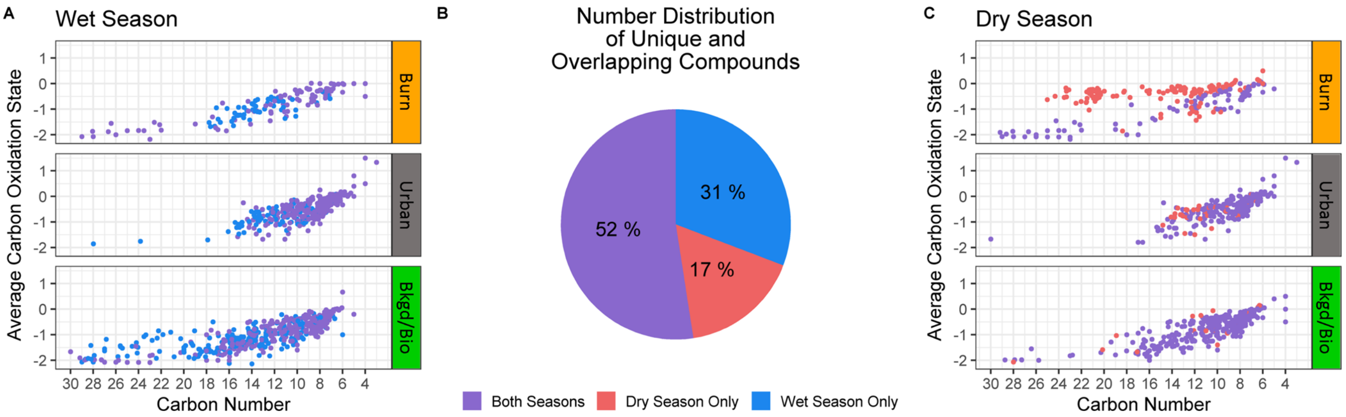

Figure 2. Compositional analysis of seasonally unique (exclusively observed in either the wet or dry seasons) and commonly observed organic compounds from GCxGC analysis of submicron aerosol collected during the GoAmazon field campaign. (A) Properties distributions of wet season compounds in $\overline{OS_c} - n_c$ space segregated by the event source clusters to which those compounds were assigned, with unique compounds indicated in blue and commonly observed products illustrated in purple. (B) Fractional contribution of wet season unique, dry season unique, and consistently observed species to the total number of compounds traced. (C) Properties distributions of dry season compounds in $\overline{OS_c} - n_c$ space segregated by the event source clusters to which those compounds were assigned.

support for and mechanistic insight into previous model-based work proposing this phenomenon in the Amazon.[4] At an average carbon number of slightly greater than 9, more than half of the products attributed to urban influence have 10 or fewer carbons, placing them within the chemical properties spaces of previously established oxidation pathways for monoterpenes in chamber conditions.[34,35] This is supported by the identification of >30 urban influence cluster products in SOA from laboratory oxidation of monoterpene precursors, as described in Supporting Information SI.1.4 and SI.2.3. These matched compounds are significant contributors to the total urban influenced organic mass, making up 22% of recovered urban influenced organic aerosol mass in the wet season and 24% in the dry season. Only four of these matched compounds are identifiable, which limits the scope of mechanistic insights which may be gained from direct comparisons between chamber and ambient samples. However, the temporal behavior of known monoterpene oxidation tracers both within and beyond the scope of products produced in the chamber oxidation studies supports the importance of anthropogenic influence for the oxidative fate of monoterpenes. In addition to the monoterpene ozonolysis products, MBTCA, a tracer for monoterpene oxidation by the hydroxyl radical,[36] was assigned to urban influence clusters in both seasons. Pinonic acid, which was identified in the monoterpene ozonolysis chamber samples and has been characterized as a tracer of monoterpene oxidation by both ozonolysis and OH oxidation,[33,37,38] followed an urban influenced variability pattern in the wet season but was not associated with anthropogenic influence in the dry season. Some enhancements in aerosol-phase monoterpene oxidation products could be attributable to partitioning onto the surfaces of primary anthropogenic aerosols and SOA from anthropogenic precursors rather than chemistry. However, inconsistencies between enhancements in different monoterpene oxidation products do not support this as a dominant enhancement mechanism. Pinic acid, an OH oxidation product of both α-pinene and β-pinene,[37] was observed in both seasons but was not associated with anthropogenic influence in either. Pinic acid falls between Pinonic Acid and MBTCA across a range of properties relevant to partitioning and physical mixing state (vapor pressure, octanol−air partitioning coefficient, air−water partitioning coefficient[39,40]), and would reasonably share the dynamics of the other monoterpene oxidation tracers if the urban influence enhancements were dominantly physical rather than chemical in nature. Together, these observations indicate the following: (i) the oxidant conditions in the urban plume shift biogenic precursor oxidation toward more oxygenated and lower carbon number products, (ii) these perturbation processes play an important role in the oxidative fate of monoterpenes, and (iii) perturbations are compound-specific among products sharing similar properties and precursors.

In contrast to the urban influenced compounds, biomass burning influenced products span a wide range of properties and demonstrate a significant interseasonal drift, with dry season burning products on average higher carbon number and more oxidized. This is primarily attributable to a population of high-carbon-number oxidized compounds that are present in the dry season but not the wet season, as will be discussed in greater detail in the Observations of Seasonally Unique Organic Aerosol Products section. Some of these products are observable in the example property distribution of a biomass burning influenced sample from the dry season, as illustrated in Figure S3 panel A. The burning influenced compound grouping contains a compositionally diverse suite of chemicals covering a particularly large range of carbon numbers, with carbon number standard deviations of 5.3 and 6.0 for the wet and dry seasons, respectively. This grouping includes products previously established as primary biomass burning products, two of which are listed in Table S2. These two well-characterized primary products, a 6-carbon sugar, levoglucosan,[41] and a 24-carbon alkanoic acid, tetracosanoic acid,[42] are illustrative of two disparate but consistently co-observed populations of biomass burning tracers, specifically low-carbon-number and highly oxidized sugars and high-carbon-number less oxidized alkanoic acids and hydrocarbons. Both groups can be seen in panel A of Figures S2 and S3. In addition to these previously characterized primary products, there are a large number of burning attributed compounds falling inside an intermediate region of $\overline{OS_c} - n_c$ space including regions typically representative of secondary organic aerosol products, as illustrated in the light gray ovals in Figure 1.[34] As discussed in the Diversity, Properties, and Importance of Unidentifiable Organics section, these com-

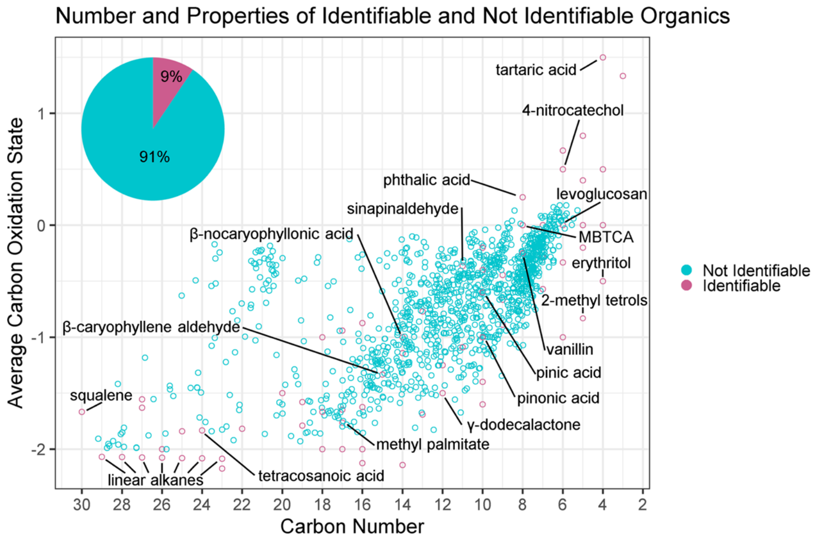

Figure 3. Chemical properties distributions in the $\overline{\mathrm{OS}}_c - n_c$ space of identifiable (pink) and not identifiable (teal) organic compounds identified in submicron aerosol collected at the GoAmazon field campaign. Identifiable compounds of interest are labeled in black. The percentage of identifiable and not identifiable compounds compared to the 1325 traced is illustrated by the pie chart in the top left. Carbon numbers of not identifiable compounds are predicted on a continuous scale and predicted carbon numbers are therefore not restricted to integer values.

pounds are largely not identifiable by mass spectral database match and represent opportunities for additional investigation into speciated secondary aerosol production from biomass burning precursors.

Background/biogenic compounds are by number the most diverse compound grouping, making up 40% of compounds traced in the dry season and 49% of compounds traced during the wet season. They cover ranges of both carbon number and carbon oxidation state properties similar to those assigned to biomass burning source groups. The seasonal compositional spaces of background/biogenic compounds are significantly different. As discussed in the Observations of Seasonally Unique Organic Aerosol Products section and illustrated in panel A of Figure 2, unique background products are observed in the wet season that are typically higher carbon number and relatively less oxidized. Overall, wet season background/biogenic products have higher carbon numbers and lower average carbon oxidation states compared to similarly categorized dry season products.

Previous work has established that the bulk organic composition of Amazonian submicron organic aerosol as assessed by AMS is more oxidized in the dry season.[2,3] While the composition of the urban influenced grouping remains statistically unchanged, the chemical distribution spaces of both biomass burning influenced and background/biogenic organic aerosol are significantly shifted toward more oxygenated species. While GCxGC analysis is not sensitive to the entire organic carbon pool and the compositional analysis presented in Figure 1 is not mass weighted, rendering the findings not directly comparable between speciated and bulk measurements, the general agreement between bulk and speciated observations highlights the utility of investigating speciated compositional shifts to better understand changes in bulk properties. Shifts in the compositional distributions indicate that not only the relative abundance of products formed but also the characteristics of products themselves play an influential role in interseasonal differences in the atmospheric chemistry of this region.

Observations of Seasonally Unique Organic Aerosol Products. Given that all samples were collected from the same location, the interseasonal consistency in the individual identities of submicron organic aerosol products detected was surprisingly low. Of the ~1300 compounds catalogued, only 52% were observed in both seasons. 31% of compounds were observed exclusively in the wet season, while 17% were observed exclusively in the dry season. This breakdown, along with the influence source breakdown and chemical properties distributions of seasonally unique and commonly observed compounds, is illustrated in Figure 2. Wet season unique species were more consistently present, with 48% observed in at least 10% of samples, while dry season unique compounds were episodic, with fewer than 20% observed in at least 10% of samples. While some of the interseasonal differences may be attributable to limits of detection (meaning that some "seasonally unique" products may have been present in the other season but always below detection limits), this does not diminish the relevance of the unique products observed. Importantly, species were only removed from analysis in early stages if they were not confidently observed in either season, and compounds were only classified as seasonally unique if they were never observed above detection limits in the other season.

Of the compounds exclusively observed in the dry season, most were attributed to biomass burning influences (75%), while 15% were attributed to urban influence and 10% attributed to background/biogenic sources. The compounds exclusively observed in wet season were mostly attributed to background/biogenic sources (61%), while 25% were attributed to urban influence and 14% were attributed to biomass burning influence. A quantitative analysis of organic aerosol mass attributed to seasonally unique species during the ~2 week continuous analysis periods of each season (Figure S4) reveals the following findings. Unique biomass burning attributed compounds of the dry season (Figure S4 panel B) dominate the seasonally unique mass concentrations but are highly episodic, particularly at the beginning of the analysis period. This is largely due to the significance and short duration of the appearance of the unique population of high-carbon-number oxidized compounds illustrated in the top left of Figure 2C, which appeared only under particularly intense burning influenced conditions. Based on their location in the $\overline{\mathrm{OS}}_c - n_c$ space, these compounds are likely high-carbon-number water-soluble organic carbon, which has been previously identified in biomass burning emissions and has been attributed to both primary emissions[43] and atmospheric oligomerization processes, specifically aqueous-phase photooxidation.[44] Examples of previously described water-soluble biomass burning products that fall into this $\overline{\mathrm{OS}}_c - n_c$ region and support the conclusion that the observed products are water-soluble and/or the result of aqueous chemistry include simple dimers of biomass burning intermediates. Syringol and guaiacol dimers, which have been observed under both ambient and laboratory conditions,[44−46] would fall into the lower carbon end of the unique biomass burning product distribution; syringol dimer and guaiacol dimer's properties in the dimensions illustrated in Figures 2 and 3 are $n_c = 16$, $\overline{\mathrm{OS}}_c = -.375$ and $n_c = 14$, $\overline{\mathrm{OS}}_c = -.43$, respectively. These compounds themselves may be present, but their identities cannot be confirmed due to a lack of available authentic standards and published derivatized mass spectra. The majority of the unidentifiable proposed water-soluble biomass burning products display mass spectral indicators of derivatization, indicating the presence of OH groups. Potential explanations for the unique observations of these compounds in the dry season include (i) preferential loss of these products to wet deposition during the wet season, likely to be particularly important due to their solubilities; (ii) production timescales requiring the longer atmospheric residence times and greater light availability typical of the dry season compared to the wet season; and (iii) differences in primary emissions from differing combustion conditions.[47,48]

During the wet season, uniquely produced biomass burning products contributed relatively little to the observed organic mass compared to the urban influenced and background/biogenic groupings, as illustrated in Figure S4. The wet season background/biogenic grouping contains a population of highly compositionally distinct products. These products, illustrated in the bottom left of Figure 2A, include a diverse group of high-carbon-number (>15) relatively low carbon oxidation state species. While previous work has identified the formation of high-carbon-number oligomers from aqueous processing of biogenic precursors in cloud droplets, the production of these products is predicted to increase in the presence of elevated urban oxidant conditions,[23,49] which is explicitly not the case for the compounds reported in this work. In fact, five of the highest-carbon-number, most oxidized members of this unique product group are anticorrelated with the urban plume tracer, producing Pearson correlation coefficients of <−0.4. Other potential explanations for this compound group include emissions of higher carbon number precursors, including sesquiterpenes and diterpenes.[32] As discussed in the Diversity, Properties, and Importance of Unidentifiable Organics section and mirroring the findings for the unique dry season biomass burning influenced products, the majority of these uniquely produced wet season biogenic species are not identifiable by database match, rendering further mechanistic insights into how these species are being produced challenging. That said, the presence and properties of interseasonally unique organic aerosol components point to differences in secondary aerosol formation processes that could guide the conditions (humidity, temperature, concentrations) for future laboratory oxidation experiments to replicate previously unmapped oxidation processes.

Diversity, Properties, and Importance of Unidentifiable Organics. Of the organic aerosol constituents catalogued in this work, very few were identifiable by match to an authentic standard or entry in the NIST/NIH/EPA mass spectral databases. Despite the compositional differences previously described, this observation was highly consistent between seasons: 91% of compounds traced during the wet season were not identifiable, while 90% of compounds traced in the dry season were not identifiable. This is consistent with findings from an analysis of on-line GC−MS data from the GoAmazon campaign, which found that approximately 90% of compounds observed could not be matched to entries in the NIST/NIH/EPA mass spectral database.[50] Of the three influence categories described in this work, urban influenced organics were by numbers the least well known, with 95% of dry season and 96% of wet season urban influenced compounds not identifiable by database match. Burning-associated compounds were consistently better known, with 85% of dry season and 83% of wet season biomass burning influenced species not available as standards or present in mass spectral databases, while the background/biogenic compounds fell in a middle ground, with 90% of wet season and 89% of dry season compounds not identifiable. The properties of identifiable and not identifiable compounds with annotations of notable identifiable compounds are illustrated in Figure 3. Both of the seasonally and compositionally unique populations described in the Observations of Seasonally Unique Organic Aerosol Products section, specifically the unique high-carbon-number dry season organics associated with biomass burning and the unique high-carbon-number wet season organics observed under background conditions were entirely not identifiable. The relevance of these species to the design of future oxidation experiments is discussed in the Implications for Future Laboratory Studies section.

The contributions of unidentifiable compounds to organic aerosol mass vary substantially but are consistently dominant under wet season highly urban influenced conditions, as illustrated in Figure 4. During significantly urban influenced sampling periods, defined as times when the urban influence plume tracer was measured at >1 standard deviation above its mean, consistently >60% of recovered aerosol mass was

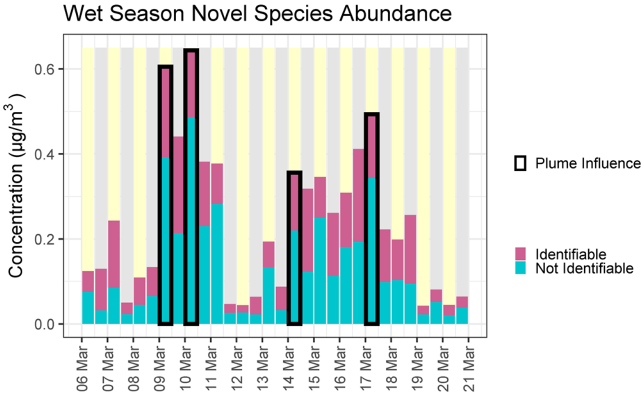

Figure 4. Contributions of identifiable (pink) and not identifiable (teal) compounds to submicron organic aerosol concentration during the wet season during the GoAmazon field campaign. Days significantly impacted by emissions from the urban plume are outlined in black, with "plume influence" defined as periods when the urban influence tracer (phthalic acid) was measured at >1 standard deviation above its mean in the wet season. Gray background bars indicate night samples (collected 18:00−6:00 local time), while yellow background bars indicate day samples (collected 6:00-18:00 local time).

attributed to unidentifiable compounds. This observation agrees with and partially explains the findings reported in Mouchel-Vallon et al., 2020,[16] which found that while model parameterizations using the volatility basis set were able to reproduce observed aerosol enhancements within the Manaus urban plume, explicit product modeling was not able to match the observed enhancement.[16] While the chemical oxidation modeling is not limited to products catalogued in mass spectral databases, the significance of unidentifiable organics to total wet season submicron organic aerosol concentrations under urban influenced conditions highlights the following challenge in improving explicit modeling of these conditions. Because the majority of individual urban influenced products cannot be identified and a dominant mass fraction (at least within the composition ranges to which GCxGC is sensitive) of organic material under urban influenced conditions is attributable to these unidentifiable compounds, the production mechanisms relevant to plume influenced secondary aerosol production cannot currently be structurally verified. Authentic synthesis and characterization of these products will significantly enhance mechanistic understandings of how urban perturbations of secondary aerosol formation occur, as will be discussed below in laboratory oxidation experiments. In the wet season, 100 compounds make up over 80% of the total recovered mass, but restricting analysis to the top individual compound contributors has the capacity to significantly skew analysis; for example, the masses of the urban influenced and background/biogenic clusters are distributed more evenly between a higher number of compounds compared to the burning influenced cluster, and restriction to the top 100 compounds would only recover only ∼70% of the mass from these two compound groups, skewing results towards biomass burning products.

Implications for Future Laboratory Studies. Generation of the unidentifiable products observed in Amazonian organic aerosol that are introduced here from known precursors under controlled conditions will play a critical role in expanding the scope of findings presented in this work. While still highly complex, emissions of gas-phase reactive organic compounds are less complex and better characterized than their aerosol-phase oxidation products.[20,21,51] As discussed in the Diversity, Properties, and Importance of Unidentifiable Organics section, the number and diversity of not identifiable products observed in this work are quite high; the time and effort required to synthesize new compounds are prohibitively high to provide a primary solution to improving the characterization of these complex mixtures. Laboratory oxidation experiments provide extremely valuable opportunities to advance understanding of these important compound populations; when aerosol produced from laboratory oxidation experiments is analyzed using the same instruments and protocols as ambient samples, unidentifiable compounds that are matched between experimental and ambient samples can be attributed to likely precursor sources and/or oxidation conditions. However, in order for these comparisons to be useful, experiments must be conducted under conditions that are sufficiently similar to those of the real atmosphere.[22] Humidity is likely to be particularly important for reproducing tropical secondary aerosol. Heterogeneous chemistry and aqueous-phase processing also deserve consideration, as aqueous-phase oligomerization has been previously reported and could potentially explain the not identifiable and seasonally unique high-carbon-number populations illustrated in Figure 2. The influence attributions and chemical properties distributions of chemically interesting compound populations such as those highlighted throughout this work can be utilized to design targeted laboratory oxidation experiments to improve mechanistic insights into the complexity of ambient aerosol formation. For example, aqueous experiments using phenolic biomass burning precursors are potential candidates for replicating the high-carbon-number dry season burning products, as previous experiments have generated products in similar properties spaces.[25]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c07260.

> Additional experimental details, supplementary results, and supporting figures, including description of the GoAmazon2014/5 field campaign, description of sample analysis protocols and uncertainties, and discussion of the results of supplementary laboratory oxidation experiments (PDF)

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☼E.B.F. analyzed ambient aerosol samples, analyzed data from ambient and laboratory-generated aerosol samples, and wrote the manuscript. L.D.Y., G.I.W., and R.A.W. collected aerosol samples. R.J.W. supported ambient sample analysis. H.Z. conducted laboratory monoterpene oxidation experiments and collected and analyzed laboratory-produced SOA. N.K. designed and implemented the aerosol sampling system. B.B.P., W.H., P.C.J., and D.A.D. conducted and analyzed data from supporting field measurements at GoAmazon. P.C.J and A.M. conducted supporting field measurements. P.A., J.J., S.T.M., and A.H.G. planned, coordinated, and oversaw field measurements. A.H.G. oversaw sample and data analysis. A.H.G., S.T.M., L.D.Y., D.A.D., P.C.J., B.B.P., P.A., H.Z., and R.A.W. reviewed and edited the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Artaxo, P.; Rizzo, L. V.; Brito, J. F.; Barbosa, H. M. J.; Arana, A.; Sena, E. T.; Cirino, G. G.; Bastos, W.; Martin, S. T.; Andreae, M. O. Atmospheric Aerosols in Amazonia and Land Use Change: From Natural Biogenic to Biomass Burning Conditions. *Faraday Discuss.* **2013**, *165*, 203−235.

(2) De Sá, S. S.; Palm, B. B.; Campuzano-Jost, P.; Day, D. A.; Hu, W.; Isaacman-Vanwertz, G.; Yee, L. D.; Brito, J.; Carbone, S.; Ribeiro, I. O.; Cirino, G. G.; Liu, Y.; Thalman, R.; Sedlacek, A.; Funk, A.; Schumacher, C.; Shilling, J. E.; Schneider, J.; Artaxo, P.; Goldstein, A. H.; Souza, R. A. F.; Wang, J.; Mckinney, K. A.; Barbosa, H.; Alexander, M. L.; Jimenez, J. L.; Martin, S. T. Urban Influence on the Concentration and Composition of Submicron Particulate Matter in Central Amazonia. *Atmos. Chem. Phys* **2018**, *18*, 12185−12206.

(3) De Sá, S. S.; Rizzo, L. V.; Palm, B. B.; Campuzano-Jost, P.; Day, D. A.; Yee, L. D.; Wernis, R.; Isaacman-Vanwertz, G.; Brito, J.; Carbone, S.; Liu, Y. J.; Sedlacek, A.; Springston, S.; Goldstein, A. H.; Barbosa, H. M. J.; Alexander, M. L.; Artaxo, P.; Jimenez, J. L.; Martin, S. T.; Paulson, J. A. Contributions of Biomass-Burning, Urban, and Biogenic Emissions to the Concentrations and Light-Absorbing Properties of Particulate Matter in Central Amazonia during the Dry Season. *Atmos. Chem. Phys* **2019**, *19*, 7973−8001.

(4) Shrivastava, M.; Andreae, M. O.; Artaxo, P.; Barbosa, H. M. J.; Berg, L. K.; Brito, J.; Ching, J.; Easter, R. C.; Fan, J.; Fast, J. D.; Feng, Z.; Fuentes, J. D.; Glasius, M.; Goldstein, A. H.; Gomes Alves, E.; Gomes, H.; Gu, D.; Guenther, A.; Jathar, S. H.; Kim, S.; Liu, Y.; Lou, S.; Martin, S. T.; Mcneill, V. F.; Medeiros, A.; De Sá, S. S.; Shilling, J. E.; Springston, S. R.; Souza, R. A. F.; Thornton, J. A.; Isaacman-Vanwertz, G.; Yee, L. D.; Ynoue, R.; Zaveri, R. A.; Zelenyuk, A.; Zhao, C. Urban Pollution Greatly Enhances Formation of Natural Aerosols over the Amazon Rainforest. *Nat. Commun.* **2019**, *10*, No. 1046.

(5) Liu, L.; Cheng, Y.; Wang, S.; Wei, C.; Pöhlker, M. L.; Pöhlker, C.; Artaxo, P.; Shrivastava, M.; Andreae, M. O.; Pöschl, U.; Su, H. Impact of Biomass Burning Aerosols on Radiation, Clouds, and Precipitation over the Amazon: Relative Importance of Aerosol-Cloud and Aerosol-Radiation Interactions. *Atmos. Chem. Phys.* **2020**, *20*, 13283−13301.

(6) Zhao, B.; Fast, J. D.; Donahue, N. M.; Shrivastava, M.; Schervish, M.; Shilling, J. E.; Gordon, H.; Wang, J.; Gao, Y.; Zaveri, R. A.; Liu, Y.; Gaudet, B. Impact of Urban Pollution on Organic-Mediated New-Particle Formation and Particle Number Concentration in the Amazon Rainforest. *Environ. Sci. Technol.* **2021**, *55*, 4357−4367.

(7) Urrutia-Pereira, M.; Rizzo, L. V.; Chong-Neto, H. J.; Solé, D. Impact of Exposure to Smoke from Biomass Burning in the Amazon Rain Forest on Human Health. *J. Bras. Pneumol.* **2021**, *47*, No. e20210219.

(8) Nawaz, M. O.; Henze, D. K. Premature Deaths in Brazil Associated With Long-Term Exposure to PM2.5 From Amazon Fires Between 2016 and 2019. *GeoHealth* **2020**, *4*, No. e2020GH000268.

(9) Davidson, E. A.; De Araüjo, A. C.; Artaxo, P.; Balch, J. K.; Brown, I. F.; Mercedes, M. M.; Coe, M. T.; Defries, R. S.; Keller, M.; Longo, M.; Munger, J. W.; Schroeder, W.; Soares-Filho, B. S.; Souza, C. M.; Wofsy, S. C. The Amazon Basin in Transition. *Nature* **2012**, *481*, 321−328.

(10) Cardil, A.; de-Miguel, S.; Silva, C. A.; Reich, P. B.; Calkin, D.; Brancalion, P. H. S.; Vibrans, A. C.; Gamarra, J. G. P.; Zhou, M.; Pijanowski, B. C.; Hui, C.; Crowther, T. W.; Hérault, B.; Piotto, D.; Salas-Eljatib, C.; Broadbent, E. N.; Zambrano, A. M. A.; Picard, N.; Aragão, L. E. O. C.; Bastin, J.-F.; Routh, D.; van den Hoogen, J.; Peri, P. L.; Liang, J. Recent Deforestation Drove the Spike in Amazonian Fires Environmental Research Letters Recent Deforestation Drove the Spike in Amazonian Fires. *Environ. Res. Lett.* **2020**, No. 121003.

(11) Shilling, J. E.; Pekour, M. S.; Fortner, E. C.; Artaxo, P.; De Sá, S.; Hubbe, J. M.; Longo, K. M.; Machado, L. A. T.; Martin, S. T.; Springston, S. R.; Tomlinson, J.; Wang, J. Aircraft Observations of the Chemical Composition and Aging of Aerosol in the Manaus Urban Plume during GoAmazon 2014/5. *Atmos. Chem. Phys.* **2018**, *18*, 10773−10797.

(12) Martin, S. T.; Artaxo, P.; Machado, L. A. T.; Manzi, A. O.; Souza, R. A. F.; Schumacher, C.; Wang, J.; Andreae, M. O.; Barbosa, H. M. J.; Fan, J.; Fisch, G.; Goldstein, A. H.; Guenther, A.; Jimenez, J. L.; Pöschl, U.; Dias, M. A. S.; Smith, J. N.; Wendisch, M. Introduction: Observations and Modeling of the Green Ocean Amazon (GoAmazon2014/5). *Atmos. Chem. Phys* **2016**, *16*, 4785−4797.

(13) Cirino, G.; Brito, J.; Barbosa, H. M. J.; Rizzo, L. V.; Tunved, P.; de Sá, S. S.; Jimenez, J. L.; Palm, B. B.; Carbone, S.; Lavric, J. V.; Souza, R. A. F.; Wolff, S.; Walter, D.; Tota, J.; Oliveira, M. B. L.; Martin, S. T.; Artaxo, P. Observations of Manaus Urban Plume Evolution and Interaction with Biogenic Emissions in GoAmazon 2014/5. *Atmos. Environ.* **2018**, *191*, 513−524.

(14) Glasius, M.; Bering, M. S.; Yee, L. D.; De Sá, S. S.; Isaacman-VanWertz, G.; Wernis, R. A.; Barbosa, H. M. J.; Alexander, M. L.; Palm, B. B.; Hu, W.; Campuzano-Jost, P.; Day, D. A.; Jimenez, J. L.; Shrivastava, M.; Martin, S. T.; Goldstein, A. H. Organosulfates in Aerosols Downwind of an Urban Region in Central Amazon. *Environ. Sci. Process. Impacts* **2018**, *20*, 1546−1558.

(15) Liu, Y.; Seco, R.; Kim, S.; Guenther, A. B.; Goldstein, A. H.; Keutsch, F. N.; Springston, S. R.; Watson, T. B.; Artaxo, P.; Souza, R. A. F.; Mckinney, K. A.; Scot, †‡.; Martin, T. Isoprene Photo-Oxidation Products Quantify the Effect of Pollution on Hydroxyl Radicals over Amazonia **2018** *4* eaar2547 DOI: 10.1126/sciadv.aar2547.

(16) Mouchel-Vallon, C.; Lee-Taylor, J.; Hodzic, A.; Artaxo, P.; Aumont, B.; Camredon, M.; Gurarie, D.; Jimenez, J. L.; Lenschow, D. H.; Martin, S. T.; Nascimento, J.; Orlando, J. J.; B Palm, B.; Shilling, J. E.; Shrivastava, M.; Madronich, S. Exploration of Oxidative Chemistry and Secondary Organic Aerosol Formation in the Amazon during the Wet Season: Explicit Modeling of the Manaus Urban Plume with GECKO-A. *Atmos. Chem. Phys.* **2020**, *20*, 5995−6014.

(17) Nascimento, J. P.; Bela, M. M.; Meller, B. B.; Banducci, A. L.; Rizzo, L. V.; Liduvino Vara-Vela, A.; Barbosa, H. M. J.; Gomes, H.; Rafee, S. A. A.; Franco, M. A.; Carbone, S.; Cirino, G. G.; Souza, R. A. F.; Mckeen, S. A.; Artaxo, P. Aerosols from Anthropogenic and Biogenic Sources and Their Interactions-Modeling Aerosol Formation, Optical Properties, and Impacts over the Central Amazon Basin. *Atmos. Chem. Phys.* **2021**, *21*, 6755−6779.

(18) Palm, B. B.; De Sá, S. S.; Day, D. A.; Campuzano-Jost, P.; Hu, W.; Seco, R.; Sjostedt, S. J.; Park, J. H.; Guenther, A. B.; Kim, S.; Brito, J.; Wurm, F.; Artaxo, P.; Thalman, R.; Wang, J.; Yee, L. D.; Wernis, R.; Isaacman-VanWertz, G.; Goldstein, A. H.; Liu, Y.; Springston, S. R.; Souza, R.; Newburn, M. K.; Lizabeth Alexander, M.; Martin, S. T.; Jimenez, J. L. Secondary Organic Aerosol Formation from Ambient Air in an Oxidation Flow Reactor in Central Amazonia. *Atmos. Chem. Phys.* **2018**, *18*, 467−493.

(19) Abou Rafee, S. A.; Martins, L. D.; Kawashima, A. B.; Almeida, D. S.; Morais, M. V. B.; Souza, R. V. A.; Oliveira, M. B. L.; Souza, R. A. F.; Medeiros, A. S. S.; Urbina, V.; Freitas, E. D.; Martin, S. T.; Martins, J. A. Contributions of Mobile, Stationary and Biogenic Sources to Air Pollution in the Amazon Rainforest: A Numerical Study with the WRF-Chem Model. *Atmos. Chem. Phys* **2017**, *17*, 7977−7995.

(20) Goldstein, A. H.; Galbally, I. E. Known and Unexplored Organic Constituents in the Earth's Atmosphere. *Environ. Sci. Technol.* **2007**, *41*, 1514−1521.

(21) Heald, C. L.; Kroll, J. H. The Fuel of Atmospheric Chemistry: Toward a Complete Description of Reactive Organic Carbon. *Sci. Adv.* **2020**, *6*, No. eaay8967.

(22) Porter, W. C.; Jimenez, J. L.; Barsanti, K. C. Quantifying Atmospheric Parameter Ranges for Ambient Secondary Organic Aerosol Formation. *ACS Earth Space Chem.* **2021**, *5*, 2380−2397.

(23) Ervens, B.; Turpin, B. J.; Weber, R. J. Secondary Organic Aerosol Formation in Cloud Droplets and Aqueous Particles (AqSOA): A Review of Laboratory, Field and Model Studies. *Atmos. Chem. Phys* **2011**, *11*, 11069−11102.

(24) Lim, Y. B.; Tan, Y.; Perri, M. J.; Seitzinger, S. P.; Turpin, B. J. Aqueous Chemistry and Its Role in Secondary Organic Aerosol (SOA) Formation. *Atmos. Chem. Phys.* **2010**, *10*, 10521−10539.

(25) Yu, L.; Smith, J.; Laskin, A.; M George, K.; Anastasio, C.; Laskin, J.; M Dillner, A.; Zhang, Q. Molecular Transformations of Phenolic SOA during Photochemical Aging in the Aqueous Phase: Competition among Oligomerization, Functionalization, and Fragmentation. *Atmos. Chem. Phys.* **2016**, *16*, 4511−4527.

(26) Fuzzi, S.; Decesari, S.; Facchini, M. C.; Cavalli, F.; Emblico, L.; Mircea, M.; Andreae, M. O.; Trebs, I.; Hoffer, A.; Guyon, P.; Artaxo, P.; Rizzo, L. V.; Lara, L. L.; Pauliquevis, T.; Maenhaut, W.; Raes, N.; Chi, X.; Mayol-Bracero, O. L.; Soto-García, L. L.; Claeys, M.; Kourtchev, I.; Rissler, J.; Swietlicki, E.; Tagliavini, E.; Schkolnik, G.; Falkovich, A. H.; Rudich, Y.; Fisch, G.; Gatti, L. V. Overview of the Inorganic and Organic Composition of Size-Segregated Aerosol in Rondônia, Brazil, from the Biomass-Burning Period to the Onset of the Wet Season. *J. Geophys. Res.: Atmos.* **2007**, *112*, No. 1201.

(27) Simoneit, B. R. T.; Cardoso, J. N.; Robinson, N. An Assessment of the Origin and Composition of Higher Molecular Weight Organic Matter in Aerosols over Amazonia. *Chemosphere* **1990**, *21*, 1285−1301.

(28) Graham, B.; Mayol-Bracero, O. L.; Guyon, P.; Roberts, G. C.; Decesari, S.; Facchini, M. C.; Artaxo, P.; Maenhaut, W.; Köll, P.; Andreae, M. O. Water-Soluble Organic Compounds in Biomass Burning Aerosols over Amazonia 1. Characterization by NMR and GC-MS. *J. Geophys. Res.: Atmos.* **2002**, *107*, LBA 14-1−LBA 14-16.

(29) Martin, S. T.; Andreae, M. O.; Artaxo, P.; Baumgardner, D.; Chen, Q.; Goldstein, A. H.; Guenther, A.; Heald, C. L.; Mayol-Bracero, O. L.; McMurry, P. H.; Pauliquevis, T.; Pschl, U.; Prather, K. A.; Roberts, G. C.; Saleska, S. R.; Silva Dias, M. A.; Spracklen, D. V.; Swietlicki, E.; Trebs, I. Sources and Properties of Amazonian Aerosol Particles. *Rev. Geophys.* **2010**, *48*, No. RG2002.

(30) Mayol-Bracero, O. L.; Guyon, P.; Graham, B.; Roberts, G.; Andreae, M. O.; Decesari, S.; Facchini, M. C.; Fuzzi, S.; Artaxo, P. Water-Soluble Organic Compounds in Biomass Burning Aerosols over Amazonia 2. Apportionment of the Chemical Composition and Importance of the Polyacidic Fraction. *J. Geophys. Res.: Atmos.* **2002**, *107*, LBA 59-1−LBA 59-15.

(31) Chen, Q.; Farmer, D. K.; Schneider, J.; Zorn, S. R.; Heald, C. L.; Karl, T. G.; Guenther, A.; Allan, J. D.; Robinson, N.; Coe, H.; Kimmel, J. R.; Pauliquevis, T.; Borrmann, S.; Pöschl, U.; Andreae, M. O.; Artaxo, P.; Jimenez, J. L.; Martin, S. T. Mass Spectral Characterization of Submicron Biogenic Organic Particles in the Amazon Basin. *Geophys. Res. Lett.* **2009**, *36*, No. 14629566.

(32) Yee, L. D.; Isaacman-Vanwertz, G.; Wernis, R. A.; Meng, M.; Rivera, V.; Kreisberg, N. M.; Hering, S. V.; Bering, M. S.; Glasius, M.; Upshur, M. A.; Bé, A. G.; Thomson, R. J.; Geiger, F. M.; Offenberg, J. H.; Lewandowski, M.; Kourtchev, I.; Kalberer, M.; De Sá, S.; Martin, S. T.; Alexander, M. L.; Palm, B. B.; Hu, W.; Campuzano-Jost, P.; Day, D. A.; Jimenez, J. L.; Liu, Y.; Mckinney, K. A.; Artaxo, P.; Viegas, J.; Manzi, A.; Oliveira, M. B.; De Souza, R.; Machado, L. A. T.; Longo, K.; Goldstein, A. H. Observations of Sesquiterpenes and Their Oxidation Products in Central Amazonia during the Wet and Dry Seasons. *Atmos. Chem. Phys* **2018**, *18*, 10433−10457.

(33) Zhang, H.; Yee, L. D.; Lee, B. H.; Curtis, M. P.; Worton, D. R.; Isaacman-Vanwertz, G.; Offenberg, J. H.; Lewandowski, M.; Kleindienst, T. E.; Beaver, M. R.; Holder, A. L.; Lonneman, W. A.; Docherty, K. S.; Jaoui, M.; Pye, H. O. T.; Hu, W.; Day, D. A.; Campuzano-Jost, P.; Jimenez, J. L.; Guo, H.; Weber, R. J.; De Gouw, J.; Koss, A. R.; Edgerton, E. S.; Brune, W.; Mohr, C.; Lopez-Hilfiker, F. D.; Lutz, A.; Kreisberg, N. M.; Spielman, S. R.; Hering, S. V.; Wilson, K. R.; Thornton, J. A.; Goldstein, A. H. Monoterpenes Are the Largest Source of Summertime Organic Aerosol in the Southeastern United States. *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 2038−2043.

(34) Kroll, J. H.; Donahue, N. M.; Jimenez, J. L.; Kessler, S. H.; Canagaratna, M. R.; Wilson, K. R.; Altieri, K. E.; Mazzoleni, L. R.; Wozniak, A. S.; Bluhm, H.; Mysak, E. R.; Smith, J. D.; Kolb, C. E.; Worsnop, D. R. Carbon Oxidation State as a Metric for Describing the Chemistry of Atmospheric Organic Aerosol. *Nat. Chem.* **2011**, *3*, 133−139.

(35) Faiola, C. L.; Pullinen, I.; Buchholz, A.; Khalaj, F.; Ylisirniö, A.; Kari, E.; Miettinen, P.; Holopainen, J. K.; Kivimäenpää, M.; Schobesberger, S.; Yli-Juuti, T.; Virtanen, A. Secondary Organic Aerosol Formation from Healthy and Aphid-Stressed Scots Pine Emissions. *ACS Earth Space Chem.* **2019**, *3*, 1756−1772.

(36) Mutzel, A.; Rodigast, M.; Iinuma, Y.; Böge, O.; Herrmann, H. Monoterpene SOA − Contribution of First-Generation Oxidation Products to Formation and Chemical Composition. *Atmos. Environ.* **2016**, *130*, 136−144.

(37) Larsen, B. R.; Di Bella, D.; Glasius, M.; Winterhalter, R.; Jensen, N. R.; Hjorth, J. Gas-Phase OH Oxidation of Monoterpenes: Gaseous and Particulate Products. *J. Atmos. Chem.* **2001**, *38*, 231−276.

(38) Koch, S.; Winterhalter, R.; Uherek, E.; Kolloff, A.; Neeb, P.; Moortgat, G. K. Formation of New Particles in the Gas-Phase Ozonolysis of Monoterpenes. *Atmos. Environ.* **2000**, *34*, 4031−4042.

(39) Aljawhary, D.; Zhao, R.; Lee, A. K. Y.; Wang, C.; Abbatt, J. P. D. Kinetics, Mechanism, and Secondary Organic Aerosol Yield of Aqueous Phase Photo-Oxidation of α-Pinene Oxidation Products. *J. Phys. Chem. A* **2016**, *120*, 1395−1407.

(40) US EPA. Estimation Programs Interface Suite for Microsoft Windows, v 4.11. https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface#citing (accessed January 26, 2023).

(41) Bhattarai, H.; Saikawa, E.; Wan, X.; Zhu, H.; Ram, K.; Gao, S.; Kang, S.; Zhang, Q.; Zhang, Y.; Wu, G.; Wang, X.; Kawamura, K.; Fu, P.; Cong, Z. Levoglucosan as a Tracer of Biomass Burning: Recent Progress and Perspectives. *Atmos. Res.* **2019**, *220*, 20−33.

(42) Oros, D. R.; Simoneit, B. R. T. Identification and Emission Factors of Molecular Tracers in Organic Aerosols from Biomass Burning Part 2. Deciduous Trees. *Appl. Geochem.* **2001**, *16*, 1545−1565.

(43) Norwood, M. J.; Louchouarn, P.; Kuo, L. J.; Harvey, O. R. Characterization and Biodegradation of Water-Soluble Biomarkers and Organic Carbon Extracted from Low Temperature Chars. *Org. Geochem.* **2013**, *56*, 111−119.

(44) Cai, J.; Zeng, X.; Zhi, G.; Gligorovski, S.; Sheng, G.; Yu, Z.; Wang, X.; Peng, P. Molecular Composition and Photochemical Evolution of Water-Soluble Organic Carbon (WSOC) Extracted from Field Biomass Burning Aerosols Using High-Resolution Mass Spectrometry. *Atmos. Chem. Phys.* **2020**, *20*, 6115−6128.

(45) Sun, Y. L.; Zhang, Q.; Anastasio, C.; Sun, J. Insights into Secondary Organic Aerosol Formed via Aqueous-Phase Reactions of Phenolic Compounds Based on High Resolution Mass Spectrometry. *Atmos. Chem. Phys.* **2010**, *10*, 4809−4822.

(46) Gilardoni, S.; Massoli, P.; Paglione, M.; Giulianelli, L.; Carbone, C.; Rinaldi, M.; Decesari, S.; Sandrini, S.; Costabile, F.; Gobbi, G. P.; Pietrogrande, M. C.; Visentin, M.; Scotto, F.; Fuzzi, S.; Facchini, M. C. Direct Observation of Aqueous Secondary Organic Aerosol from Biomass-Burning Emissions. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*, 10013−10018.

(47) Rissler, J.; Swietlicki, E.; Zhou, J.; Roberts, G.; Andreae, M. O.; Gatti, L. V.; Artaxo, P. Physical Properties of the Sub-Micrometer Aerosol over the Amazon Rain Forest during the Wet-to-Dry Season Transition-Comparison of Modeled and Measured CCN Concentrations. *Atmos. Chem. Phys* **2004**, *4*, 2119−2143.

(48) Fuentes, J. D.; Chamecki, M.; Dos Santos, R. M. N.; Von Randow, C.; Stoy, P. C.; Katul, G.; Fitzjarrald, D.; Manzi, A.; Gerken, T.; Trowbridge, A.; Freire, L. S.; Ruiz-Plancarte, J.; Maia, J. M. F.; Tóta, J.; Dias, N.; Fisch, G.; Schumacher, C.; Acevedo, O.; Mercer, J. R.; Yañez-Serrano, A. M. Linking Meteorology, Turbulence, and Air Chemistry in the Amazon Rain Forest. *Bull. Am. Meteorol. Soc.* **2016**, *97*, 2329−2342.

(49) Ervens, B.; Sorooshian, A.; Aldhaif, A. M.; Shingler, T.; Crosbie, E.; Ziemba, L.; Campuzano-Jost, P.; Jimenez, J. L.; Wisthaler, A. Is There an Aerosol Signature of Chemical Cloud Processing? *Atmos. Chem. Phys.* **2018**, *18*, 16099−16119.

(50) Kim, S.; Lerner, B. M.; Sueper, D. T.; Isaacman-Vanwertz, G. Comprehensive Detection of Analytes in Large Chromatographic Datasets by Coupling Factor Analysis with a Decision Tree. *Atmos. Meas. Tech.* **2022**, *15*, 5061−5075.

(51) Jardine, A. B.; Jardine, K. J.; Fuentes, J. D.; Martin, S. T.; Martins, G.; Durgante, F.; Carneiro, V.; Higuchi, N.; Manzi, A. O.; Chambers, J. Q. Highly Reactive Light-Dependent Monoterpenes in the Amazon. *Geophys. Res. Lett.* **2015**, *42*, 1576−1583.