

Detailed chemical characterization of submicrometer organic aerosol particles in the Amazon rainforest

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Johannes Gutenberg-Universität with the Max Planck-Graduate Center

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This work is dedicated to Joshua Micheel

** November 23, 1987 – † May 23, 2024*

*With gratitude for his love and encouragement, and for his support that continues
beyond these pages.*

Zusammenfassung

Organische Aerosole (OA) sind ein zentraler Bestandteil der Atmosphäre und beeinflussen Klima, Wolkenbildung, den Strahlungshaushalt und die Luftqualität und damit auch die menschliche Gesundheit. Trotz erheblicher Fortschritte in der analytischen Charakterisierung bestehen weiterhin grundlegende Wissenslücken hinsichtlich niedrig- und halbflüchtiger Verbindungen, hochoxidierter Moleküle und reaktiver organischer Spezies. Ziel dieser Dissertation ist es, die molekulare Zusammensetzung, Bildungsprozesse sowie natürliche und anthropogene Einflüsse auf organische Aerosole mithilfe hochauflösender Massenspektrometrie (HR-MS) systematisch zu untersuchen und in einen atmosphärischen und ökologischen Kontext einzuordnen.

Die Arbeit zeigt, dass die extreme chemische Vielfalt organischer Aerosole eine Kombination aus hochauflösender Massenspektrometrie und chromatographischer Trennung erfordert, um isomere Strukturen, funktionelle Gruppen und Oxidationszustände zuverlässig aufzulösen. Nicht-zielgerichtete HR-MS-Ansätze ermöglichen die Erfassung tausender Molekülformeln, während zielgerichtete Analysen eine quantitative Beschreibung spezifischer Vorläufer- und Markerkomponenten erlauben. Am Beispiel atmosphärischer Aerosole aus dem zentralen Amazonasgebiet wird gezeigt, dass biogene sekundäre organische Aerosole aus der Oxidation von Isopren, Mono- und Sesquiterpenen die Hintergrundzusammensetzung dominieren, wobei ausgeprägte saisonale Unterschiede zwischen Trocken- und Regenzeit auftreten. Die molekulare Zusammensetzung variiert systematisch mit Partikelgröße und Höhe in der Atmosphäre, was auf unterschiedliche Bildungswege, Alterungsprozesse und Quellbeiträge in ultrafeinen und feinen Partikeln hinweist. Insbesondere ultrafeine Partikel sind eng mit spezifischen biogenen Oxidationsprodukten verknüpft und spielen eine wichtige Rolle für die Neubildung und das frühe Partikelwachstum.

Die Ergebnisse belegen zudem, dass meteorologische Prozesse wie Niederschlagsereignisse die chemische Umgebung im Waldkronenbereich stark verändern und lokale Neubildung ultrafeiner Partikel auslösen können, die innerhalb weniger Stunden in klimarelevante Größenbereiche wachsen. Darüber hinaus wird gezeigt, dass die Verfügbarkeit biogener Vorläuferstoffe nicht allein durch atmosphärische Chemie bestimmt wird, sondern wesentlich durch bodenchemische und ökologische Prozesse kontrolliert wird. Die molekulare Charakterisierung gelöster organischer Substanz in Amazonböden weist auf ausgeprägte Phosphorlimitierung sowie mögliche Ko-Limitierungen durch Stickstoff und Schwefel hin und verdeutlicht den Einfluss der Nährstoffdynamik auf die Bereitstellung biogener Emissionsvorläufer.

Anthropogene Einflüsse werden anhand von Organosulfaten untersucht, die einen wichtigen Beitrag zur organischen Aerosolmasse leisten, deren Quantifizierung bislang jedoch stark unterschätzt wurde. Durch die Kombination aus Festphasenextraktion, HR-Orbitrap-MS und Charged Aerosol Detection wird gezeigt, dass ein erheblicher Anteil der Organosulfate in chromatographisch nicht aufgelösten Fraktionen vorliegt und somit in bisherigen Studien nicht erfasst wurde. Dies unterstreicht die Bedeutung der Schwefelemissionen für die Bildung organischer Aerosole und zeigt das Potenzial gezielter Emissionsminderungsstrategien für die Luftqualität.

Insgesamt liefert diese Dissertation eine integrierte, molekular aufgelöste Betrachtung organischer Aerosole, die chemische Detailinformationen mit Partikeleigenschaften, meteorologischen Prozessen, ökologischen Steuergrößen und anthropogenen Einflüssen verknüpft. Die Ergebnisse verdeutlichen die zentrale Rolle hochauflösender massenspektrometrischer Methoden für das Verständnis der Entstehung, Umwandlung und

klimatischen Wirkung organischer Aerosole und leisten einen Beitrag zur Verbesserung ihrer Repräsentation in atmosphärischen Modellen sowie zur Bewertung ihrer Bedeutung für Klima und Luftqualität.

Abstract

Organic aerosols (OA) are a major component of the atmosphere and strongly influence climate, cloud formation, radiative forcing, air quality, and human health. Despite substantial advances in analytical chemistry, fundamental knowledge gaps remain regarding low- and semi-volatile compounds, highly oxidized species, and reactive organic molecules. This dissertation aims to improve the molecular-level understanding of organic aerosols by applying high-resolution mass spectrometry (HR-MS) to investigate their chemical composition, formation pathways, and environmental and anthropogenic controls within an integrated atmospheric and ecosystem framework.

The results demonstrate that the extreme chemical complexity of organic aerosols requires the combined use of high-resolution mass spectrometry and chromatographic separation to resolve isomeric structures, functional groups, and oxidation states. Non-targeted HR-MS approaches detect thousands of molecular formulas, while targeted analyses provide quantitative insights into specific precursor and marker compounds. Observations from the central Amazon rainforest show that biogenic secondary organic aerosols derived from isoprene, monoterpene, and sesquiterpene oxidation dominate the background composition, with pronounced seasonal differences between wet and dry periods. Molecular composition varies systematically with particle size and sampling height, reflecting distinct formation pathways, aging processes, and source contributions in ultrafine and fine particles. In particular, ultrafine particles are closely linked to specific biogenic oxidation products and play a key role in new particle formation and early growth.

Meteorological processes, especially rainfall events, strongly modify the chemical environment within the forest canopy and can trigger local new particle formation, followed by rapid growth to climatically relevant particle sizes. In addition, the availability of biogenic precursor compounds is shown to depend not only on atmospheric chemistry but also on soil biogeochemical processes. The molecular characterization of dissolved organic matter in Amazonian soils reveals pronounced phosphorus limitation and potential nitrogen and sulfur co-limitations, highlighting the role of nutrient cycling in controlling the supply of biogenic emissions that ultimately contribute to secondary organic aerosol formation.

Anthropogenic influences are addressed by investigating organosulfates, which constitute an important fraction of organic aerosol mass but are difficult to quantify due to their molecular diversity. By combining solid-phase extraction, HR-Orbitrap-MS, and charged aerosol detection, this work demonstrates that a substantial fraction of organosulfates occurs in chromatographically unresolved form and has therefore been largely underestimated in previous studies. These findings emphasize the importance of sulfur emissions for organic aerosol formation and highlight the potential of emission control strategies to improve air quality.

Overall, this dissertation provides an integrated, molecularly resolved perspective on organic aerosols that links chemical composition with particle properties, meteorological drivers, ecosystem controls, and anthropogenic emissions. The results highlight the central role of high-resolution mass spectrometry in unraveling the complexity of organic aerosols and contribute to a more mechanistic understanding of their formation, transformation, and impacts on climate and air quality.

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ZUSAMMENFASSUNG I

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1 Introduction

1.1 The role of the Amazon rainforest

The Amazon Basin is one of the most biodiverse and ecologically significant environments on Earth, covering approximately 6.9 million km² in South America. About 80 % of this region is still covered by rainforests, accounting for roughly 40 % of all tropical forests worldwide (Andreae et al., 2015; Goulding, Barthelm, & Ferreira, 2003; Malhi et al., 2006). However, the Amazon is increasingly threatened by deforestation, climate change, and anthropogenic pressures, which are rapidly altering its ecological and biogeochemical dynamics (Boulton, Lenton, & Boers, 2022; Gloor et al., 2013; Lovejoy & Nobre, 2018). The total carbon content of the Amazon forest is estimated at 80–120 Pg C (Boulton et al., 2022; Malhi et al., 2006; Saatchi et al., 2011), underscoring its critical role in global climate regulation and the provision of ecosystem services.

A defining characteristic of the Amazon system is the tight coupling between the forest and the hydrological cycle. Large amounts of water are recycled through evapotranspiration, sustaining deep convection and frequent precipitation. This recycling creates a vertically and horizontally connected system in which surface processes influence cloud formation and rainfall, and vice versa (Gloor et al., 2013; Hoorn et al., 2010; Spracklen, Arnold, & Taylor, 2012; Wittmann et al., 2013). Atmospheric composition plays a central role in this coupling, as trace gases and aerosol particles modulate cloud microphysics and radiative transfer, thereby influencing the spatial and temporal structure of precipitation (Andreae et al., 2018; Andreae & Rosenfeld, 2008; Pöschl et al., 2010). The forest–atmosphere system thus operates as a coupled biophysical and biogeochemical engine, in which chemical and physical processes are inseparable.

The Amazon is also characterized by exceptionally strong biological control over atmospheric composition. Vegetation emits large quantities of reactive trace gases (e.g., isoprene, monoterpenes, and sesquiterpenes), while soils and surface waters exchange a wide range of chemical species with the lower atmosphere. These fluxes shape the regional atmosphere's oxidative capacity and influence the formation and transformation of particulate matter (Andreae et al., 2015; Claeys et al., 2004b; Yáñez-Serrano et al., 2020). In turn, atmospheric processing alters the chemical form and reactivity of deposited compounds, feeding back into ecosystem nutrient cycles. This bidirectional exchange establishes a continuous chemical linkage between the biosphere and the atmosphere, connecting molecular-scale processes with ecosystem-scale dynamics (Artaxo et al., 2013b; Longo et al., 2020).

The Amazon's sensitivity to environmental change further underscores the need to understand its atmospheric processes. Changes in vegetation composition, forest cover, or soil moisture directly affect the fluxes of water and reactive compounds to the atmosphere. These changes propagate upward through the boundary layer and into cloud-forming regions, potentially altering precipitation patterns and chemical processing pathways (Boulton et al., 2022; Gloor et al., 2013; Lovejoy & Nobre, 2018). Because these feedbacks operate across multiple spatial and temporal scales, the Amazon can act as both a stabilizing component of the Earth system and a source of nonlinear responses to disturbance, including potential tipping points (Lenton et al., 2008; Nobre et al., 2016; Staal et al., 2020).

A comprehensive understanding of the Amazonian atmosphere, therefore, requires an ecosystem perspective in which biological activity, atmospheric composition, and hydrological dynamics are treated as parts of a unified system (Hoorn et al., 2010; Wittmann et al., 2013).

Rather than viewing aerosols, trace gases, and clouds as isolated phenomena, they must be interpreted as emergent properties of coupled biosphere–atmosphere interactions. Establishing this conceptual framework is a prerequisite for resolving the chemical and physical mechanisms that govern organic matter cycling, cloud formation, and precipitation in the region. The following sections build upon this perspective by progressively focusing on the molecular and chemical processes that underpin these large-scale ecosystem–atmosphere linkages.

1.2 Organic aerosols

Organic aerosols (OA) represent a central interface between biological activity and atmospheric processes. In regions such as the Amazon rainforest, where emissions are dominated by vegetation and soils, organic aerosol particles largely originate from biologically derived precursor compounds, primarily isoprene, monoterpenes, and sesquiterpenes (Claeys et al., 2004b; Lee et al., 2006; Yáñez-Serrano et al., 2020), and their subsequent atmospheric transformation. OA therefore embodies the chemical imprint of ecosystem functioning in the atmosphere and provides a mechanistic link between surface processes, cloud formation, and radiative transfer (Andreae et al., 2015; Pöschl et al., 2010).

Organic aerosols influence the atmospheric radiation budget both directly and indirectly. Through direct interactions with solar and terrestrial radiation, aerosol particles scatter and, depending on their chemical composition, absorb incoming and outgoing radiation. The magnitude and sign of this radiative effect depend on particle size, phase state, and molecular composition, which determine optical properties such as refractive index and hygroscopic growth. In biogenically dominated systems, organic aerosols are often weakly absorbing and predominantly scattering, leading to a cooling influence at the surface, while still modifying the vertical distribution of radiative heating (Bond et al., 2013; Change, 2014; Jimenez et al., 2009; Liu et al., 2020).

Indirectly, organic aerosols affect the radiation budget by serving as cloud condensation nuclei (CCN). By controlling cloud droplet number and size distributions, they alter cloud albedo, lifetime, and vertical structure. In the Amazon system, where cloud formation is frequent and tightly coupled to surface fluxes, such aerosol–cloud interactions constitute a critical pathway through which biological activity feeds back onto the atmospheric energy balance. Changes in organic aerosol abundance or chemical nature can therefore translate into changes in cloud reflectivity and precipitation efficiency, linking ecosystem processes to radiative forcing (Andreae et al., 2018; Andreae & Rosenfeld, 2008; Fan et al., 2018; Rosenfeld et al., 2019).

From an ecosystem perspective, these radiative effects are not merely atmospheric phenomena; they also influence biological functioning at the surface. Modifications in cloud cover and light scattering affect the quantity and spectral quality of radiation reaching the forest canopy, with consequences for photosynthesis and evapotranspiration (ALTON, NORTH, & LOS, 2007; Mercado et al., 2009; Rap et al., 2018). Organic aerosols thus participate in regulating the distribution of energy between the atmosphere and the biosphere, embedding them within the broader forest–climate coupling.

Organic aerosols can further modify the radiation budget through chemical aging. As biogenic precursor compounds undergo oxidation and multiphase processing, their molecular structures evolve toward higher oxygen content and greater polarity. These changes influence particle phase state and water uptake, thereby modifying optical properties and cloud activation behavior (Donahue, Robinson, Stanier, & Pandis, 2006; Gilardoni et al., 2016; Palm et al., 2017; Shiraiwa et al., 2011). In this way, chemical processing pathways leave a radiative

signature that connects molecular-scale transformations with ecosystem-scale energy exchange.

Understanding organic aerosols in the Amazon, therefore, requires considering their dual role as chemical products of biological activity and as regulators of atmospheric radiation. This perspective provides the conceptual basis for examining their formation mechanisms and molecular composition in the following sections, with attention to the chemical pathways governing their emergence and transformation.

1.3 Molecular characterization

To resolve the role of organic aerosols within coupled biosphere–atmosphere processes, it is necessary to move beyond bulk measurements and towards analytical techniques capable of capturing their intrinsic chemical complexity. Organic aerosol particles consist of thousands of distinct organic compounds spanning wide ranges in molecular size, functionalization, and oxidation state. Their environmental behavior volatility, hygroscopicity, optical properties, and reactivity, emerge from this molecular diversity rather than from total mass alone (Goldstein & Galbally, 2007; Hallquist et al., 2009; Nozière et al., 2015a).

Mass spectrometry has become the central analytical technique for this purpose, as it enables the detection and characterization of complex organic mixtures with high sensitivity. The development of high-resolution mass spectrometry (HR-MS), particularly Orbitrap (Makarov, 2000) and Fourier-transform ion cyclotron resonance (FT-ICR) MS (Marshall, Hendrickson, & Jackson, 1998), represents a pivotal advance in atmospheric and environmental chemistry. HR-MS enables the distinction of individual molecular species within extremely complex matrices such as organic aerosol extracts and cloud or rainwater samples (Beck, Brüggemann, van Pinxteren, & Herrmann, 2022; Bianco et al., 2018; Burgay et al., 2023; Spolnik, Wach, Rudziński, Szmigielski, & Danikiewicz, 2020). By resolving small differences in mass-to-charge ratio, HR-MS enables assignment of elemental compositions to detected ions and describes organic aerosol composition in terms of molecular formula distributions rather than unresolved signal envelopes (Hughey, Hendrickson, Rodgers, Marshall, & Qian, 2001; Kendrick, 1963).

This capability fundamentally changes how organic aerosol can be conceptualized. Instead of treating OA as a chemically uniform substance, HR-MS reveals it as a structured ensemble of molecules organized along gradients of oxidation, unsaturation, and heteroatom content (Nozière et al., 2015a). Molecular formula information can be transformed into chemically meaningful metrics, such as oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) ratios, and degrees of unsaturation, providing direct links to underlying chemical processes, such as oxidation, fragmentation, and oligomerization (Badertscher, Bischofberger, Munk, & Pretsch, 2001; Hughey et al., 2001; Kroll et al., 2011; Rivas-Ubach et al., 2018; Zhang, Wang, Tong, Huang, & Hoffmann, 2021).

High-resolution mass spectrometry is particularly important for studying organic aerosols in biogenically dominated systems, where precursors are chemically diverse and reaction pathways are strongly influenced by multiphase processing. Oxidation products formed from biological emissions often differ only subtly in mass and composition, and their separation requires resolving power beyond that of conventional low-resolution techniques (Hallquist et al., 2009; Kroll & Seinfeld, 2008; Nizkorodov, Laskin, & Laskin, 2011; Yassine et al., 2014).

Moreover, HR-MS supports the investigation of chemical continuity between atmospheric and aqueous organic matter. Because the same molecular formulas can be identified in aerosol

particles, cloud water, and precipitation, molecular-level comparisons can be made across physical phases (Burgay et al., 2023; Mazzoleni et al., 2012; Vogel et al., 2016; Vogel et al., 2019; Wozniak, Bauer, Sleighter, Dickhut, & Hatcher, 2008). This provides a basis for linking atmospheric oxidation products to deposited organic matter and for tracing chemical processing pathways across the atmosphere–biosphere interface. In this sense, HR-MS serves not only as a descriptive tool but as a bridge between atmospheric chemistry and ecosystem biogeochemistry.

The importance of high-resolution mass spectrometry lies, therefore, not only in its analytical precision but in its conceptual implications. By rendering complex organic mixtures chemically legible, it enables process-oriented interpretation of organic aerosol formation and evolution. Molecular-level characterization provides the foundation for connecting ecosystem emissions, atmospheric transformation, and radiative and hydrological effects within a unified chemical framework. Without such resolution, key reaction pathways remain obscured within bulk measurements, limiting the ability to identify mechanisms and feedbacks.

High-resolution mass spectrometry thus represents a methodological turning point in the study of organic aerosols. It allows chemical complexity to be quantified rather than approximated and supports a shift from phenomenological descriptions toward mechanistic understanding. In the context of this thesis, HR-MS forms the analytical core for investigating how biological emissions and atmospheric processing generate chemically distinct organic aerosol populations and how these populations participate in coupled biosphere–atmosphere interactions.

1.4 Motivation and thesis objectives

Organic aerosols are key components of the atmosphere, influencing climate, cloud formation, precipitation, and air quality, with direct implications for human health. Despite advances in high-resolution mass spectrometry and complementary analytical approaches, important knowledge gaps remain:

1. **Molecular characterization of complex OA:** Many OA constituents are low- or semi-volatile, highly oxidized, or reactive. Traditional mass spectrometry approaches often target specific analytes, leaving a substantial fraction of organic mass and structural diversity insufficiently characterized.
2. **Source-specific formation pathways:** Biogenic emissions, biomass burning, and long-range transport strongly influence OA composition, yet the molecular pathways underlying particle formation, aging, and transformation, particularly as a function of particle size, remain poorly constrained.
3. **Meteorological influences on particle dynamics:** Rainfall, canopy interactions, and other environmental processes can affect new particle formation. The mechanistic connections among meteorology, precursor availability, and particle growth remain poorly understood, requiring a combined observational and analytical approach.
4. **Ecosystem context for biogenic emissions:** The molecular composition and nutrient status of dissolved organic matter (DOM) in Amazon soils govern the release of biogenic volatile organic compounds, which serve as precursors for secondary OA. However, it remains unclear how variations in soil chemistry, nutrient limitations, and seasonal dynamics translate into changes in biogenic volatile organic compound (VOC) emissions and subsequent OA formation, leaving a critical gap in linking ecosystem processes to atmospheric aerosol composition.

5. **Anthropogenic contributions and chemical diversity:** Sulfur-containing organosulfates and other anthropogenically influenced OA strongly affect air quality and climate, yet their molecular diversity and contribution to total OA remain challenging to quantify.

Motivation: Addressing these questions drives the integrated application of comprehensive mass spectrometric techniques and particle-resolved measurements. By combining advanced analytical methods with environmental and ecosystem observations, this dissertation aims to achieve a comprehensive molecular-level understanding of OA and their formation, transformation, and ecosystem interactions.

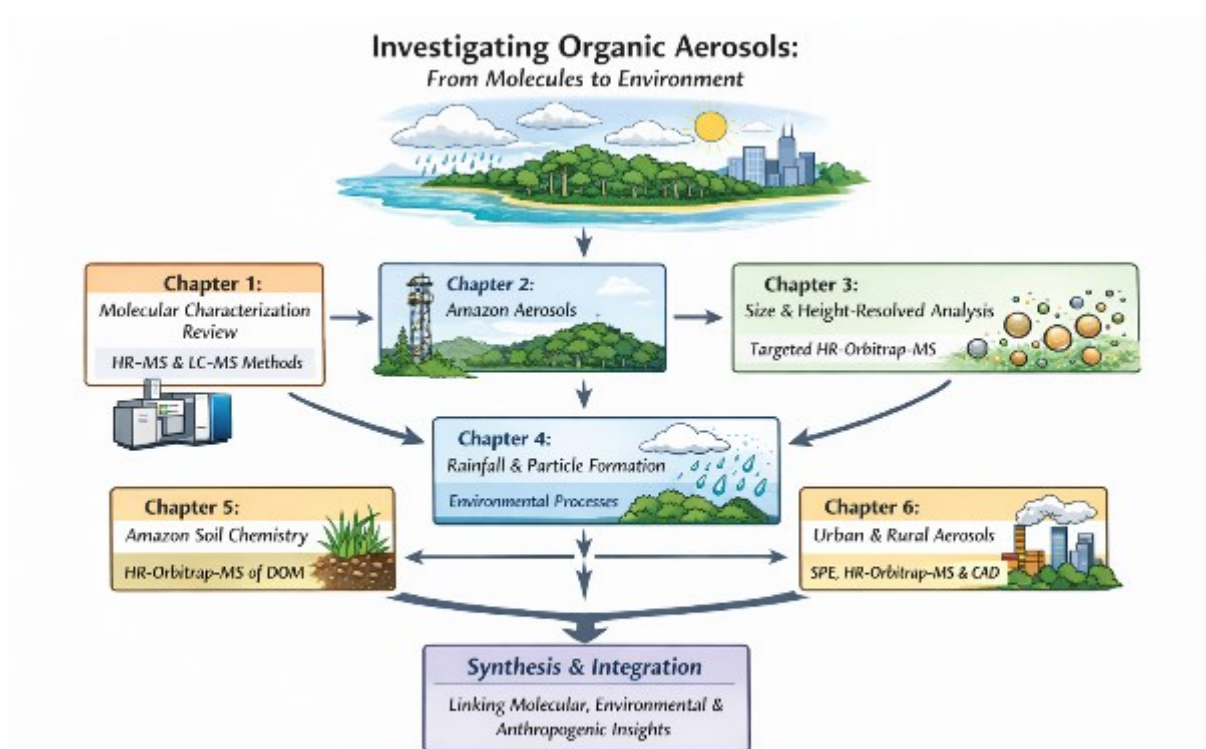


Figure 1.4-1: Overview of the dissertation structure showing how Chapters 1–6 are linked methodologically and thematically, highlighting the use of HR-Orbitrap-MS, SPE, and CAD to study molecular, environmental, and anthropogenic aspects of organic aerosols (figure by ChatGPT, 2026).

This dissertation investigates the molecular composition, formation processes, and environmental and anthropogenic influences of organic aerosols using high-resolution mass spectrometry. Organic aerosols play a central role in the Earth's climate system, impacting cloud formation, precipitation, and atmospheric radiation, while also affecting air quality and human health. Despite considerable progress in characterizing organic aerosol constituents, key knowledge gaps remain, particularly regarding low- and semi-volatile compounds, highly oxidized species, and reactive organics. Understanding these gaps requires an integrated approach that combines advanced analytical techniques, environmental observations, and ecosystem context.

The first chapter of the thesis is based on a review article that provides a comprehensive overview of the current state of molecular characterization of OA. This work discusses the analytical challenges posed by the chemical complexity of organic aerosols, including the diversity of functional groups, volatility classes, and oxidative states. It highlights the opportunities and limitations of one- and multidimensional liquid chromatography coupled with mass spectrometry, and contrasts targeted versus non-targeted approaches. Chapter 1 establishes the methodological and conceptual foundation for the subsequent studies, demonstrating how advanced HR-MS techniques can be applied to resolve the structural and chemical diversity of atmospheric organic matter.

Building on this foundation, chapters 2 and 3 present applications of these analytical methods to aerosols collected in the Amazon rainforest. Chapter 2 employs non-targeted HR-MS to identify thousands of molecular formulas in ambient aerosol samples collected at the Amazon Tall Tower Observatory (ATTO), revealing the predominance of biogenic secondary organic aerosols derived from isoprene and monoterpene oxidation and the seasonal modulation of these compounds by wet and dry periods.

Chapter 3 extends this approach by performing size- and height-resolved targeted analyses of primary and secondary organic aerosol markers. These measurements demonstrate how particle composition varies systematically with particle size, altitude, season, and atmospheric conditions, highlighting the distinct formation and aging pathways of ultrafine and fine particles, as well as the interplay among primary biological markers, secondary organic aerosols, and organosulfates. Together, chapters 2 and 3 illustrate how molecular-level characterization can be combined with particle-resolved observations to elucidate sources, transformation processes, and atmospheric transport of organic aerosols in a tropical environment.

Chapter 4 provides the environmental context for aerosol formation by examining nanoparticle bursts triggered by rainfall events within the forest canopy. This study shows how precipitation and canopy-mediated processes influence the nucleation of new particles and the potential generation of cloud condensation nuclei. These observations establish a mechanistic link between environmental dynamics and the chemical processes observed in chapters 2 and 3, emphasizing the importance of meteorology and vertical gradients in understanding aerosol formation in pristine tropical forests.

Chapter 5 situates these atmospheric observations within the ecosystem context by analyzing the molecular composition and nutrient limitations of dissolved organic matter (DOM) in Amazonian soils using non-targeted HR-Orbitrap-MS. This approach enables the comprehensive characterization of phosphorus-, nitrogen-, and sulfur-containing organic compounds, providing detailed insights into the potential precursors of biogenic volatile organic compounds that subsequently contribute to secondary organic aerosol formation. Although this work focuses on soil and nutrient dynamics rather than aerosol chemistry, it highlights the ecological controls on precursor availability and illustrates the interconnectedness between ecosystem chemistry and atmospheric processes.

Finally, chapter 6 examines the role of anthropogenic influences on organic aerosols, focusing on organosulfates in ambient aerosol samples from urban and rural environments. The analytical challenge of quantifying organosulfates in ambient organic aerosol samples is addressed by presenting a novel solid-phase extraction (SPE) method coupled with high-resolution Orbitrap mass spectrometry (HR-Orbitrap-MS) and charged aerosol detection (CAD). This multi-method approach revealed significant differences between urban and rural aerosols and highlighted the substantial impact of sulfur emissions on both air quality and

climate-relevant aerosol chemistry. By combining SPE, HR-Orbitrap-MS, and CAD, this work not only provides a detailed molecular-level characterization of anthropogenic organosulfates but also extends the methodological framework established in chapter 1, demonstrating the broader applicability of advanced mass spectrometric approaches to environmental aerosol studies.

Taken together, chapters 1 through 6 provide a multi-scale, integrated perspective on organic aerosols, bridging molecular-level chemical analyses, particle-resolved atmospheric observations, environmental processes, ecosystem controls, and anthropogenic contributions. The dissertation emphasizes the necessity of high-resolution mass spectrometry as a tool for unraveling the complexity of organic aerosols, while situating these measurements within the environmental and ecological context in which aerosols form, evolve, and impact climate and air quality.

2 Analytical approaches to enable the molecular characterization of organic aerosols

This chapter has been published in *Trends of Analytical Chemistry* (Hildmann & Hoffmann, 2024) :

Summary

The first chapter of the thesis is based on a review article that provides a comprehensive overview of the current state of molecular characterization of organic aerosols. This work discusses the analytical challenges posed by the chemical complexity of organic aerosols, including the diversity of functional groups, volatility classes, and oxidative states. It highlights the opportunities and limitations of one- and multidimensional liquid chromatography coupled with mass spectrometry, and contrasts targeted versus non-targeted approaches. Chapter 1 establishes the methodological and conceptual foundation for the subsequent studies, demonstrating how advanced high-resolution mass spectrometry techniques can be applied to resolve the structural and chemical diversity of atmospheric organic matter.

I am the first author of this paper and led the conceptualization, literature research, and synthesis of current advancements in the molecular characterization of organic aerosols. My work involved critically evaluating the analytical challenges posed by the chemical complexity of organic aerosols, contrasting targeted and non-targeted mass spectrometry approaches, and establishing a methodological framework that bridges liquid chromatography–mass spectrometry with the structural and chemical diversity of atmospheric organic matter.

Characterisation of atmospheric organic aerosols with one- and multidimensional liquid chromatography and mass spectrometry: State of the art and future perspectives

Stefanie Hildmann, Thorsten Hoffmann

2.1 Abstract

Aerosol particles are important components of the Earth's atmosphere and affect air quality and climate. They are small enough to penetrate deep into human lungs and are associated with serious short- and long-term health effects. They also affect Earth's climate directly through scattering and absorption of solar radiation and indirectly through their role as cloud condensation nuclei. A large fraction (~50%) of the submicron aerosol mass in the troposphere consists of organic material. In recent years progress has been made in the molecular characterisation of individual target analytes and in the determination of the physicochemical properties of organic aerosol constituents. However, knowledge gaps remain, especially information on low- and semi-volatile, often highly oxidized organic compounds or highly reactive compounds. For these classes of compounds, different liquid chromatography-mass spectrometry (LC-MS) systems have become preferred analytical methods in recent years. Although these methods offer a wide range of applications, they can be limited to specific analytes. Therefore, multidimensional LC and MS methods have also been introduced in atmospheric sciences to increase either the fraction of organic mass analysed or the degree of identification of individual components. In this review article, we present the main applications of advanced one- and multidimensional LC and MS methods in the analysis of atmospheric particles in non-targeted and targeted approaches, highlight their opportunities and limitations, and outline the main challenges for future application in atmospheric sciences.

Keywords: atmospheric aerosol; (multidimensional) liquid chromatography; (high-resolution) mass spectrometry; chemical characterisation/identification; (non/semi)-targeted approach

Abbreviations

2,4-DNPH	2,4-dinitrophenylhydrazine
HULIS	Humic like substances
ACN	Acetonitrile
AMS	Aerosol mass spectrometer
APCI	Atmospheric pressure ionisation
APPI	Atmospheric pressure photo ionisation
ASM	Active solvent modulation
BVOC	Biogenic volatile organic compound
CIMS	Chemical ionisation mass spectrometer
CPLC	Chiral phase LC
DBE	Double bond equivalence
DOAS	Differential optical absorption spectroscopy
EI	Electron ionisation
ESI	Electrospray ionisation
FLD	Fluorescence detector
FT-ICR-MS	Fourier transform ion cyclotron resonance MS
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HILIC	Hydrophilic lipophilic interactions chromatography
HOM	Highly oxidized molecules
HPLC	High performance liquid chromatography
IR-MS	Isotope ratio MS

IT-MS	Ion trap MS
LC-LC	Heart cut LC
LCxLC	Comprehensive LC
LOQ	Limit of quantification
MCR	Maximum carbonyl ratio
mLC-LC	Multiple heart cut LC
MRM	Multiple reaction monitoring
MS	Mass spectrometry
MS ⁿ	Tandem mass spectrometry
MW	Molecular weight
NPLC	Normal phase LC
NTA	Non-targeted analysis
O/N-PAHs	Oxygenated and nitro-substituted PAHs
OA	Organic aerosols
OS	Organosulphates
PAH	Polycyclic aromatic hydrocarbon
PERCI	Photoelectron resonance capture ionisation
PFBHA	Pentafluorobenzyl hydroxylamine
PI	Photo ionisation
PTR	Proton transfer reaction
Qq-ToF-MS	Quadrupole time of flight MS
ROS	Reactive oxygen species
RPLC	Reversed phase LC
SCX	Strong cation exclusion chromatography
SEC	Size exclusion chromatography
SOA	Secondary organic aerosols
SPAM	Stationary phase assisted modulation
SPE	Solid phase extraction
SRM	Selected reaction monitoring
STA	Semi-targeted analysis
TA	Targeted analysis
ToF-MS	Time of flight mass spectrometry
tQ-MS	Triple quadrupole MS
UHR-MS	Ultra high resolution mass spectrometry
VEM	Vacuum evaporation modulation

2.2 Introduction

One of the current analytical challenges in atmospheric sciences is the chemical characterisation of atmospheric organic aerosol (OA) particles. Due to their impact on human health (Chaturvedi et al., 2023; Jo et al., 2023; Mauderly & Chow, 2008; Shiraiwa et al., 2017), climate and geochemical cycles, there is great interest in elucidating their chemical composition. Based on the latest chemical and physicochemical understanding of the processes leading to the formation of atmospheric aerosols (Elm et al., 2023; Stolzenburg et al., 2023), quantitative information on low- and semi-volatile, often highly oxidized organic compounds in the ultra-trace region is particularly needed. However, the chemical and physicochemical properties of aerosol-bound organics such as volatility, polarity, reactive oxygen content, reactivity, and complexity, which classify these compounds as interesting target analytes, at the same time make it difficult to reliably measure their concentration. Despite some progress in this field, the search for techniques to identify and quantify suitable tracers for understanding atmospheric processes as well as source attribution continues, with liquid chromatography-mass spectrometry (LC-MS) emerging in recent years as popular analytical techniques for the determination of organic compounds in aerosols. (Johnston &

Kerecman, 2019; Parshintsev & Hyötyläinen, 2015) LC-MS methods, while offering a wide range of applications, are limited in a basic design to specific analyte classes only. Therefore, multidimensional LC and MS methods have been introduced in atmospheric sciences to increase either the fraction of organic mass analysed or the degree of identification of individual components. This review article therefore aims to present the main applications of advanced one- and multidimensional LC and MS methods for the analysis of organic aerosol components in the atmosphere, but also to highlight their limitations and outline the main challenges for future applications in atmospheric sciences.

2.2.1 Identification factor I

The degree of identification of an organic compound is described by the identification factor I . I is defined by the number of possible compounds corresponding to the information requested or measured by a particular analytical technique. For a compound determined by mass spectrometric techniques, I is defined by Equation 2.2-1:(Nozière et al., 2015c)

$$I = \text{number of molecules matching MW} \times \text{number of possible isomers and spatial configurations} \quad \text{Equation 2.2-1}$$

Depending on the ionisation technique and the mass resolution that the chosen mass spectrometer provides, identification factors can range from $1 \leq I \leq 100$. Using hard ionisation techniques, such as electron ionisation (EI), leads to high fragmentation ions that cannot always be deconvoluted. The factor I decreases drastically with upstream chromatography since a second dimension on information, e.g. retention time, is added. Mass analysers with low mass resolution, i.e. unit-resolution MS, lead to several compounds that can be assigned to a specific molecular weight (MW) what increases I . I is now the number of isobaric compounds that are ionised and eluted simultaneously, for example, the number of possible (non-separated) structural or stereoisomers. The use of a high-resolution mass spectrometers (HR-MS) result in smaller numbers of compounds due to the unique molecular formula that can be assigned to a specific m/z . If a suitable, authentic standard of the compound to be characterised is available, a complete characterisation can be achieved by an appropriate matching ($I = 1$). (Nozière et al., 2015c).

2.2.2 From functional group to molecular analysis of OA

Different atmospheric research questions need distinctive levels of identification of organic components that can be provided by various analytical techniques. For example, to study optical properties for the global energy budget of secondary organic aerosol (SOA) precursors, it is not necessary to identify the compounds individually but to quantify them based on common property. Typically, functional group analyses (i.e. optical spectroscopies: Fourier transform infrared spectroscopy (FTIR), differential optical absorption spectroscopy (DOAS), ...)(Christian et al., 2004; Faber, Drewnick, Bierl, & Borrmann, 2017; Hak et al., 2005; Moise, Flores, & Rudich, 2015) can be used that would provide identification with $I \geq 100$. Also, for real-time monitoring to capture the chemistry in a turbulent atmosphere, excellent time resolutions with time scales of seconds to minutes are prioritised rather than complete identification of individual compounds. For these purposes, online analytical techniques such as aerosol mass spectrometers (AMS) are often used. AMS systems are operated at high vaporisation temperature (~ 600 °C) and use electron ionisation (~ 70 eV). This allows the characterisation of chemical features due to similar structures and functionalities that lead to similar fragmentation patterns at excellent time scales.(Canagaratna et al., 2007; Jeon et al.,

2023; Lanz et al., 2010; Zhang et al., 2011) On the other hand, due to highly fragmentation ions, mass spectra from different molecules that simultaneously vaporise from the probe cannot be deconvoluted what leads to a loss of molecular information (higher I -factor). When coupled with high-resolution mass analysis to separate isobaric ions (decreasing I), quantitative information can be gained about the elemental composition of organic matter in atmospheric particles and how it changes with time. (Ge, Sun, Trousdell, Chen, & Zhang, 2024; Niedek et al., 2023) To circumvents the drawbacks of hard ionisation techniques, soft ionisation approaches were developed for online-MS devices. Examples are chemical ionisation (CI) (Hearn & Smith, 2004; Yatavelli & Thornton, 2010; Zhang et al., 2023), proton-transfer-reaction (PTR) ionisation (Holzinger et al., 2010b; Smith, Moore, McMurry, & Eisele, 2004; Thornberry et al., 2009), photo ionisation (PI) (Oktem, Tolocka, & Johnston, 2004) and photoelectron resonance capture ionisation (PERCI) (LaFranchi & Petrucci, 2006) where high-resolution mass analysers (Aljawhary, Lee, & Abbatt, 2013; Holzinger, Kasper-Giebl, Staudinger, Schauer, & Röckmann, 2010a; Yatavelli et al., 2012) can provide additional molecular specificity. Additionally, tandem-MS can be performed in an ion trap (IT) mass analyser. (Thornberry et al., 2009) Using the mentioned online techniques for OA characterisation can provide excellent time resolution and $10 \leq I \leq 100$ depending on the chosen ionisation method and mass resolution of the analyser. Summarising, there are several online-MS techniques and devices that have been implemented in the past and are constantly being further developed to enable chemical characterisation of OA in a turbulent atmosphere in real-time. Interested readers who want deepen their knowledge of these techniques are referred to the excellent reviews (Johnston & Kerecman, 2019; Nozière et al., 2015c; Zhang et al., 2023).

However, for certain atmospheric questions, a relative ($I \leq 2-3$) or complete ($I = 1$) identification of individual organic components is necessary. Molecular analysis is needed to identify molecular markers that can be attributed to a specific source or process that generates OA. Furthermore, molecular analysis methods are inherently adaptable for quantitative analysis what is crucial for determining relative contributions that various sources or processes make to OA. Molecular marker analysis can elucidate mechanisms and rates of aerosol formation and decay or reconstruct physicochemical properties (i.e. fraction of light absorbing molecules in particles correlates with ability to absorb solar radiation (Laskin, Laskin, & Nizkorodov, 2015; Rincón, Guzmán, Hoffmann, & Colussi, 2009)). Nevertheless, molecular analysis of OA is analytically challenging due to chemical diversity, low concentrations, matrix effects, chemical transformations and sampling artifacts. (Hallquist et al., 2009) Atmospheric levels of organic particulate matter (PM) are in the order of $1 - 10 \mu\text{g}/\text{m}^3$ with individual compounds in the pg/m^3 to ng/m^3 level. (Nozière et al., 2015c; Pöschl, 2005a) As a result, sensitivity limitations of analytical instruments can hinder the accurate measurement of low-concentration species. Organic PM is composed of a diverse mixture of compounds originating from various sources such as biogenic emissions, combustion processes, and anthropogenic activities and can contain thousands of different organic compounds with a wide range of chemical structures and properties, i.e. volatility or polarity. (Donahue, Robinson, Trump, Riipinen, & Kroll, 2014; Donahue, Tischuk, Marquis, & Huff Hartz, 2007; Kroll & Seinfeld, 2008; Shrivastava et al., 2017) Analysing this chemical diversity requires techniques capable of detecting and characterising a broad spectrum of molecules. Furthermore, the presence of other aerosol components, such as inorganic salts and water, can interfere with the analysis of organic compounds. Matrix effects can affect the performance of analytical techniques and lead to biased results if not adequately accounted for. (Parshintsev & Hyötyläinen, 2015) Furthermore, organic aerosols undergo chemical transformations during atmospheric aging

processes, such as oxidation reactions.(Donahue et al., 2014; Rudich, Donahue, & Mentel, 2007) These transformations can alter the composition and properties of organic compounds, complicating their identification and quantification. Lastly, collection and storage of aerosol samples can introduce artifacts or losses of volatile or semi-volatile compounds, affecting the representativeness of the analysis results.(Kanakidou et al., 2005) To face these challenges, MS detectors with upstream gas- or liquid-chromatography are typically used for molecular analysis of OA.

2.3 GC- and LC-MS for molecular analysis

GC-MS and LC-MS techniques are well-suited for comprehensive analysis of OA and addressing the challenges associated with their molecular characterisation. These techniques combine separation power, sensitivity, selectivity, identification and quantification. Mass spectrometric detectors are the closest approach to a universal detector for organic compounds, offering high sensitivity combined with high time resolution. It is suited to ultra-trace analysis like no other technique, and has without question already contributed significantly to advances in our understanding of the role of organic compounds in the atmosphere. In particular, offline MS techniques that allow the use of tandem MS experiments (MS_n) or high-resolution mass analysers enable near-complete characterisation of atmospherically relevant compounds at trace concentrations.(Nizkorodov, Laskin, & Laskin, 2011) This selectivity is crucial for distinguishing between different organic species in complex aerosol samples and reducing interference from matrix components.(Visentin & Pietrogrande, 2014) Furthermore, MS systems can be easily coupled to chromatography systems like GC or LC what provides even higher sensitivity, selectivity and $1 \leq I \leq 2-3$ due to excellent separation power, since separation of a complex OA mixture into individual compounds leads to higher signal-to-noise ratios and smaller matrix effects.(Mahilang, Deb, & Pervez, 2021; Parshintsev & Hyötyläinen, 2015) While compounds are separated based on their affinity for the stationary phase in the LC column, separation in GC is achieved based on differences in volatility.(Harris, 2010) Depending on the stationary phase that is chosen for the separation columns, LC-MS and GC-MS can be used for analysing a wide range of organic compounds, including polar and non-polar species.(Flores & Doskey, 2014; Tiusanen, Ruiz-Jimenez, Hartonen, & Wiedmer, 2023) This versatility makes them suitable for studying the diverse chemical composition of organic aerosols originating from various sources and undergoing different atmospheric processes. Lastly, LC-MS and GC-MS enable the accurate quantification of organic compounds in aerosol samples by comparing the signal intensity of target analytes to that of internal or external standards.(Harris, 2010) This quantitative capability allows to determine concentration levels and to assess the contributions of different sources to OA composition.

Applications of GC-MS for the molecular characterisation of atmospheric OA can be dated back to the late 1970s(Cautreels & van Cauwenberghe, 1976; M. Claeys, R. Vermeylen, A. Kubatova, & J. Cafmeyer and W. Maenhaut, 1970; Pitts, Grosjean, van Cauwenberghe, Schmid, & Fitz, 1978) where a limited range of compound classes could be investigated. During the past decades, GC-MS could significantly contribute to our understanding of the contribution of OA and its specific sources to atmospheric aerosol. Experiments in which particles from specific sources were analysed by GC-MS allowed a rigorous identification of molecular source signatures while simultaneously expanding the number of compounds analysed. Examples are fossil fuel combustion from motor vehicles(Rogge, Hildemann, Mazurek, Cass, & Simoneit, 1993), biomass burning(Simoneit, 2002), cooking(Rogge, Hildemann, Mazurek, Cass, & Simoneit, 1991) or cigarette smoke(Rogge, Hildemann,

Mazurek, Cass, & Simoneit, 1994; Schwanz et al., 2019). Molecular markers identifying each source could consist of an individual compound, i.e. Levoglucosan as the most prominent marker for wood burning.(Simoneit et al., 1999) While GC-MS is a mature, robust method for molecular identification and quantification, significant limitations exist. Firstly, only a certain range of compounds can be eluted from the GC columns because many organic compounds are highly polar or thermally labile. Secondly, a certain amount of eluted organic compounds cannot be chromatographically resolved and identified since EI is usually used for quantitative GC-MS what significantly increases *I*.(Williams et al., 2007) To partially overcome the limitation, that many compounds are difficult to vaporise and to elute by GC, molecular derivatisation methods have been developed, where silylation(Flores & Doskey, 2015) is the most prominent one.(Claeys et al., 2004b; Jaoui, Kleindienst, Lewandowski, Offenber, & Edney, 2005) To address the problem that atmospheric aerosol is complex on a molecular level and one-dimensional separations are unable to resolve the large number of compounds present, two-dimensional (2D)-GC methods have been implemented in atmospheric science.(Flores & Doskey, 2014) These approaches were used with an emphasis on coupling 2D-GC with a Time of Flight (ToF) mass analyser.(Franklin et al., 2022; Franklin et al., 2023; Hamilton et al., 2004; Hatch et al., 2015; Kallio et al., 2003; Welthagen, Schnelle-Kreis, & Zimmermann, 2003) These techniques enabled increasing the peak capacity, in which the effluent from a non-polar primary column was collected at regular intervals and eluted through a polar secondary column.(Hamilton, 2010; Liu & Phillips, 1991) With this method, the number of distinct chemical species found in an atmospheric sample was reported to be as high as 10 000.(Hamilton, 2010) GC-MS is commonly favoured over LC-MS for atmospheric aerosol analysis due to its superior separation efficiency, high sensitivity, and relative resistance to ion signal quenching effects. Furthermore, 2D-GC couplings are easier adaptable since modulation techniques are well implemented nowadays compared to 2D-LC setups.(Duarte, Brandão, & Duarte, 2023) Nonetheless, LC-MS plays a crucial role in identifying polar, non-volatile, and thermally labile molecules that cannot be eluted by GC, even with derivatisation.

An early study utilizing LC-MS with a reverse-phase column and electrospray ionisation (ESI) to investigate atmospheric aerosols revealed a complex array of species within the 100–800 *m/z* range.(Gao et al., 2006) Many nominal *m/z* values exhibited multiple chromatographic peaks, indicating the presence of isomeric and/or isobaric compounds. These findings underscored the necessity for high-resolution mass measurements to differentiate isobaric elemental formulas and the need for authentic standards to confirm molecular assignments and enable quantitative analysis.(Johnston & Kerecman, 2019) Furthermore, a distinct advantage of using LC-MS in aerosol science is that it allows to analyse high molecular weight (MW) compounds, such as dimers and oligomers of secondary organic aerosols (SOA).(Hamilton, Lewis, Carey, & Wenger, 2008; Yasmeen et al., 2010) Our understanding of SOA dimers and high MW compounds in atmospheric chemistry is still incomplete but a lot of effort has been taken in the last years. These compounds can constitute a significant portion of the organic aerosol mass and can serve as precursors for nucleation and particle growth by serving as condensation nuclei or by providing reactive functional groups for further chemical reactions.(Hamilton et al., 2008; Kourtchev et al., 2015; Kourtchev et al., 2016a; Müller, Reinnig, Hayen, & Hoffmann, 2009) Analysing SOA dimers and high MW compounds is crucial for gaining a comprehensive understanding of the composition, origin, and atmospheric impact of OA in the atmosphere. Lastly, a big emphasis has to be taken on the capability to operate LC-MS systems with soft ionisation techniques, such as ESI, atmospheric pressure chemical ionisation (APCI) and atmospheric pressure photo ionisation (APPI). Electrospray ionisation is most often used for OA analysis with LC-MS but several applications of APCI(Wang, Zhu, Shi,

& Li, 2023a) and APPI(Adelhelm, Niessner, Pöschl, & Letzel, 2008; Lintelmann, França, Hübner, & Matuschek, 2010; Robb & Blades, 2008; Ruiz-Jiménez et al., 2012) also exist, especially when aromatic compounds are studied. The use of soft ionisation techniques dramatically decreases I what allows to identify new molecular markers. Moreover, it enables detailed non-targeted analysis by identifying several thousands of organic compounds on the molecular levels.(Kourtchev et al., 2015; Vogel et al., 2019) In combination with high resolution MS techniques, $I \leq 2-3$ can still be guaranteed what is not possible with GC-EI-MS techniques. Nevertheless, compared to GC-MS, LC has to face the same challenge of being limited to analyse and to resolve only a certain range of compounds. While GC-MS is limited to compounds that are volatile and stable enough, LC-MS is limited to specific polarity ranges depending on the stationary phase used in the separation column. To circumvent this drawback, the use of multidimensional LC techniques lends itself. While 2D-GC-MS approaches have found increasing application in atmospheric chemistry, the number of applications for multidimensional LC techniques is comparatively small, although they are already well utilised in polymer analysis, biopharmaceutics or proteomics.(Duarte et al., 2023; Pirok, Stoll, & Schoenmakers, 2019; Stoll & Carr, 2017)

Accordingly, this review article discusses to what extent and for which atmospheric questions and samples one- and multidimensional LC techniques are applicable nowadays or when even the one-dimensional techniques are superior. Besides adding a second LC dimension, the addition of another detector dimension, such as coupling UV/Vis with MS detection or tandem MS experiments, is also discussed as an alternative way to obtain extended information.

2.4 Analytical approaches and resulting analytical conditions

In the chemical characterisation of organic aerosols, there are essentially three analytical approaches, which must satisfy different instrumental criteria: targeted analysis (TA), non-targeted analysis (NTA) and semi-targeted analysis (STA). Figure 2.4-1 shows the schematic representation of exemplary data generated with TA, NTA and STA approaches in the field of atmospheric organic aerosol research.

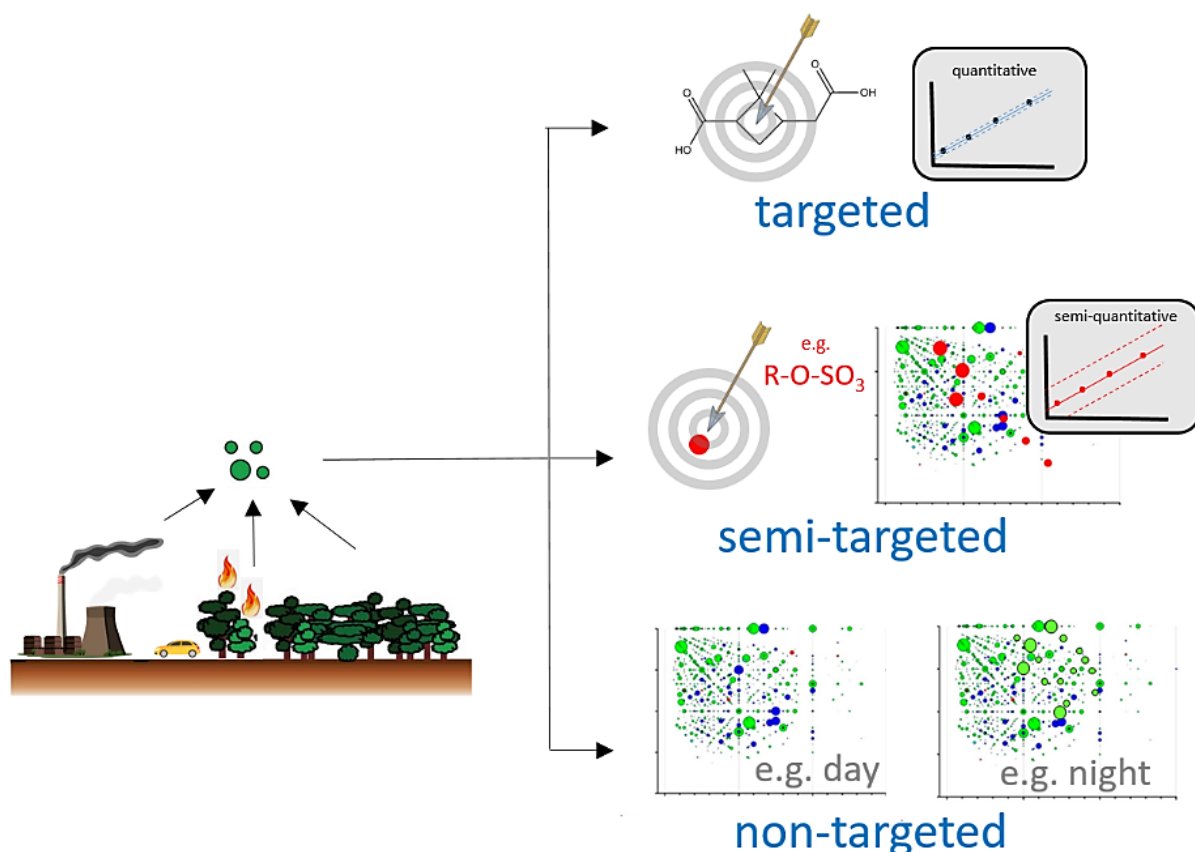


Figure 2.4-1: Schematic representation of TA, NTA and STA approaches in the field of atmospheric organic aerosol research. While pinic acid, as a biogenic SOA marker, can be precisely quantitatively determined in the TA, the determination of organosulphates in the STA is only semi-quantitative. For the NTA, for example, a qualitative comparison of two van Krevelen plots is made to visualise diurnal influences on the chemical composition of OA.

2.5 The targeted approach

In the context of TA, a selected number of previously determined target compounds are analysed. The selection of the analytes is subject to their atmospheric chemical significance or uniqueness as so-called marker substances for sources or source processes. Targeted methods have very high selectivity and often better sensitivity than non-targeted methods and are therefore especially suitable for the quantification of ultra-trace concentrations. However, TA can only be performed if an authentic standard of the analyte is available. A number of target analytes representing oxidation products of important biogenic volatile organic compounds (BVOCs) in the atmosphere, such as isoprene, monoterpenes, and sesquiterpenes, are commercially available. (Nozière et al., 2015c) For many other oxidation products of both, anthropogenic and biogenic origin, the same is not true and those products have to be synthesised in the laboratory. An excellent overview of synthesised reference standards for corresponding oxidation products that are not commercially available can be found in (Nozière et al., 2015c; Upshur et al., 2023). The quantification of the analytes is comparatively straightforward due to the use of internal and external standards for the selected analytes. In addition, the desired performance criteria of the method, i.e. thresholds for selectivity, sensitivity, accuracy, and precision, are well defined, generally accepted, and adaptable to any application. (Fisher, Peter, Newton, Schaub, & Sobus, 2022)

The determination of molecular markers in submicrometer aerosol is important because it can provide information about aerosol sources or ageing processes such as oxidation or formation of light-absorbing compounds. Interested readers will find a good review article on markers for biomass combustion in (Simoneit, 2002) and on markers for SOA formation from isoprene in (Claeys & Maenhaut, 2021). Furthermore, there are numerous individual articles on suitable marker substances for SOA formation from monoterpenes and sesquiterpenes (Glasius et al., 2000; Parshintsev et al., 2008; Spolnik et al., 2020; Steimer et al., 2018; van Eijck, Opatz, Taraborrelli, Sander, & Hoffmann, 2013) as well as aged organic aerosol (Jaoui et al., 2019; Witkowski, Al-Sharafi, Błaziak, & Gierczak, 2023). In addition, interest in the dedicated determination of stereoisomers in aerosol chemistry, particularly from biogenic hydrocarbons, has increased in recent years (Bellcross, Bé, Geiger, & Thomson, 2021; Ebben et al., 2011; Stokes et al., 2009; Zhu, Kais, Zeng, Francisco, & Gladich, 2017). For example, Leppla et al. 2023 quantified the optical isomers of α -pinene oxidation products in OA using a chiral stationary phase (CP) by LC-MS measurements and showed, using vertical profiles in the Amazon rainforest, that the chiral ratio of α -pinene oxidation products varied at different heights above the forest canopy. The authors concluded that characteristic emissions of chiral aerosol precursors from different forest ecosystems could provide large-scale information on differential contributions to biogenic SOAs through analysis of chiral particle-bound degradation products (Leppla et al., 2023). In addition to the increasingly specialised markers for terrestrial biogenic SOA sources, there is further work on biomarkers for marine aerosol (Claeys et al., 2010b; Rinaldi et al., 2010), fungal spores (Elbert, Taylor, Andreae, & Pöschl, 2007; Zhang et al., 2010a), and anthropogenic sources (Al-Naiema & Stone, 2017; Bryant et al., 2020).

Clearly, the TA is a very popular approach in organic aerosol research which is constantly expanding and requires excellent LC-MS methods to enable identification and quantification at trace concentrations. The most commonly operated LC technique is reversed-phase chromatography (RPLC), as it allows separation of a wide range of medium-polar to non-polar compounds. For highly polar species, variations of normal phase chromatography (NPLC), such as hydrophilic interaction liquid chromatography (HILIC), are applied. For more specialised applications, ion exchange (IEC) or size exclusion chromatography (SEC) are also used. In terms of detectors, mass spectrometers with MS/MS capabilities such as ToF-MS or triple quadrupole mass spectrometers (tQ-MS) are commonly applied for TA. An overview of current and known LC-MS methods is given in Table 2.5-1.

Table 2.5-1: List of examples for applying different one- and multidimensional LC and MS methods and analytical approaches to characterise atmospheric organic aerosols in different samples in recent years. Multidimensional LC methods are written bold.

<i>Targeted approaches</i>				
Analytes	Sample, Analytical approach	Extraction	Analysis Technique	References
Aliphatic & aromatic carboxylic acids	Filter	Water	RPLC-ESI-ToF-MS	(Mirivel, Riffault, & Galloo, 2011)
Aliphatic & aromatic aldehydes and ketones	Speleothems Filter Filter SPE	MeOH ACN/Water 1/1 +2,4-DNPH MeOH/Water 1/1 + 2,4-DNPH	RPLC-ESI-HR-Orbitrap-MS RPLC-UV/Vis RPLC-UV/Vis-ESI-IT-MS/MS	(Homann, Oster, Wet, Breitenbach, & Hoffmann, 2022)

		ACN/Water + 2,4-DNPH	RPLCxRPLC-UV	(Liggio & Mclaren, 2003) (Kampf, Bonn, & Hoffmann, 2011; Kampf, Jakob, & Hoffmann, 2012b) (Kootstra & Herbold, 1995)
Phenols	Filter	ACN/Water	RPLC-ESI-IT-MS	(Ogrizek, Kroflíč, & Šála, 2022)
Nitroaromatics	Filter	MeOH	RPLC-ESI-MS/MS	(Kitanovski, Grgić, Vermeulen, Claeys, & Maenhaut, 2012a)
Heterocyclic & aliphatic amines	Filter Filter Filter	Water MeOH MeOH	RPLC-ESI-QqToF- MS/MS RPLC-ESI-IT- MS/RPLC-APCI-IT- MS/RPLC-APPI-IT-MS RPLC-UV	(Samy & Hays, 2013) (Ruiz- Jiménez et al., 2012) (Huang, Deng, Zhuang, Lin, & Xiao, 2016)
Terpene- oxidation products Pinic acid, Pinonic acid	Filter Ice cores Filter Filter	Water Evaporation MeOH/Water 9/1 Water	RPLC-ESI-IT-MS mRPLC-CP-ESI-HR- Orbitrap-MS CP-ESI-HR-Orbitrap- MS RPLC-ESI-tQ-MS/MS	(Claeys et al., 2012) (Schäfer, Burgay, Singer, Schwikowski, & Hoffmann, 2023) (Leppla et al., 2023) (Feltracco et al., 2018)
Anhydrosugars	Speleothems	MeOH	RPLC-ESI-HR-Orbitrap- MS	(Homann et al., 2023)
Sugar alcohols	Filter	MeOH	NPLC-ESI-MS	(Wan & Yu, 2006)
Polycyclic aromatic hydrocarbons	Filter Filter, PUF	Ethylacetate ACN	RPLC-MS/MS RPLC-UV/Vis	(Lintelmann, Fischer, & Matuschek, 2006)

				(El Mais et al., 2023)
<i>Semi-targeted approaches</i>				
Analytes	Sample, Analytical approach	Extraction	Analysis Technique	References
Aliphatic & aromatic carboxylic acids	Filter Filter Filter	MeOH Water MeOH/Water 9/1	SCXxRPLC-ESI-ToF-MS NPLC-ESI-MS/MS RPLC-ESI-QqToF-MS	(Pól, Hohnová, Jussila, & Hyötyläinen, 2006) (Stone, Hedman, Sheesley, Shafer, & Schauer, 2009) (Zhang et al., 2010b)
Organosulphates	Filter Filter Filter Rain, snow, hail	MeOH Water Water MeOH Evaporation	mRPLC-RPLC-ESI-IT-MS NPLC-ESI-MS/MS HILIC-ESI-MS/MS HILIC-ESI-QToF-MS RPLC-ESI-HR-MS	(Iinuma et al., 2007a) (Stone et al., 2009) (Bryant et al., 2020) (Cui et al., 2018a) (Spolnik et al., 2020)
Carbohydrate-like substances	Filter	Water	NPLC-ESI-MS/MS	(Stone et al., 2009)
Nitroaromatics	Filter Filter	MeOH MeOH/Water 9/1	RPLC-UV/Vis RPLC-ESI-QqToF-MS	(Kitanovski, Grgić, Yasmeen, Claeys, & Cusak, 2012b) (Zhang et al., 2010b)
Heterocyclic amines	Filter	MeOH/ACN 1/1	RPLC-ESI-QqToF-MS	(Gao, Zhang, Liu, Yang, & Zhu, 2021)
Terpene-oxidation products	Filter Filter Filter	MeOH MeOH MeOH/Water 9/1	SCXxRPLC-ToF-MS RPLC-ESI-HR-Orbitrap-MS/MS RPLC-ESI-QqToF-MS	(Pól et al., 2006) (Jaoui et al., 2019) (Zhang et al., 2010b)
Pinic acid, Pinonic acid	Filter	MeOH	SCXxRPLC-ESI-ToF-MS	(Pól et al., 2006)
<i>Non-targeted approaches</i>				
Identified species	Sample	Extraction	Analysis Technique	References
Organic acids, anhydrosugars,	Ice cores	Evaporation	HILIC-RPLC-ESI-HR-Orbitrap-MS	(Beschnitt, Schwikowski,

sugar alcohols, terpen-oxidation products				& Hoffmann, 2022)
Organic acids, nitrophenols	Rainwater, filter	Evaporation, ACN/Water 1/1	RPLC-ESI-HR-Orbitrap-MS	(Beck et al., 2022)
Organic acids, aldehydes & ketones, phenols, nitroaromatics, benzenes	Filter	MeOH	RPLC-ESI-ToF	(Sato et al., 2012)
Terpen-oxidation products	Filter	MeOH	RPLC-ESI-HR-Orbitrap-MS	(Kourtchev et al., 2015)
Terpene-oxidation products, nitroaromatics, organosulphates	Ice cores, filter	SPE, MeOH/Water 14/1	RPLC-ESI-HR-Orbitrap-MS	(Vogel et al., 2019)
Organosulphates, reduced N-containing compounds, PAHs	Filter	Water, SPE	mSEC-RPLC-ESI-FT-ICR-MS	(Spranger, van Pinxteren, & Herrmann, 2017; Spranger, van Pinxteren, Reemtsma, Lechtenfeld, & Herrmann, 2019)
Organosulphates	Filter	ACN/Water 1/1	RPLC-ESI-HR-Orbitrap-MS	(Brüggemann, van Pinxteren, Wang, Yu, & Herrmann, 2019)
Plasticisers, flame retardants, pesticides, drug metabolites	Dust, filter	MeOH, SPE	RPLCxRPLC-ToF-MS	(Ouyang, Weiss, Boer, Lamoree, & Leonards, 2017)
Sum of water soluble organic matter	Filter Filter	Water Water	HILICxSEC-UV-FLD* HILICxSEC-UV/Vis*	(Paula, Matos, Duarte, & Duarte, 2016) (Matos, Freire, Duarte, & Duarte, 2015)

*No molecular analysis

2.6 The non-targeted approach

An NTA ideally searches for all organic components present in the sample, both known and unknown, maximising the number of compounds detected. By recording and storing all detectable signals, an inventory of the chemical composition of each sample is permanently available for further analysis. Non-targeted approaches are most appropriate for detecting unexpected changes in chemical composition. The goal is to maximise the number of substances detected providing the opportunity to observe unexpected changes. NTA also makes it possible to find new molecular markers for atmospheric processes or sources, which

is essential for the advancement of atmospheric chemistry research. In particular, important atmospheric processes where more knowledge is still needed, such as the role of organic compounds in nucleation, cloud formation processes or in the ageing and processing of aerosol components, would benefit from the identification and characterisation of new molecular markers. The challenges here are generally similar to those in environmental science, engineering, and regulation, where a variety of known but also unknown organic contaminants exist, and the use and advancement of non-target methods based on high-resolution mass spectrometry have greatly expanded the analytical window in recent years.(Hollender, Schymanski, Singer, & Ferguson, 2017) However, while the performance evaluation of analytical methods in TA is already widely known and accepted, the performance criteria for analytical NTA methods are not yet universally defined. Interested readers will find a discussion on the definition of NTA performance criteria in (Fisher et al., 2022).

HR-MS instruments suitable for routine analysis are now affordable and capable of detecting thousands of substances almost simultaneously and sensitively, if necessary, within the short time required for chromatographic separation. The essential criteria for high-resolution mass spectrometry are a high mass resolving power, but also a high mass accuracy. Initially, Qq-ToF-MS were used, but in recent years, Fourier transform mass spectrometers (FT-ICR-MS) and Orbitraps, have been increasingly operated (see Table 2.5-1). This allows the determination of unique molecular formulas for each ion peak. This development has given NTA a tremendous momentum, also in the analysis of organic aerosol constituents. The organic fraction of atmospheric aerosols contains hundreds to thousands of species in an m/z range of 100-500, and often more than 10 compounds are observed within 0.1 Dalton (Da), emphasising the need for high mass resolution.(Kourtchev et al., 2016b; Nozière et al., 2015c) Therefore, compared to a TA, an NTA can be used to analyse a larger fraction of the organic mass. The number of matching theoretical formulas, and thus the I - value, depends on the accuracy with which the measured MW is determined and increases exponentially with MW. For $MW > 300$, identification also requires additional information, such as isotopic composition or fragmentation (tandem MS).

Nevertheless, the high mass resolution of HR-MS allows direct input of the collected aerosol samples into an ion source, usually in the form of filter extracts (aqueous or organic solvents) by direct infusion. The idea is obvious since the omission of chromatographic preseparation increases the number of compounds detected (limited by the choice of solvent for extraction and detectability) and allows higher measurement frequencies. For these reasons, methods using direct infusion have also been successfully applied several times in atmospheric aerosol analysis.(Divisekara, Schum, & Mazzoleni, 2023; Kourtchev et al., 2020; Zielinski et al., 2018)However, this method always includes the risk of producing artifacts due to adduct formation in the ion source, thereby also increasing complexity and, last but not least, raising questions about quantification by ion suppression. Particularly with the goal of building the non-target approach on the detection of real individual substances (avoiding ion source artifacts), the coupling with LC is advised, accepting that the fraction of the analysed organic mass may decrease. Currently, reversed-phase (RP)LC-HR-MS methods are most commonly used for the characterisation of OC in NTA in aerosol chemistry because they can cover a comparatively wide polarity range of analytes.(Beck et al., 2022; Kourtchev et al., 2015; Vogel et al., 2019)

The increasing complexity and size of the datasets in terms of individual compounds imposes new requirements and challenges regarding the interpretation and visualisation of NTA results. Discussion and interpretation of data generated by NTA is usually facilitated by visualisation

methods that categorise and group data sets to identify patterns (see Figure 2.4-1). For example, these patterns allow discrimination between different sampling locations or different atmospheric processes. Popular visualisation methods include plotting double bond equivalents (DBE)(An et al., 2019; Jia & Xu, 2020), element ratios (e.g. van Krevelen diagrams)(Kourtchev et al., 2015; Kourtchev et al., 2016b; Vogel et al., 2019), degree of oxidation(Kourtchev et al., 2015; Kourtchev et al., 2016b; Vogel et al., 2019), or are based on Kendrick mass analysis(Jia & Xu, 2020). Recently, Zhang et al. also introduced the maximum carbonyl ratio (MCR) as a new index and visualisation method for structural classification of SOA components in NTA.(Zhang et al., 2021) More detailed explanations of the various methods can be found in (Nozière et al., 2015c).

2.7 The semi-targeted approach

Semi-targeted methods are a hybrid between untargeted and targeted approaches. This approach aims to quantify a large number of substances whose identity is often known only in terms of their substance class. This method usually uses a calibration curve generated for one or a few reference compounds for a whole class of substances (i.e. compounds with a similar chemical structure) instead of generating a separate calibration curve for each target analyte. The approach therefore allows the quantification (or semi-quantification) of analytes for which there is no authentic standard for the generation of external calibrations. For STA, as for NTA, high-resolution mass spectrometers are required, which is why Orbitrap-MS or Quadrupole-ToF-MS are often used.

In the field of SOA analysis, STA are currently widely used for the analysis of monoterpene and isoprene SOA markers and organosulphates (OS).(Gómez-González et al., 2008; Maenhaut et al., 2017) In recent years, numerous studies have been conducted on the molecular characterisation, formation mechanisms, and source attribution of SOAs from isoprene. For molecular characterisation, mass spectrometric methods combined with separation techniques play a crucial role. Chamber experiments and tandem MS measurements have allowed the identification of many organic markers, and the preparation of some reference compounds has enabled unambiguous structural characterisation.(Bondy et al., 2018; Cui et al., 2018a; Jaoui et al., 2019; Nestorowicz et al., 2018; Zhang et al., 2012) Interested readers will find an excellent review article on the current state of research on SOA formation of isoprene in (Claeys & Maenhaut, 2021). Chemically structurally similar standards are often used for the quantification of isoprene SOA markers, in this case erythritol and threitol for the quantification of 2-methyltetroles and C₅-alkentrioles.⁵(Clements & Seinfeld, 2007; Kourtchev, Warnke, Maenhaut, Hoffmann, & Claeys, 2008) Furthermore, response factors of camphorsulfonic acid, methanesulfonic acid, and octylsulfate have been used for the quantification of organosulphates. (Brüggemann et al., 2019; Kristensen & Glasius, 2011) In addition to isoprene SOA and OS markers, imidazoles also represent a class of compounds in atmospheric aerosol particles that require the use of STA due to an insufficient number of authentic standards. Recently, a STA was combined with data driven acquisition and auto-MS/MS scans measurements using UHPLC-HR-MS/MS to quantify ten imidazoles using reference standards, identify five imidazoles without standards, and discover three imidazoles that had never been measured before.(Gao et al., 2021; Teich, van Pinxteren, Kecorius, Wang, & Herrmann, 2016) In this example, using a STA is superior to a TA in terms of effectiveness and information gain. Nevertheless, using response factors for accurate quantification of marker substances can lead to significant over- or underestimation of the specific concentrations. For example, camphorsulfonic acid, methanesulfonic acid and octylsulfate show a large difference in ESI response than authentic terpene-derived organosulphates what

has led to an underestimation of several orders of magnitudes of OS concentrations in PM.(Beck et al., 2022) It should be memorised, that STA can only give trends of concentration while reliable quantitative results can only be achieved with TA.

Generally applicable performance criteria exist for the STA in hybrid form. First, performance can be judged by the generally applicable thresholds for selectivity, sensitivity, trueness, and precision of the method, relative to the standards used. For the identification of new compounds, the current state of performance evaluation is the same as for NTA methods, whose evaluation the interested reader will find in(Fisher et al., 2022). Analytically, the same requirements are necessary for an STA as for a TA.

2.8 Instrumental approaches

Figure 2.8-1 gives an overview of the most often used multidimensional LC or MS techniques applied to characterise atmospheric organic aerosol and discussed in this chapter. In terms of multidimensional LC and MS techniques, it is possible to either add a second LC or a second detector (UV/Vis or MS) dimension. In general, adding a second detector or LC dimension significantly decreases *I*. In terms of the fraction of organic mass analysed, adding a second detector dimension (LC-UV/Vis-MS or LC-MSⁿ) decreases the fraction whereas adding a second LC dimension can do both, increase and decrease the fraction of organic mass analysed depending on the specific coupling of the two LC dimensions: comprehensive LC-MS (LCxLC-MS), heart-cut LC-MS (LC-LC-MS) or multiple heart-cut LC-MS (mLC-LC-MS).

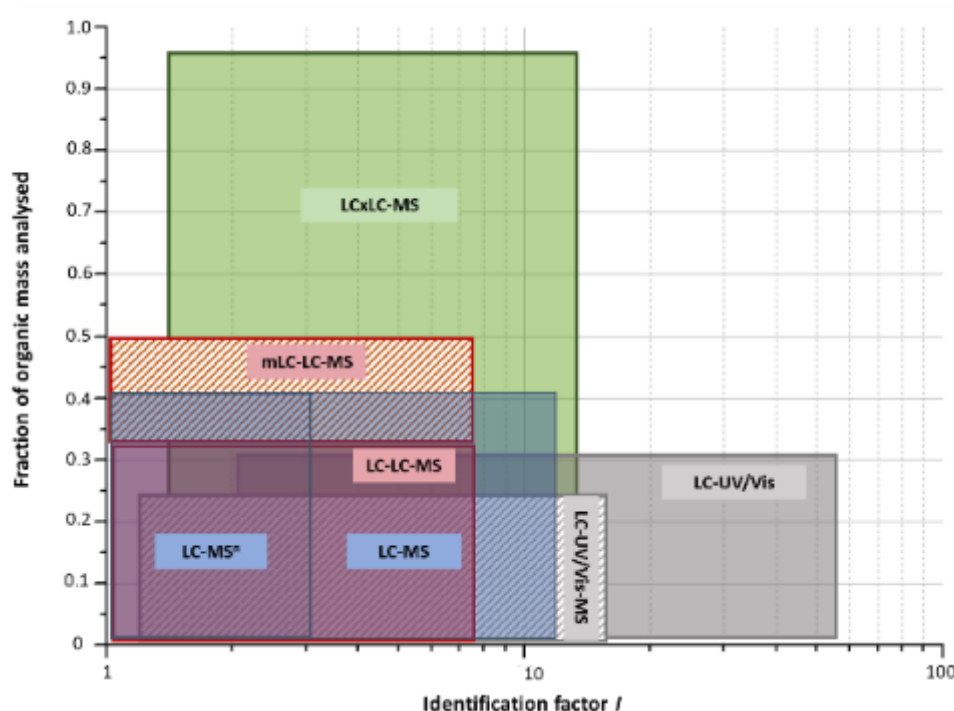


Figure 2.8-1: Summary of the most often used multidimensional LC or MS techniques applied to characterise atmospheric organic aerosols as function of their *I* factor. A decreasing *I* factor describes the increasing ability of the corresponding technique to identify the molecular structure of a compound and is based on literature values. The y-axis represents an educated guess of the fraction of the total organic mass of atmospheric aerosols characterised by a technique. Modified from Noziere et al. 2015.

2.9 LC-UV/Vis and LC-UV/Vis-MS

Based on years of availability and widespread use alone, abundant work exists on LC-UV/Vis or LC-MS analyses for the characterisation of organic aerosol components. UV/Vis spectroscopy is comparatively nonspecific in the characterisation of atmospheric aerosols, allowing mainly the identification of specific compounds or functional groups ($I \geq 100$). Coupling with LC significantly improves the level of identification as it provides information on retention times and allows comparison with reference standards what makes it extremely suitable for TA. LC-UV/Vis analysis has become particularly important for the determinations of harmful compounds such as PAHs, which are strong UV chromophores due to their aromatic structure. Although the introduction of more sensitive GC-MS methods has led to a decrease in work using UV absorption alone, the UV detector continues to be a reliable and easy-to-use detector that responds universally to chromophoric compounds. Interested readers can find an informative review article on the current state of instrumental analysis of PAHs in aerosols in (Galmiche, Delhomme, François, & Millet, 2021).

For the analysis of non-chromophoric compounds, a derivatisation step must be performed when UV/Vis is used as detection system. On one hand, this increases the time required for method development and sample preparation and limits the proportion of organic matter analysed, but at the same time increases selectivity and allows $I < 10$. In aerosol analysis, carbonyl compounds are usually detected using this method. For these, 2,4-dinitrophenylhydrazine (2,4-DNPH) or pentafluorobenzyl hydroxylamine (PFBHA) are most commonly used for derivatisation, providing comparable detection limits to GC-MS methods. (Ho & Yu, 2004; Lee, Szulejko, & Kim, 2018; Michoud et al., 2018) In addition, pre-column or post-column derivatisation methods have been developed. Over time, LC-UV/Vis methods have been further improved by performing couplings with tandem MS detections. The coupling of LC-UV/Vis detection with mass spectrometers allows very good degrees of identification, since the information of optical properties and polarities is extended by the information dimensions of MW or even fragmentation patterns. This methodology is particularly attractive in aerosol analysis for the characterisation of light-absorbing organic species (brown carbon). (Budisulistiorini et al., 2017; Hettiyadura et al., 2021; Lin et al., 2016) A good overview of the different analytical techniques for humic substances and brown carbon can be found in (Duarte & Duarte, 2011; Laskin et al., 2015). For example, by coupling UV/Vis with MS detectors, the selectivity in the detection of glyoxal and methylglyoxal in aerosol samples could be significantly increased. (Kampf et al., 2011; Kampf et al., 2012a) In addition, this approach has been used in the study of chromophoric nitrogen-containing compounds such as nitroaromatics and imidazoles. (Claeys et al., 2012; Kampf et al., 2012b)

2.10 LC-MSⁿ

Due to the increasing use of MS/MS capable mass spectrometers (also called tandem MS, MS² or MSⁿ), more and more laboratories are using these instruments for organic aerosol analysis. Here, the selection of selected ions of a particular mass followed by fragmentation of these ions and detection of the fragments provides additional information which is extremely helpful in both, identification and quantification. Fragmentation of the selected m/z can occur spontaneously or through an activation process. In addition, it is possible to increase the number of fragmentation steps (MSⁿ with $n > 2$) and further fragment the ions formed in the first fragmentation step. Interested readers will find an excellent review article on the fundamentals and instrumental capabilities of MS/MS techniques in (Hoffmann, 2006), while here we only discuss the possible applications of corresponding MSⁿ experiments with respect to atmospheric aerosol analysis.

Depending on instrumental requirements and availability, four types of tandem MS experiments are possible: product ion scanning, precursor ion scanning, neutral loss scanning, and selected/multiple reaction monitoring. Figure 3 shows a schematic explanation of the different types of MSn experiments.

2.10.1 Product ion scanning

Product ion scanning in combination with LC is commonly utilized in the analysis of organic aerosols with mass analysers such as tripl-quadrupole-MS(Feltracco et al., 2018) (see Figure 2.10-1), ion traps(Surratt et al., 2007; Warnke, Bandur, & Hoffmann, 2006; Yasmeeen et al., 2011), Orbitraps(Gómez-González et al., 2008; Wang, Zhang, Zhang, Liang, & Shi, 2021), FT-ICR-MS(Hall & Johnston, 2012) and Qq-ToF-MS(Kanawati, Herrmann, Joniec, Winterhalter, & Moortgat, 2008). In product ion scanning, a precursor ion species is first selected and analysed in the first mass spectrometric dimension (e.g. first quadrupole in case of tQ-MS). Subsequently, this precursor ion species is deliberately fragmented, either by collision with a neutral gas in a collision cell or by other fragmentation mechanisms. The resulting fragments, also known as product ions, are then scanned in a second MS dimension (e.g. second quadrupole), and their m/z are detected. This scan mode provides the highest degree of molecular identification and has therefore been widely used in the past to elucidate the molecular structures of aerosol components. It is particularly useful for obtaining structural information on small organic molecules ($MW < 300$) and has been applied successfully, especially in the field of SOA research. Structural information includes both, characteristic product ions and neutral losses, which provide information not only about functional groups but also about other structural features such as the location of functional groups. Product ion spectra have also proven useful in deriving structural information about the monomeric units of dimers or high MW oligomers.(Hall & Johnston, 2012) Based on the work with product ion scanning of the target analytes, multiple reaction monitoring (MRM) methods for their quantification are finally worked out for the selected components (see below).

2.10.2 Precursor ion scanning

Compared to product ion scanning, precursor ion scanning detects fragment ions of a specific m/z in the second mass spectrometric dimension, while all m/z that produce the selected fragment ion are scanned in the first dimension. In this way, the precursor ions of the specific fragment can be detected. Precursor ion scanning is commonly utilized with triple-quadrupole-MS(Dron, Abidi, Haddad, Marchand, & Wortham, 2008) (see Figure 2.10-1) but applications with i.e. ion traps(Szmigielski et al., 2007b) or Orbitraps(Wang, Ge, Bi, Liang, & Shi, 2022) also exist. It has occasionally been used for screening complex atmospheric aerosol samples. For example, the method has been used to monitor nitroaromatic compounds leading to m/z 46 ($-NO_2$).(Dron et al., 2008; Dron et al., 2010)

2.10.3 Neutral Loss Scan

Neutral loss scans are usually utilized by triple-quadrupole-MS to analyse OA. In the neutral loss scan, two quadrupole analysers (Q1 un Q3) are scanned with a constant mass offset x . Thus, if an ion of a certain m/z ratio fragments into q_2 with the defined mass difference x , these ions can successfully pass Q3 and be detected (see Figure 2.10-1). Similar to precursor ion scanning, this scanning mode is useful when the analysis of specific functional groups is desired, i.e., when the focus is not necessarily on individual compounds but on entire compound classes. For example, the neutral loss scan has been used to monitor carboxylic acids after conversion to methyl esters by detecting the loss of methanol (m/z 32)(Dron, Eyglunent, Temime-Roussel, Marchand, & Wortham, 2007), to determine carbonyl compounds

after conversion to hydrazones and a neutral loss from hydrazone fragmentation(Dron et al., 2010) or to identify organic hydroperoxides(Zhou, Rivera-Rios, Keutsch, & Abbatt, 2018). In addition, nitroaromatic compounds have also been analysed, in this case by the loss of NO (m/z 30).(Dron et al., 2007; Dron et al., 2008)

2.10.4 Selected Reaction Monitoring

In selected reaction monitoring (SRM), or multiple reaction monitoring (MRM), only selected m/z are recorded in the first and second mass spectrometric dimensions. Accordingly, no scanning takes place. Here, ions selected by the first mass analyser are detected only when they produce a specific fragment by a selected reaction. Since no scanning occurs, the precursor and fragment ions can be in focus for extended periods of time, which increases both, sensitivity and selectivity. High selectivity corresponds to a low probability of detecting an interfering compound, reducing background noise and eliminating most interferences (see smaller background in the LC chromatogram in Figure 2.10-1). SRM and MRM are commonly utilized in the analysis of organic aerosols with triple-quadrupole-MS(Kitanovski et al., 2012b; Kitanovski et al., 2012a; Kundu et al., 2013; Olson et al., 2011b; Yassine, Suski, & Dabek-Zlotorzynska, 2020) (see Figure 2.10-1) or ion traps(Kitanovski et al., 2012b; Kitanovski et al., 2012a; Wang, Ren, Huang, Tong, & Yu, 2017c). Monitoring of selected/multiple reactions is particularly useful for confirming beyond doubt both, the presence and amount, as well as the identity, of compounds in atmospheric samples. For example, this has been used to detect carboxylic acids and nitroaromatics(Kitanovski et al., 2012a) as markers of biomass combustion.(Kitanovski et al., 2012b) The MRM scan mode is specific and very sensitive, but can only be performed with an STA or TA because the target analyte must be known in advance and well characterised.

It is clear that tandem MS experiments have significant potential for the analysis of atmospheric organic aerosols. When combined with LC, they represent very advanced analytical tools for both, detection and detailed mass spectrometric characterisation of organic components in complex atmospheric samples. LC-MSn methods have an increased capacity through efficient structure elucidation and selective detection capability, high sensitivity, and enable rapid analyses of complex mixtures.

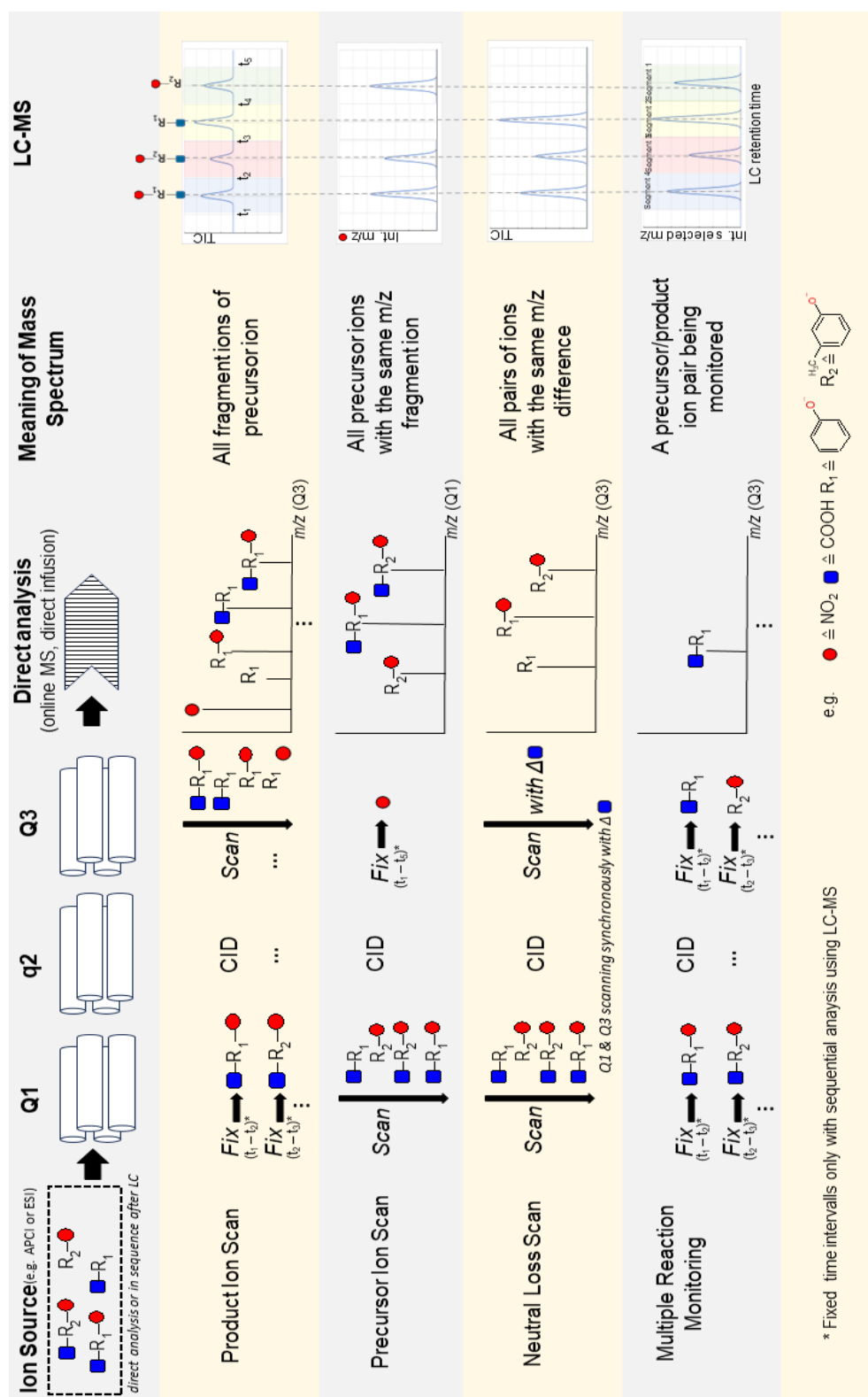


Figure 2.10-1: Tandem mass spectrometry scan modes. (1) Product ion scan: selection of precursor ion with Q1 and scanning with Q3. (2) Precursor ion scan: scan all precursor ions in Q1 that produce a specific fragment ion that is selected in Q3. (3) Neutral loss scan: scanning all ions with a constant mass difference in Q1 and Q3 simultaneously. (4): Multiple reaction monitoring: selection of precursor ion in Q1 and monitoring one or more selected fragment ions in Q3.

2.11 Two-dimensional liquid chromatography

The essential concept of 2D LC is to collect one or more fractions from the 1D column (sampling) and transfer them to a 2D column (modulation). The task of the second column is to separate all analytes that were not resolved in the first dimension in the second dimension based on a different selectivity. If the selectivities, i.e., the retention mechanisms, are independent in two dimensions, the separations are called orthogonal. The latter should be aimed at in order to obtain as much information as possible about the sample under investigation. In liquid chromatographic aerosol analysis, HILIC is usually coupled with RPLC, SEC with RPLC, or CP with RPLC (see Table 2.5-1). In the following, we discuss three different instrumental possibilities of how this 2D separation procedure is performed in practice: heart-cut LC (LC-LC), multiple heart-cut LC (mLC-LC), and comprehensive LC (LCxLC). Figure 2.11-1 shows an explanatory illustration of the three modes. Readers interested in learning the detailed instrumental chromatographic setup of each mode are referred to the excellent reviews (Pirok et al., 2019), (Stoll & Carr, 2017) and (Pursch & Buckenmaier, 2015).

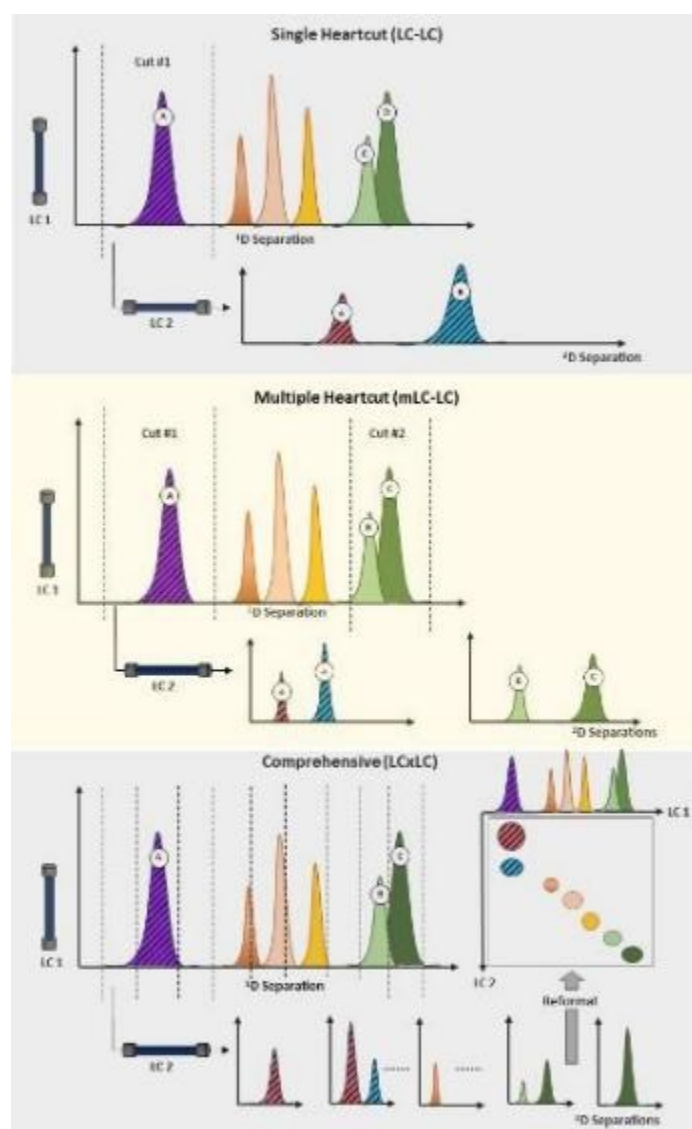


Figure 2.11-1: Illustration of three different modes of 2D LC separation: Heart-cut LC where one (single heart-cut) or more (multiple heart-cut) selected fractions of the 1st dimension are collected and injected into a 2nd column and comprehensive LC where the whole 1D effluent is injected into the 2D column. Modified from (Pirok et al., 2019).

2.11.1 Heart-cut LC (LC-LC)

Heart-cut LC is particularly suitable for TA and represents the two-dimensional method with the smallest fraction of organic mass analysed, but also the smallest *I*-value. In this 2D approach, a single fraction of the first dimension is collected and then injected into a 2D column for further separation. This is usually done via a second valve equipped with a sample loop whose volume is sufficient to hold the entire 1D eluent fraction of interest. LC-LC methods are useful for separating a single target analyte from a complex matrix or for reducing assignment uncertainty. In general, high-purity analyte signals are obtained. Therefore, heart-cut LC methods are ideally suited for aerosol analysis, e.g., to separate stereoisomers. Other advantages of heart-cut LC methods are the very high resolving power, the additional selectivity provided by the second dimension, the wide range of different retention mechanisms, and the ease of combination with MS and tandem MS techniques. (Pirok et al., 2019) However, high-precision quantifications are difficult to achieve with heart-cut methods, e.g., because retention time changes can be caused by matrix effects in real samples or by minor variations in solvent composition. In addition, lower detection sensitivities and problems with incompatibility of phase systems in the two dimensions can be challenging.

As indicated above, cutting out a retention time window of the first separation makes the fraction of the analysed organic mass quite small, thus not at all comprehensive in the sense of detecting the largest possible number of components present. This is different if the heart-cut is the void volume region of the first separation, since e.g. in the case of a separation on HILIC phases, the majority of the less polar compounds leave the column at this stage. If this volume is now subsequently separated with an RP phase, one could speak of a quasi-comprehensive analysis. Beschnitt et al. used exactly this type of coupling to study organic atmospheric components in ice cores using an NTA. The researchers collected the void volume of the HILIC column in a sample loop, analysed the separated signals within the first HILIC dimension, and then, while the HILIC column was running in re-equilibration settings, the void volume was analysed in the second RP dimension. In this way, information from the first HILIC dimension was retained while additional information on lower polarity compounds was provided without the need to extend the run time of the method. The method provided good reproducibility and very low detection limits. An example of the obtained results is shown in Figure 2.11-2. While the one-dimensional HILIC method provided 177 signals, significantly more signals were obtained with the dead-time heart-cut method, beneficial for both, TA and NTA. (Beschnitt et al., 2022)

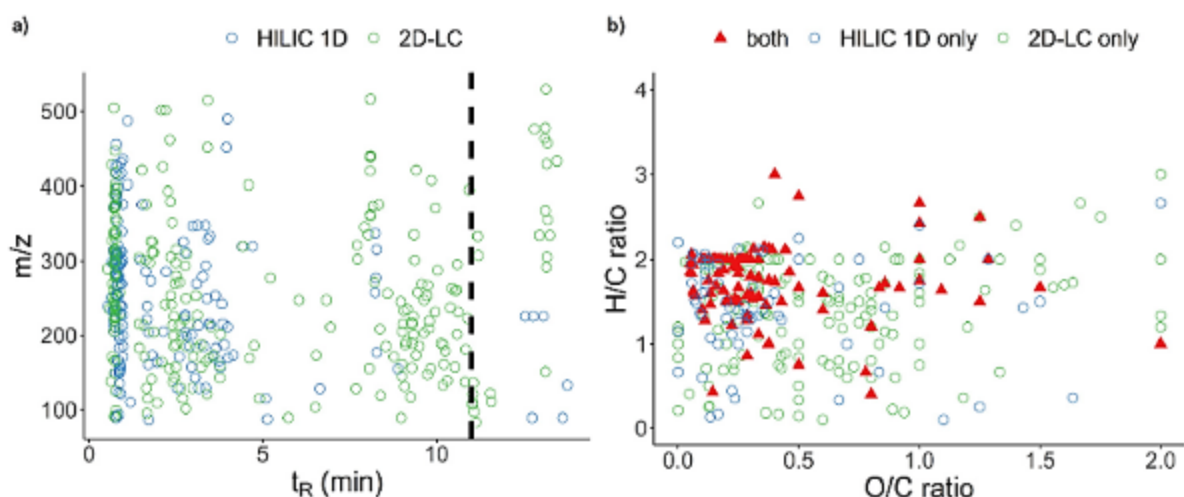


Figure 2.11-2: Example of obtained results by using HILIC-RPLC-HR-Orbitrap-MS as quasi-comprehensive analysis to characterise organic aerosols in ice core samples. The void volume of the 1st HILIC dimension was heart-cut and injected into the 2nd RPLC dimension. (a) plot of m/z to retention time (t_R) of signals detected only in the 1D HILIC method (blue) and only in the 2D approach (green). The switch between the two dimensions is marked at $t_R=11$ min (black). (b) Van-Krevelen plot of H/C to O/C ratios of all signals detected in the 1D HILIC method (blue), 2D HILIC-RPLC method (green), and signals detected by both methods (red). Modified from (Beschnitt et al., 2022).

2.11.2 Multiple heart-cut LC (mLC-LC)

The mLC-LC method is a simple extension of heart-cut LC-LC in which individual fractions from several 1D peaks are successively transferred to the second dimension for further separation. This expands the proportion of organic matter analysed, as more analytes can be detected in a single chromatogram. (Pursch & Buckenmaier, 2015) Similar to heart-cut LC-LC methods, mLC-LC systems are particularly suitable for TA, but also open up possibilities for STA.

An interesting application of one type of mLC-LC analysis was a two-dimensional offline chromatographic fractionation for the characterisation of HULIS in atmospheric aerosol particles. PM₁₀ was collected on filters, extracted, followed by a solid phase extraction (SPE) and then separated into five molecular size fractions (SEC) in the first dimension. The five fractions were collected, processed and separated into more eleven fractions with different polarities in the second reversed phase dimension. The RP fractions were collected and processed again and then analysed with direct infusion ESI-FT-ICR-MS by applying a NTA. An interesting result was that the number of assigned molecular formulas increased by a factor of 2.3 for the fractionated sample (18144) compared to bulk sample analysis without fractionation (7819) and allowed the identification of 71240 isomeric compounds. (Spranger et al., 2017; Spranger et al., 2019) Accounting for these isomers with an mLC-LC method could provide both, better identification levels (lower I -values) and a higher fraction of organic mass analysed compared to direct infusion MS. Other researchers used a type of mRPLC-RPLC method to elucidate the structure of specific organosulphate derivatives and coupled two LC columns simultaneously to an ESI-IT-MS_n and ESI-ToF-MS. The 1D separation was used to obtain the MW distribution of the analytes, to tentatively quantify organosulphates and nitroxy-organosulphates and to clean up for the 2D separation. Selected 1D fractions were further analysed using the second column to perform tandem MS experiments for compounds with isobaric isomers. This approach ensured that dimers, oligomers and organosulphates detected

in the 1D chromatogram were not caused by artifact formation in the ion source. The researchers found out that the MW of nitroxy-organosulphates can be as high as those of dimers previously detected in monoterpene oxidation experiments. Furthermore, these compounds showed very high abundance in night time samples. Using a 2D LC approach in this early work enabled separation of isobaric compounds providing lower *I*-values and obtain a relative identification that was significantly important to understand possible missing parts of organic mass in ambient aerosols due to lacking knowledge of night time chemistry in aerosol formation. (Iinuma et al., 2007a)

2.11.3 Comprehensive LC (LCxLC)

In general, LCxLC methods aim to obtain as much information about the sample as possible from a single 2D run. Therefore, comprehensive 2D LC is particularly suitable for NTA of atmospheric aerosols, as it is able to analyse a large fraction of the organic mass when two orthogonal stationary phases are used. There is a wide range of different retention mechanisms and additional selectivity due to the second dimension. The chromatograms obtained are structured and easy to interpret, and groupwise separation of analyte classes is possible. Compared with 1D LC methods, the uncertainty of peak assignment is much lower, and coupling with MS and tandem MS techniques is possible. (Pirok et al., 2019) In addition, high peak capacities (1.000 – 10.000) and high peak reproduction rates (typically 1 peak per second) are routinely enabled. It should be noted, however, that very few LCxLC systems have been used in atmospheric aerosol analysis. (Duarte et al., 2023) In 2006, Pól et al. coupled a strong cation exclusion (SCX) column with a RP column in an LCxLC-ESI-ToF-MS setup to study acidic components in rural and urban atmospheric samples following a STA approach. The authors concluded that the comprehensive 2D LC setup was simple and easy to use, and identification from contour plot positions together with mass spectral information was more reliable than in the 1D LC-MS setup. Many compounds and their possible isomers could be determined in one run. Quantification of individual compounds was also reliable and reproducible, providing detection limits of 2-200 ppb. (Pól et al., 2006)

It is clear that 2D LC methods have great potential for aerosol analytical applications, especially for NTA and STA, but have found comparatively little acceptance in atmospheric science. There are certainly several reasons for why this is the case. In contrast to GC, multidimensional LC presents both, a difficulty in mobile phase compatibility and a greater risk of undersampling the effluent from the first dimension. (Pirok et al., 2019) Also, the low detection limits essential in the analysis of atmospheric aerosols are difficult to achieve with existing 2D LC methods. At the very least, this leads to the need to use the optimal column combinations and chromatographic separation conditions in both dimensions, the latter requiring the optimisation of several parameters (mobile phase composition, isocratic and/or gradient elution, sampling rate and loop volume of the modulator, column dimensions and flow rates). Last but not least, the very small number of instruments and software packages for LC × LC available on the market hinders a widespread use of this technique also in aerosol analysis. A more detailed discussion of this issue in the context of environmental analysis can be found in (Duarte et al., 2023).

2.12 Future perspectives

The developed analytical techniques and their application presented in this review highlight the tremendous increase in interest in organic aerosols over the past few decades, as well as the considerable progress that has been made in analytical techniques for their study. Certainly, this has provided a clearer picture of the myriad organic compounds in the

atmosphere, their sources, and their contribution to important processes such as air quality, or their role in chemical cycles between biosphere and atmosphere. By identifying markers, not only sources of aerosol components are accessible but also changes in aerosol composition during their atmospheric lifetime, especially for biogenic and anthropogenic secondary organic aerosols but also in the context of aerosol particles formed by biomass combustion. Thus, the understanding of the close relationship between gas and particle chemistry, the resulting SOA formation and its contribution to atmospheric chemistry and climate has made considerable progress, especially the quantitative treatment of organic aerosols e.g. in air quality and climate modelling.

But many challenges remain. In recent years, interest in the chemical characterisation of primary aerosols, especially bioaerosols, has increased significantly. Bioaerosols are natural primary aerosols (primary biological aerosol particles, PBAPs) from living or dead biological organisms, such as fungal spores, bacteria, viruses, and pollen. Estimated total global emissions of PBAPs range widely from 10 to 1000 Tg/yr, depending on size and range and whether cell fragments are included in the estimate.(Després et al., 2022) Bioaerosols are known to act as very effective ice nuclei, and are estimated to be particularly important for ice formation in warm clouds (temperature > -15 °C). These biological samples with their complex matrix impose high demands on organic trace analysis, and it is in this area that progress can also be expected in aerosol research, driven in part by the enormous developments in high-resolution mass spectrometry and proteome and metabolome analysis which could benefit from multidimensional LC and MS systems.(Emetere, Oloke, Afolalu, & Joshua, 2021; Ghosh, Lal, & Srivastava, 2015; Li et al., 2022; Myers, Sumner, Li, Barnes, & Du, 2017)

However, many problems in the analysis of organic compounds in aerosols can also be solved with one-dimensional LC-MS setups, since the chromatographic separation and the use of MS already allow excellent quantification and identification of even complex mixtures. For multidimensional LC, optimisation approaches offer the possibility for further development of 2D LC separations. Following the goal to improve detection sensitivity, active modulation techniques have to be further implemented. The three most commonly used active modulation techniques are active-solvent modulation (ASM), stationary-phase-assisted modulation (SPAM), and vacuum evaporation modulation (VEM).

Briefly, the principle of ASM relies on diluting the 1D eluent stream with an elution-weak solvent to focus the area of analyte at the inlet of the 2D column.(Stoll, Shoykhet, Petersson, & Buckenmaier, 2017) In SPAM, low volume enrichment columns, called traps, are used. These traps contain stationary phases designed to retain the analytes of the 1D effluent while the 1D solvent mixture leaves the chromatographic system without retention. The valve is then switched and the 2D mobile phase elutes the trapped analytes as sharp, concentrated bands into the 2D column.(Uijl et al., 2022; Vonk et al., 2015) The principle of the VEM is based on evaporating part of the 1D effluent before injection into the 2D column. It is mainly used to overcome incompatibility problems when combining NPLC and RPLC separations.(Ding, Xu, Wang, Duan, & Guan, 2010; Tian, Xu, Xu, & Guan, 2006) Although most applications of modulation techniques have been tested with respect to the coupling of HILIC with RPLC(Pardon, Chapel, Witte, & Cabooter, 2023; Pirok et al., 2019), which is also the most popular coupling in the analysis of organic atmospheric compounds (see Table 2.5-1), to our knowledge no modulation techniques have yet been implemented in the 2D LC analysis of aerosols. This represents a possible branch for the future of multidimensional LC systems in aerosol analysis, as they can significantly improve detection sensitivities.

Work has also already been done on implementing predictive tools and optimization algorithms to establish optimal conditions for the chosen 2D chromatographic separation problem. (Pirok, Gargano, & Schoenmakers, 2018) In the future, effort should be taken in aerosol science to use these implementations for overcoming the time-consuming trial-and-error optimization approach for 2D LC method developments. Furthermore, user-friendly softwares for data analysis and visualization should be developed. (Matos, Duarte, & Duarte, 2012; Stoll & Carr, 2017)

In recent years, one increasingly encounters the term 'aerosolomics', i.e., in reference to the life sciences, the description of the goal of current aerosol research to identify, characterise, and quantify those molecules that are important for the composition, origin, processing, phase state, and especially the effects of aerosol particles in the atmospheric environment. (Thoma, Bachmeier, Gottwald, Simon, & Vogel, 2022) We have certainly come closer to this target, as usual also as a result of immense progress in the field of instrumental analytics. But challenges still exist, such as the role of organic compounds in particle formation, where extremely small amounts of substance in nanometer particles must be analysed, or in cloud formation, where unusually difficult sampling and stark external conditions (e.g., low temperatures) complicate analysis. However, the study of particles that are harmful to human health (e.g. reactive oxygen species (ROS)) also remains a challenge. (Zhang et al., 2022) The study of these processes requires further analytical developments, some of which are already underway and could benefit other chemical disciplines. Moreover, high efforts are also already taken to build up databases for NTA as aerosolomic tools to enable the application to organic aerosol samples by including tandem-MS experiments. (Thoma et al., 2022) This can be expected to become a branch of atmospheric science where more work will be invested in the future.

The increasing widespread use and performance of HR-MS and the consequent impact on atmospheric aerosol analysis have already been mentioned. Related to this, concerning future developments in this research area, would be the analysis of stable isotopes by HR-MS. The analysis of stable isotopes and exploitation of chemically or physically induced fractionation processes of the elements is a widely used method, especially in the geosciences, to trace elemental cycles or to collect paleoclimate data. Typically, stable isotope ratios are measured after the analyte has been converted to a low molecular weight gas by combustion, pyrolysis, microbial fermentation, or other chemical treatments. The gas is then analysed using a magnetic sector isotope ratio mass spectrometer (IR-MS). However, in these methods, much of the intramolecular isotopic information is erased during gas formation and by destructive ionisation in the IR-MS. The very high mass resolution of especially the new generations of orbitrap mass spectrometers allows the resolution of many near isobaric interferences for compounds containing H, C, N, O and/or S, without question the elements that are also the most important in the field of atmospheric aerosol research. (Csernica, Bhattacharjee, & Eiler, 2023; Neubauer et al., 2018; Neubauer et al., 2020) The sensitivity of today's instruments allows analysis of subnanomolar samples and quantification of multi-substituted species. The site-specific capabilities arise from the fact that mass spectra of molecular analytes typically contain different fragment ion species, each of which samples a specific subset of molecular sites.

2.13 Conclusion

In conclusion, the molecular characterisation of atmospheric aerosol particles poses significant analytical challenges due to their diverse chemical composition and complex physicochemical properties. The importance of understanding these particles lies in their profound impact on human health, climate dynamics, and geochemical cycles. Despite advancements in analytical

techniques, particularly the emergence of LC-MS methods that undisputably already contributed significantly to our understanding of aerosol formation and growth, such as on particular aerosol sources and sinks, accurately quantifying low- and semi-volatile organic compounds in ultra-trace amounts remains a formidable task. While LC-MS offers versatility, its inherent limitations in analysing specific analyte classes necessitate the development of multidimensional LC and MS methods. These advanced techniques aim to enhance both, the scope of organic mass analysis and the identification of individual components. While progress has been made, challenges still persist. The integration of high-resolution mass spectrometry and multidimensional LC systems holds promise for addressing these challenges and enhancing our understanding of aerosol chemistry. Future research efforts should focus on optimising analytical methodologies (e.g. modulation strategies), developing user-friendly software tools, and advancing the field of aerosolomics to better characterise and quantify aerosol components. Additionally, the utilisation of high-resolution mass spectrometry for stable isotope analysis represents a promising avenue for further exploration, offering enhanced sensitivity and site-specific capabilities. Overall, advancements in atmospheric chemistry are closely linked to advancements in analytical chemistry, being essential unravelling the complexities of organic aerosols and their impacts on atmospheric chemistry and climate.

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CRedit authorship contribution statement

Stefanie Hildmann: Investigation, Methodology, Writing – original draft, Writing – review & editing. **Thorsten Hoffmann:** Conceptualization, Formal analysis, Funding acquisition, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Thorsten Hoffmann reports financial support was provided by Deutsche Forschungsgemeinschaft - DFG. Thorsten Hoffmann reports financial support was provided by Bundesministerium für Bildung und Forschung - BMBF. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

3 Molecular characteristics and seasonality of organic particulate matter in the Amazon rainforest

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Summary

In this chapter, non-targeted high-resolution mass spectrometry (HR-MS) is applied to characterize the molecular composition of organic aerosols at the Amazon Tall Tower Observatory (ATTO), revealing distinct seasonal and vertical patterns. By identifying thousands of molecular formulas, this study demonstrates the dominance of biogenic secondary organic aerosols (SOA) derived from isoprene and monoterpene oxidation, as well as the influence of biomass burning during dry periods. The height-resolved analysis highlights localized emissions near the forest canopy, while seasonal variations reflect changes in atmospheric processing and deposition. This chapter establishes a molecular-level understanding of organic aerosol dynamics in the Amazon, providing a methodological and conceptual foundation for investigating aerosol–climate interactions in tropical ecosystems.

I am the first author of this paper (shared first authorship). I was responsible for validating and optimizing non-targeted high-resolution mass spectrometry (HR-MS) methods, performing height-resolved data evaluation to assess vertical gradients in aerosol composition, and writing the manuscript. My work included ensuring the robustness of the HR-MS workflow for identifying thousands of molecular formulas in ambient aerosol samples, analyzing the altitudinal distribution of early terpene oxidation products, and synthesizing these findings into a coherent narrative that highlights the seasonal and vertical dynamics of organic aerosols in the Amazon rainforest.

Comprehensive non-targeted molecular characterization of organic aerosols in the Amazon rainforest

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3.1 Abstract

The Amazon rainforest plays a crucial role in the global climate system, hydrological cycle, and earth's energy balance. As one of the planet's least industrialized regions, it allows investigation of organic aerosol formation and constituents under almost pristine conditions. Nevertheless, human activities are known to affect this ecosystem— especially during the dry seasons. In this study, ambient aerosol samples collected at the Amazon Tall Tower Observatory (ATTO) during two dry and two wet seasons were characterized by high-resolution mass spectrometry (HR-MS). Comprehensive non-targeted data evaluation was applied to identify thousands of molecular formulae. Most were found to be associated with oxidation products of isoprene and monoterpenes, highlighting the predominance of biogenic secondary organic aerosols (SOA) at ATTO. The chemical composition exhibited distinct seasonal patterns with more processed organic compounds during the dry season, which can be explained by an increase of later-generation oxidation products due to reduced wet deposition and enhanced long-range transport. Mono- and polycyclic heteroaromatic components from biomass burning (BB) sources were enhanced during the dry seasons and the second wet season. The wet seasons were generally characterized by less oxidized compounds, associated with freshly formed SOA particles. Height-resolved measurements showed biogenic emissions with higher concentrations of early terpene oxidation products at lower altitudes. Overall, our results provide new insights into the molecular characteristics and seasonality of organic particulate matter at ATTO, helping to constrain the sources and interactions of aerosols, clouds, and precipitation in the Amazon rainforest.

3.2 Introduction

Organic particulate matter (PM) accounts for up to 90 % of the total atmospheric aerosol mass ((Jimenez et al., 2009; Kanakidou et al., 2005; Kroll & Seinfeld, 2008). While primary organic aerosols (POA) are emitted directly into the atmosphere (e.g., combustion of biomass), secondary organic aerosols (SOA) are produced by oxidative processes and transformations of volatile organic compounds (VOC), followed by their oxidation products' nucleation and/or condensation in the atmosphere. (Seinfeld & Pankow, 2003) Numerous studies have illustrated the complex chemical composition of organic aerosols covering various compound classes and thousands of different organic species (; Goldstein & Galbally, 2007; Nizkorodov et al., 2011; Tolocka et al., 2004; Wozniak et al., 2008) Organic aerosols have a substantial impact on climate and human health (Hallquist et al., 2009; Pöschl, 2005b). Consequently, clarifying the chemical composition of organic aerosols is an essential task of atmospheric-related studies.

Compounds in OA feature a huge variety of functionalities, polarities, and volatilities at various concentration regimes (Goldstein & Galbally, 2007) which poses major challenges for analytical techniques (Nozière et al., 2015b). Traditional gas chromatography and liquid chromatography systems coupled with mass spectrometry (GC/MS, LC/MS) have proven useful in identifying certain OA species (Hoffmann, Huang, & Kalberer, 2011). However, these methods are limited to compounds with specific physicochemical properties and, thus, not

adequate to resolve complex organic mixtures (Hildmann & Hoffmann, 2024). Hence, high-resolution mass spectrometry (HR-MS) with enhanced resolving power ($\geq 100\,000$) and high mass accuracy (≤ 5 ppm) has received more and more attention in atmospheric aerosol research (Burgay et al., 2023; Nozière et al., 2015b; Xie & Laskin, 2024). The combination with soft ionization methods, such as electrospray ionization (ESI), allows a detailed characterization of complex OA samples (Nizkorodov et al., 2011). Several studies have already proven the potential of HR-MS in smog chamber experiments (Frauenheim, Offenber, Zhang, Surratt, & Gold, 2024; Thoma et al., 2022). Hundreds of different organic species have been detected in SOA samples generated by isoprene and monoterpene oxidation (Bateman et al., 2008; Nguyen et al., 2010; Tolocka et al., 2004). Additionally, OA samples from urban and pristine environments have been analyzed by HR-MS to identify transformation processes and potential sources of aerosol constituents (Hettiyadura & Laskin, 2022; Kourtchev et al., 2013; Lin, Fleming, Nizkorodov, Laskin, & Laskin, 2018; Tong et al., 2016; Wang et al., 2017b).

The Amazon basin is one of the most pristine ecosystems on Earth, comprising approximately 40% of all tropical forests (Baccini et al., 2012; Goulding et al., 2003). The ecosystem impacts the earth's climate through its role in the hydrological cycle, its role as storage for atmospheric carbon, and the radiative effects of its associated cloud systems. However, the Amazon region is heavily impacted by anthropogenic activities such as deforestation (Andreae et al., 2015). Observations and modelling studies show that climate change and deforestation affect the carbon and hydrological cycles in Amazonia, changing to carbon neutrality and affecting precipitation downwind (Artaxo et al., 2022). Consequently, significant seasonal fluctuations in OA concentrations are observed, influencing the radiation balance and cloud processing (Artaxo et al., 2013a; Pöhlker et al., 2023; Pöschl et al., 2010). Despite the Amazon's pivotal role in the Earth's atmosphere, our comprehension of the underlying atmospheric processes remains incomplete. For instance, the role of organic compounds in nucleation, cloud formation processes, or the aging and processing of aerosol components remains unresolved. An understanding of these processes is a fundamental prerequisite for assessing the future of the ecosystem in the context of climate and land use change (Shrivastava et al., 2019). To address such questions, a molecular characterization of organic aerosol in the Amazon rainforest is required.

In this study, LC-HR-MS was applied to analyze aerosol filter samples collected at the ATTO site during multiple campaigns across 2018 and 2019. Organic aerosols were sampled at distinct heights (0 m, 42 m, 80 m, 150 m, and 320 m) to investigate vertical gradients in chemical composition. This height-resolved sampling strategy was designed to capture the influence of biogenic emissions near the forest canopy, photochemical transformation processes above the canopy, and the impact of regionally transported, aged aerosol in the upper boundary layer. In particular, sub-canopy and near-canopy samples reflect local sources and early secondary organic aerosol formation, whereas the 320 m platform provides insight into regional and long-range transport contributions. These data enable a more detailed separation of local and regional influences on OA composition. It is important to note, however, that vertical differences are strongly influenced by seasonal and diurnal meteorological variability, including boundary layer dynamics, atmospheric mixing, and air mass history. Thus, height-dependent measurements must be interpreted within the broader context of meteorological conditions. Non-targeted high-resolution analytical techniques were employed to characterize the molecular composition of OA in relation to emission sources, (trans)formation processes, and atmospheric conditions. This molecular-level understanding contributes to improved representation of aerosol–cloud–climate interactions in atmospheric

chemistry and climate models, particularly for pristine yet rapidly changing tropical regions such as the Amazon.

3.3 Experimental section

3.3.1 Aerosol sampling

Ambient PM_{2.5} aerosol samples were collected in the Amazon rainforest at the Amazon Tall Tower Observatory (ATTO). In total, four measurement campaigns were performed to investigate seasonal variations of the SOA chemical composition. The sampling time covered the wet season 2018 (14/Apr/2018 – 19/Apr/2018), the dry season 2018 (22/Oct/2018 – 31/Oct/2018), the wet season 2019 (04/Mar/2019 – 14/Mar/2019), and the dry season 2019 (20/Sep/2019 – 26/Sep/2019). The research site allows height-resolved measurements on a 325 m tall tower in the central Amazon basin (coordinates: S 02°08.752' W 59°00.335') and is described in detail by Andreae et al. (2015). Shortly, the nearest urban region is Manaus which is located approximately 150 km southwest of ATTO. The station is part of the Uatumã Sustainable Development Reserve (UDSR) and is reached via the roughly 12 km distant Uatumã river. The tower is located at about 120 m above sea level on a plateau that is embedded in a dense, non-flooded forest (terra firme) with adjacent floodplain forests and white-sand soil savannas (campinas) and forests (campinaranas). The area at ATTO is characterized by a canopy height of about 35 m. The meteorological conditions at ATTO depend on the location of the Intertropical Convergence Zone (ITCZ) providing clean and rainy circumstances from February until May and polluted and drier conditions from August to November with strong contributions from anthropogenic deforestation and land-use change (Pöhlker et al., 2019). Relevant meteorological parameters were constantly measured and are shown in the supporting information. The corresponding wind profiles and backward trajectories were generated by the HYSPLIT Trajectory Model (Rolph, Stein, & Stunder, 2017; Stein et al., 2015).

Ambient PM_{2.5} filter samples were collected at three different heights at the tower (wet season 2018: 42 m – 15 filters + 2 blank filters, 150 m – 14 filters + 2 blank filters, 320 m – 15 filters + 2 blank filters; dry season 2018 : 80 m - 18 filters + 2 blank filters, 150 m – 18 filters + 2 blank filters, 320 m – 18 filters + 2 blank filters; wet season 2019: 80 m – 22 filters + 2 blank filters, 150 m – 22 filters + 2 blank filters, 320 m – 22 filters + 2 blank filters ; dry season 2019: 0 m – 16 filters + 2 blank filters, 80 m – 14 filters + 2 blank filters, 320 m – 16 filters + 2 blank filters,) using borosilicate glass microfiber filter bonded with PTFE (Pallflex® Emfab, 70 mm diameter). A pre-separator (Digitel, DPM2.3) was set up in front of the filter to only collect the size fraction with aerodynamic particle diameters below 2.5 µm at constant flow rates of 38 L min⁻¹. The sampling duration was set to 10 h – 14 h to allow daytime and nighttime related sample collection while ensuring sufficient particle mass on the filter material. Blank filters were collected according to the mentioned procedures but with disabled pumps. In total, 204 filter samples were collected and stored in the freezer at -18 °C before their analysis.

3.3.2 Sample preparation and analysis

One half of each filter sample was extracted three times by adding 1.5 mL of a 9:1 mixture of methanol and water (Fisher Scientific, Optima™ grade). The samples were subsequently agitated for 30 min on a laboratory shaker. The combined liquid phases were filtered afterward through a 0.2 µm PTFE syringe filter (Carl Roth, Rotilabo® KC 94.1) and evaporated completely by a gentle stream of N₂. The residue was then reconstituted in 700 µL of a 9:1 mixture of water and acetonitrile (Fisher Scientific, Optima™ grade).

Ten microliters of each sample were analyzed three times by ultra high-performance liquid chromatography (UHPLC) (ThermoFisher Scientific, UltiMate 3000) coupled to a high-resolution Orbitrap mass spectrometer (MS) (ThermoFisher Scientific, Q Exactive™). A heated electrospray ionization (ESI) source was installed and operated in the negative ionization mode. The instrument was externally calibrated with a calibration solution (Fisher Scientific, Pierce™) and a 2 mM sodium acetate aqueous solution providing mass accuracies below 1 ppm. The sample analysis was performed in the range of m/z 50 – 750 at a mass resolving power of 140 000 at m/z 200. The following ESI-MS parameters were used for the measurements: ESI capillary temperature 300 °C; spray voltage –3.2 kV; sheath gas flow 30; auxiliary gas flow 10, S-lens RF level 50%. The UHPLC system was operated with a HSS T3 column (100 × 2.1 mm ID, 1.8 μm, Waters, ACQUITY UPLC®) and the mobile phase A (water with 2% acetonitrile and 0.04% formic acid) and mobile phase B (acetonitrile with 2% water). The conditions for gradient elution were as follows: 0 – 2 min 0% B, 2 – 9 min linear increase to 30% B, 9 – 15 min linear increase to 95% B, 15 – 17.5 min 95% B, 17.5 – 19 min linear decrease to 0% B, 19 – 21 min 0% B at a constant flow rate of 350 μL min⁻¹.

3.4 Non-Targeted Data Evaluation

The LC/MS data were processed by MzMine 2.30 to obtain molecular formulae $C_cH_hO_oN_nS_s$ with the following limitations: $2 \leq C \leq 40$, $2 \leq H \leq 100$, $0 \leq O \leq 40$, $0 \leq N \leq 4$, $0 \leq S \leq 2$. Fluorine was not taken into account in the data evaluation, although recent studies show that fluorine compounds in the form of per- and polyfluoroalkyl substances (PFAS) can also be detected in traces in aerosols over tropical rainforests (Kourtchev et al., 2024). The mass tolerance for the formula assignment was set to ± 2 ppm considering isotope patterns. Adducts were removed and only ions present in all three repeated measurements were retained. The signal intensities per sample were averaged afterward. Blank samples were processed accordingly and subtracted. Only compounds with signal-to-background ratios ≥ 3 were kept for further evaluations.

The number of rings and double bonds was described by the double bond equivalent (DBE) for each assigned formula providing information on the degree of unsaturation and calculated by equation (2.1) (Badertscher et al., 2001):

$$DBE = nc - \frac{n_H}{2} + \frac{n_N}{2} + \frac{n_S}{2} + 1 \quad (2.1)$$

where n describes the number of the respective element.

Based on the DBE values the aromaticity equivalent (X_c) was calculated by equation (2.2) to identify mono- and polycyclic aromatic compounds (Yassine, Harir, Dabek-Zlotorzynska, & Schmitt-Kopplin, 2014):

$$X_c = \frac{3(DBE - (p \cdot n_o + q \cdot n_s)) - 2}{DBE - (p \cdot n_o + q \cdot n_s)} \quad (2.2)$$

where p and q represent the fraction of oxygen and sulfur atoms that are involved in the π -bond structure of the molecule. Consequently, these values can vary according to different compound classes. While $p = q = 0.5$ is suggested for carboxylic acids, esters, and nitro

functional groups, p and q are set to either 0 or 1 for aldehydes, ketones, alcohols, ethers, and nitroso classes. In the present study, $p = q = 0.5$ was used to calculate X_c considering that negative ESI analysis is highly sensitive to carboxylic acids (Kourtchev et al., 2016b; Wang et al., 2017b). According to Yassine et al. (2014), $X_c \geq 2.50$ and $X_c \geq 2.71$ are indicating monocyclic and polycyclic aromatic compounds, respectively.

The carbon oxidation state (OSC) for CHO compounds was calculated following the simplified equation (2.3) (Kroll et al., 2011):

$$OSC \approx 2 \cdot \frac{n_O}{n_C} - \frac{n_H}{n_C} \quad (2.3)$$

with the elemental ratios O/C and H/C , respectively.

Furthermore, the saturation vapor pressure (C^0) has been calculated to predict the volatility of OA compounds according to equation (2.4) (Donahue, Epstein, Pandis, & Robinson, 2011; Li, Pöschl, & Shiraiwa, 2016):

$$\log_{10} C^0 = (n_C^0 - n_C) \cdot b_C - n_O b_O - 2 \cdot \frac{n_C n_O}{n_C + n_O} \cdot b_{CO} - n_N b_N - n_S b_S \quad (2.4)$$

where n_C^0 describes the reference carbon number, b represents the contribution of each element to $\log_{10} C^0$, and b_{CO} denotes the carbon-oxygen nonideality. The C^0 values have been calculated for compound classes containing C, H, O, N, and S atoms. The parameters for the calculation based on Li et al. (2016) are listed in the supporting information Table S11.1-1.

Kendrick mass (KM) analysis was used to assign homologous series of the detected compounds, which vary only in the number of a defined base unit (; Hughey et al., 2001). In the present study, CH_2 was chosen as the base unit by rescaling the exact mass of 14.01565 to 14.00000. KM_{CH_2} was calculated according to equation (2.5) for each compound by renormalizing the exact mass scale (Hughey et al., 2001):

$$KM_{CH_2} = exact\ mass \cdot \left(\frac{14.00000}{14.01565} \right) \quad (2.5)$$

Subsequently, the Kendrick mass defect (KMD) was calculated by equation (2.6):

$$KMD_{CH_2} = nominal\ KM - KM_{CH_2} \quad (2.6)$$

where *nominal KM* describes the KM rounded to the next integer. Consequently, compounds differing only in their number of CH_2 units have the same KMD values. Homologous series can be identified as horizontal lines in KMD plots.

3.5 Results and Discussion

The chemical complexity of the OA samples is highly influenced by stochastic regional events and the respective meteorological conditions between sampling days, such as the height of the mixing layer and the wind direction. In order to take these influences into account, a distinction is made in the present study between background, variable and total organic aerosol compounds. Only compounds that were observed in more than 75 % of all samples based on their presence (identical molecular formula + retention time) were defined as background compounds. They presumably describe the local OA characteristics, as it is assumed that they are not dependent on individual emission events. For the variable OA characteristics, the evaluation was carried out by subtracting the peak areas of the previously determined background compounds from the peak areas of the total number of identified compounds (= background compounds + variable compounds). The variable compounds are attributed to irregular atmospheric events, presumably caused by different meteorological conditions. Compounds that were only detected once in the respective data set were excluded as they were not considered representative.

3.5.1 Total OA characteristics

All detected compounds were separated by reversed-phase HPLC prior to MS analysis, which increases the number of measurable compounds and reduces the risk of ion suppression in the ESI source. The chemical composition of the SOA samples was mainly influenced by seasonal effects during the measurement campaigns. A total of 2336 molecular formulas could be assigned, of which 699 were in the range of < 250 Da, 1309 between 250 Da and 450 Da, and 328 above > 450 Da. Typical mass spectra are shown in Figure S 11.1-20. Molecular weights (MW) in the range below 250 Da could be assigned to the majority of observed substances in both seasons, while the aerosol composition in the dry season additionally showed signals in the oligomeric range between 300 and 450 Da with lower intensity. While several studies have shown that ozonolysis of biogenic VOCs (e.g. α -pinene, β -pinene, isoprene) in smog chamber experiments produces compounds with high molecular weight and increased signal intensities in the oligomeric range (Kourtchev et al., 2014a; Reinhardt et al., 2007), molecules with MW above 450 Da contributed insignificantly to the total number of compounds in the present filter samples.

All filter samples reveal a high chemical diversity with 875 – 1940 unambiguously assigned molecular formulae with a large fraction of isomeric compounds (69% – 85%) Table 3.5-1, highlighting the importance of pre-separating the samples by HPLC. The identified molecular formulae were divided into four subgroups according to their elemental composition: CHO, CHON, CHONS, and CHOS. The CHO subgroup is predominant with (56 ± 6) % in all samples, followed by CHON with (20 ± 7) %, CHOS (17 ± 5) %, and CHONS (7 ± 1) %, although the contribution of sulfur- and/or nitrogen-containing compounds increases at higher MWs. This trend is in good agreement with similar studies from remote environments (e.g. Amazonia, Brazil: CHO⁽⁻⁾ with 58-63 %, CHON⁽⁻⁾ with 25-30 %, CHOS⁽⁻⁾ with 10 %, CHONS⁽⁻⁾ with 2 %, (Kourtchev et al., 2016b); Hyytiälä, Finland: CHO⁽⁻⁾ with 54.8 ± 2.2 %, CHON⁽⁻⁾ with 21 ± 3 %, CHOS⁽⁻⁾ with 16 ± 3 %, CHONS⁽⁻⁾ with 5.4 ± 2.2 %, (Kourtchev et al., 2013)), while studies from a suburban and urban environment revealed enhanced contributions of CHON and CHONS compounds (Pearl River Delta region, China: CHON⁽⁻⁾ with 34 %, CHONS⁽⁻⁾ with 8 %, (Lin, Rincon, Kalberer, & Yu, 2012); Cambridge, UK: CHON⁽⁻⁾ with 33 %, CHONS⁽⁻⁾ with 21-26 %, (Rincón, Calvo, Dietzel, & Kalberer, 2012); Shanghai, China: CHON⁽⁻⁾ with 21-23.7 %, CHONS⁽⁻⁾ with 11.2-16.6 % , (Wang et al., 2017b)), proving an increased relevance of nitrogen and sulfur chemistry in more polluted areas. The total calculated elemental ratios are

highly variable throughout the seasonal measurement campaigns with 0.60 ± 0.37 (mean value $\pm$ standard deviation of the data set) and 1.47 ± 0.49 for O/C and H/C during the dry season and 0.49 ± 0.32 and 1.56 ± 0.45 during the wet season, respectively. The wide variability indicates a high chemical complexity within the data set. Comparable values were reported from the boreal forest in Hyytiälä, Finland (0.58 and 1.54 for O/C and H/C, respectively) (Kourtchev et al., 2013). Additionally, the elemental ratios obtained in this study are consistent with smog chamber experiments using certain biogenic VOCs for SOA generation, e.g. α -pinene (0.42 – 0.55 for O/C and 1.5 for H/C, (Putman et al., 2012)) and limonene (0.5 – 0.6 for O/C and 1.5 – 1.6 for H/C, (Kundu, Fisseha, Putman, Rahn, & Mazzoleni, 2012)). Vertical profiles of α -pinene and limonene were measured at ATTO showing different chemical speciations between day and night (Yáñez-Serrano et al., 2018; Zannoni et al., 2020). The averaged total oxidation states of CHO compounds in the wet seasons ($-0.681 \leq \text{OSC} \leq -0.486$) are lower than in the dry seasons ($-0.525 \leq \text{OSC} \leq -0.324$) indicating more processed organic aerosol in the dry seasons than in the wet seasons. Furthermore, the averaged total aromaticity indices ($X_c \leq 2.50$) do not suggest a significant portion of mono- or polycyclic hydrocarbons.

Table 3.5-1: Summary of all observed MS signals with unambiguous molecular formula assignment for the four measurement campaigns in 2018 and 2019 (wet season = WS, dry season = DS). The signals are divided into four subgroups regarding their elemental composition. The relative contribution of the subgroups was calculated by dividing the number of compounds of the particular subgroup by the total number of compounds. Additionally, the average values¹ of molecular weight (MW), carbon oxidation state (OSC), aromaticity index (Xc), and isomeric fraction are listed.

Season	Height m	Number of compound s detected	CHO %	CHON %	CHONS %	CHOS %	MW Da	OSC ²	Xc	Isomers %
WS18	42	1095	54	30	6	10	271	– 0.647	0.872	77
	150	875	67	15	7	11	261	– 0.606	0.977	80
	320	1293	43	41	7	9	293	– 0.681	0.822	70
DS18	80	1856	51	19	7	23	245	– 0.324	1.050	83
	150	1940	51	18	8	23	240	– 0.353	1.051	85
	320	1720	52	18	8	22	245	– 0.330	1.070	84
WS19	80	1555	55	19	5	21	250	– 0.535	0.907	81
	150	1081	57	18	7	18	252	– 0.486	0.922	81
	320	1287	62	17	6	15	255	– 0.558	1.017	82
DS19	0	1328	60	17	5	18	237	– 0.425	0.831	69
	80	1225	61	14	6	19	233	– 0.439	0.906	84
	320	1050	62	15	6	17	246	– 0.525	0.975	77

¹Average values are calculated based on the molecular composition of each compound.

²Only CHO compounds are considered in the calculation of OSC.

3.5.2 Background OA characteristics

A clear seasonality characterizes the molecular background composition of organic aerosols at ATTO. Air masses at ATTO are in response to the annual north-south migration of the ITCZ (Intertropical Convergence Zone) leading to a seasonal alternation between north-easterly winds during the wet seasons and south-easterly winds during the dry seasons. Seven-day HYSPLIT backward trajectories (Stein et al., 2015) show that air masses need approximately 6 – 7 days from the west coast of Africa to pass the Atlantic Ocean towards ATTO (Figure S 11.1-4, Figure S 11.1-5). Higher wind speeds of up to 15 – 20 m s⁻¹ were observed during the wet seasons (dry seasons 10-15 m s⁻¹), leading to a dilution of the particles at ATTO (Figure S 11.1-3). Comparable to cleaner marine air masses from the ocean, lower background signals are detected during the wet seasons. In contrast, the dry seasons are considerably influenced by biomass burning (Table S 11.1-3) and other anthropogenic emissions from the eastern regions in Brazil (Andreae et al., 2015; Artaxo et al., 2002), resulting in higher concentrations of particulate matter (PM) (Figure S 11.1-6, Figure S 11.1-7). Concentrations up to 15 µg m⁻³ have been observed during the dry periods while approximately ten times lower concentrations were detected during the wet season.

The chemical composition of background OA also reflects these seasonal changes in meteorological conditions. 72 – 215 organic compounds were detected during the dry seasons, while 28-60 different compounds were observed during the wet seasons (Table S11.1-2). The molecular formulae in the wet seasons are predominated by the CHO subgroup (90 ± 7) %, followed by CHOS with (8 ± 7) %, CHONS (1 ± 1) %, and CHON (1 ± 2) %. The dry seasons show a comparable predominance of the CHO subgroup (93 ± 3) % and an equal contribution of CHONS compounds (1 ± 1) % but an increased fraction of CHON compounds (4 ± 1) % and a decreased fraction of CHOS compounds (3 ± 2) %. Furthermore, the averaged background aromaticity indices ($X_c \leq 2.50$) do not suggest a significant portion of mono- or polycyclic hydrocarbons in both seasons.

3.5.2.1 Van-Krevelen diagrams

Van Krevelen diagrams (VK diagrams) are used to visualize similarities and differences, e.g. between measuring locations, measuring heights, daily or seasonal influences. In a VK diagram, the H/C ratio is shown as a function of the O/C ratio for each molecular formula detected in a sample. This helps for example to visualize the degree of oxidation of the particle phase organics as the most oxidized molecules are located at the lower right corner (Zhang et al., 2021). Consequently, the most saturated and reduced species are found in the upper left region. VK diagrams of the wet and dry season 2018 at different sampling heights are shown in Figure 3.5-1. The corresponding VK diagrams for the wet and dry season 2019 show very similar patterns and can be found in Figure S 11.1-9. The signal intensity is proportional to the size of the symbols. However, the signal intensities of the various compounds certainly only provide semi-quantitative results and should therefore only be converted into concentrations to a limited extent, as different substances are detected with different sensitivities due to the selectivity of the electrospray ionization with regard to ion yield. The most intense ion signals are summarized in **Table 3.5-2** with their molecular formula, their possible identity and the precursor species.

General: The background compounds in the wet seasons are all non-aromatics with a high O/C-ratio ($O/C \geq 0.5$) and either C4-5 or C7-8 backbones, probably resulting from isoprene and monoterpene (mainly α -pinene, β -pinene, and limonene) oxidation (Hammes, Lutz, Mentel, Faxon, & Hallquist, 2019; Kleindienst et al., 2007; Nguyen et al., 2010; Worton et al., 2013). These precursor compounds are the most prevalent biogenic VOCs in the Amazon

rainforest, released by a large diversity of terrestrial vegetation (Greenberg et al., 2004; Guenther et al., 1995; Zannoni et al., 2020). The more complex chemical background of the dry seasons is clearly illustrated in the VK diagram in **Figure 3.5-1**. Especially the dry season 2018 was characterized by a high abundance of signals with H/C ratios ≥ 1.5 and O/C ratios ≤ 0.5 . These compounds are commonly attributed to aliphatic species, which can be related to both, biogenic and anthropogenic sources. Simultaneously, several compounds with low elemental ratios (H/C ≤ 1.0 and O/C ≤ 0.5) were identified as background compounds, typically associated with aromatic hydrocarbons (Mazzoleni et al., 2012; Wozniak et al., 2008). Species within this region were exclusively observed during the dry season 2018, where the highest particle concentrations were detected.

Isoprene SOA: The ion at m/z 149.0455 ($C_5H_{10}O_5$) was observed in all analyzed filter samples with high intensities. This component has been detected in isoprene oxidation chamber experiments and field studies using SOA filter sampling (Chen et al., 2020; Krechmer et al., 2015). $C_5H_{10}O_5$ was identified to be the most dominant species produced during the photooxidation of isoprene hydroxy hydroperoxides (ISOPOOH), which are important products of the isoprene oxidation under low-NO conditions (Krechmer et al., 2015; Nagori et al., 2019; Paulot et al., 2009). As shown in Figure S 11.1-8, NO and NO₂ mixing ratios were generally <0.5 ppb and <1 ppb at 73.3 m and <2 ppb and <0.5 ppb at 0.05 m for the dry season 2018. For the wet seasons 2018 and 2019 NO mixing ratios were <0.25 ppb at 79.3 m and <1.5 ppb at 0.05 m whereas NO₂ mixing ratios were <0.05 ppb at 79.3 m and <0.1 ppb at 0.05 m. NO_x data for the dry season 2019 are lacking due to instrument issues. These conditions are consistent with what is commonly defined as low-NO regimes in previous chamber studies (e.g., Krechmer et al., 2015; Nagori et al., 2019; Paulot et al., 2009). OH-initiated oxidation of ISOPOOH leads to only 2.5% to organic aerosols including $C_5H_{10}O_5$, while approximately 90% result in the formation of isoprene epoxydiol (IEPOX) and other gas-phase products (Krechmer et al., 2015). However, $C_5H_{10}O_5$ was also observed during isoprene ozonolysis and during isoprene photooxidation under high-NO conditions (Jaoui et al., 2019). Consequently, the latter pathways appear to be the dominant reactions during the dry seasons with increased NO concentrations (Figure S 11.1-8), while the ISOPOOH-SOA pathway under low-NO conditions is presumed during the wet seasons.

IEPOX-OS: The samples from the 2018 wet season showed the ion at m/z 215.0231 ($C_5H_{12}O_7S$) as the most intense signal related to IEPOX-derived organosulfates (OS) (Surratt et al., 2006b; Surratt et al., 2008). It is established that these OSs are formed from the reactive uptake of IEPOX on acidic sulfate particles under low-NO conditions, which is in agreement with our findings. IEPOX-OS was also found on filter samples from the Amazon rainforest in another study (Kourtchev et al., 2016b). The authors observed the highest intensities on filters highly affected by surrounding forest fires. Interestingly, the lowest number of active fires was recorded during the wet season 2018 campaign (Table S 11.1-3) (Instituto Nacional de Pesquisas Espaciais, 2020). Sulfate concentrations during the wet seasons are mainly attributed to biogenic and marine sources (Andreae et al., 2015), while increased levels during drier seasons are related to combustion activities (Pöhlker et al., 2018b). Sulfur compounds can also be emitted from soils showing higher emissions with higher soil moisture (Pugliese et al., 2023) leading to a significant organosulfur source from the forest itself. This suggests that IEPOX-OS is a relevant SOA constituent, regardless of the current season, and is consistent with the idea of mixed anthropogenic and biogenic sources.

Monoterpene SOA: The wet season 2019 campaign was characterized by intense ion signals at m/z 157.0506 ($C_7H_{10}O_4$) and m/z 171.0662 ($C_8H_{12}O_4$) (Figure S 11.1-9), attributed to

limonene and α -pinene oxidation products, among others (Eddingsaas et al., 2012; Florou et al., 2024; Hammes et al., 2019; Thoma et al., 2022) suggesting that biogenic sources are dominant contributors to SOA loading at ATTO. Furthermore, the intensities of α -pinene oxidation products were higher in the dry than in the wet seasons. This can be explained by increased ambient temperatures (Figure S 11.1-1, Figure S 11.1-2) and photosynthetic active radiation facilitating the emission rates of monoterpenes (Guenther, Monson, & Fall, 1991; Kesselmeier & Staudt, 1999). This also affects the diel variation with prevalent concentrations during the day.

Aromatics: All detected ions were classified by their aromaticity equivalent X_c according to Yassine et al. (2014), in order to identify mono- and polycyclic aromatic species. While monocyclic structures such as benzene and functionalized derivatives are indicated by values of $X_c \geq 2.50$, condensed polycyclic aromatic compounds are described by $X_c \geq 2.71$. Naphthalene is the smallest polycyclic structure meeting this criterion (Wang et al., 2017b; Yassine et al., 2014). The dry season campaigns were accompanied by an increased number of active fires and biomass burning (Table S 11.1-3). Consequently, the detected aromatic hydrocarbons are mainly attributed to anthropogenic sources (Henze et al., 2008).

Hydrocarbons: The dry season 2018 was characterized by the occurrence of several aromatic species with X_c values ≥ 2.50 (Figure S 11.1-8). The most intense signals correspond to the ions at m/z 149.0243 ($C_8H_6O_3$), m/z 164.0353 ($C_8H_7NO_3$), m/z 193.0505 ($C_{10}H_{10}O_4$), and m/z 207.0298 ($C_{10}H_8O_5$), each with DBE values ≥ 6 . These compounds were already identified as relevant components of biomass burning activities. $C_8H_6O_3$ and $C_{10}H_8O_5$ were observed during naphthalene photooxidation experiments in a chamber study (Chhabra et al., 2015; Kautzman et al., 2009; Thoma et al., 2022). Naphthalene and other polycyclic aromatic hydrocarbons (PAH) have been related to wood combustion processes in the literature and are considered to impact human health (Baumann et al., 2023; Chan et al., 2009; Samburova et al., 2016; Schauer, Kleeman, Cass, & Simoneit, 2001). $C_{10}H_{10}O_4$ might be a product formed during the degradation of cellulose and lignin, two important biopolymers (Kong et al., 2021). The MS^2 spectrum (Figure S 11.1-11) revealed two fragments, CO_2 and $C_3H_4O_2$ (acrylic acid), leading to a tentative structure of ferulic acid.

Nitro-hydrocarbons: $C_8H_7NO_3$ was assigned to a nitro-phenolic structure, which can be formed during biomass pyrolysis. This compound class is a major contributor to brown carbon (BrC) (Lin et al., 2016) and has been detected earlier in SOA samples from the Amazon rainforest (Claeys et al., 2012). The ion appeared in almost every sample of the dry season 2019 in high intensities, suggesting this compound to be an important biomass burning marker in this study. Another intense background ion was 4-nitrocatechol at m/z 154.0146 ($C_6H_5NO_4$), which has been previously considered as a marker compound for biomass burning OA (Claeys et al., 2012; Iinuma, Böge, Gräfe, & Herrmann, 2010; Kourtchev et al., 2016b).

Polycycles: The ion at m/z 219.0455 ($C_{15}H_8O_2$) appeared in the dry season 2019 samples and has already been reported in another study (Bruns et al., 2015). The authors identified this compound as an oxygenated PAH produced during wood combustion with a pyrene core structure, which seems reasonable according to the increased X_c Value of 2.82 and 12 DBE.

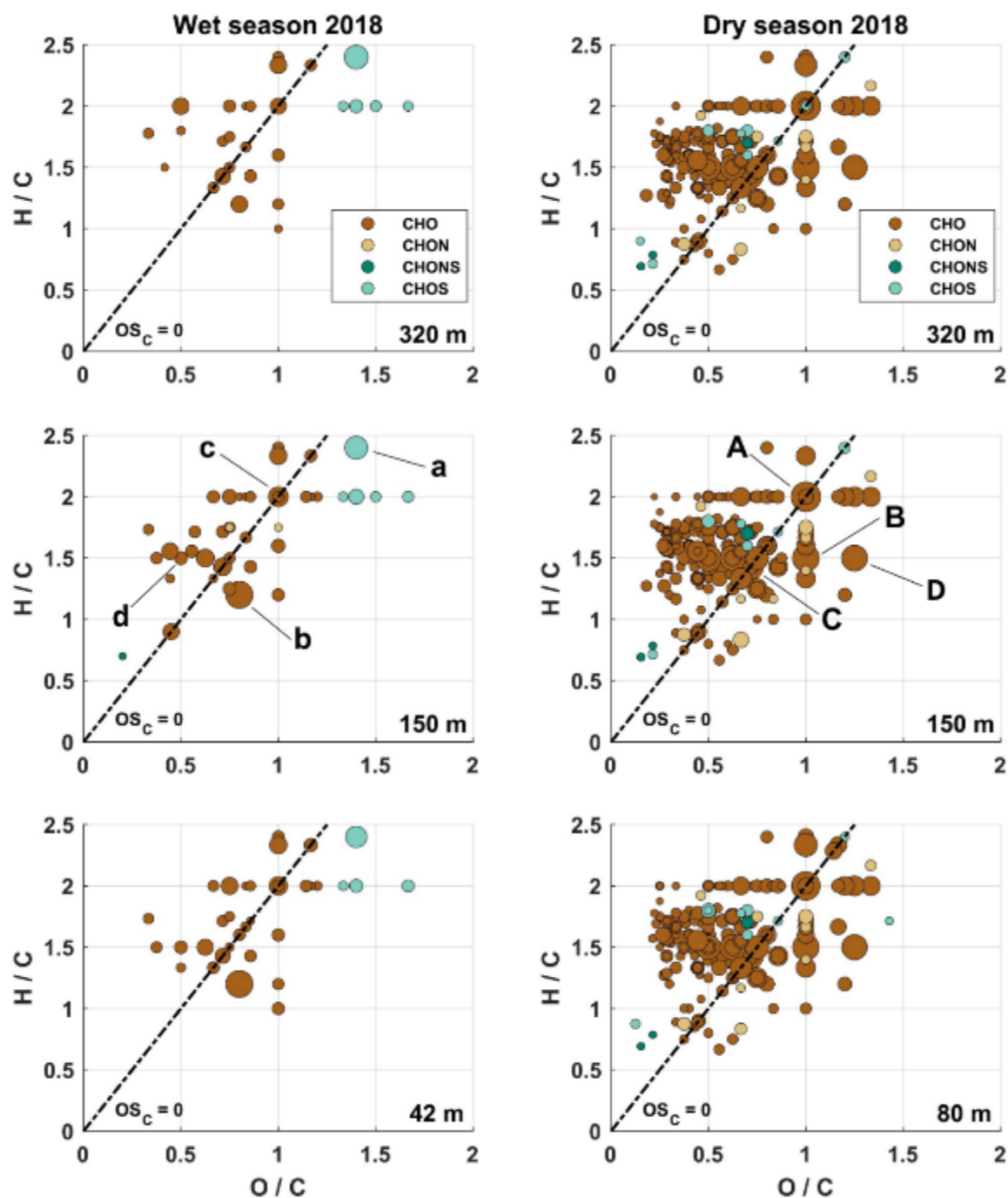


Figure 3.5-1: Van Krevelen plots from the wet season 2018 (left panel; sampling heights: 320 m, 150 m, 42 m) and the dry season 2018 (right panel; sampling heights: 320 m, 150 m, 80 m). Included are only molecular formulae that were present in more than 75% of the samples, respectively. The size of the data points represents the signal intensity of the corresponding peak. The four subgroups are distinguished with different colors. Compounds located on the black dashed line have an average carbon oxidation state of 0 ($OS_C = 0$). The labels a-d and A-D correspond to the most intense signals further characterized in Table 3.5-2.

Table 3.5-2: Possible identities and precursors for the most intense signals from the background ions for the different seasons.

Season	ID ¹	Formula	m/z	OSC	Possible identity	Precursor	Reference
WS18	a	C ₅ H ₁₂ O ₇ S	215.0231	-	IEPOX-OS	Isoprene	(Worton et al., 2013) (Kourtchev et al., 2016)
	b	C ₅ H ₆ O ₄	129.0194	0.4	Dicarboxylic acid / Peroxy acid	Methylfuran	(Joo et al., 2019)
	c	C ₅ H ₁₀ O ₅	149.0455	0.0	Carbonyl-tetrol / Epoxyl-tetrol / Carboxyl-triol	Isoprene	(Krechmer et al., 2015) (Chen et al., 2020)
	d	C ₈ H ₁₂ O ₄	171.0662	-0.5	Ketolimononic acid / Terpenylic acid	Limonene / α -pinene	(Hammes et al., 2019) (Eddingsaas et al., 2012)
DS18	A	C ₅ H ₁₀ O ₅	149.0455	0.0		See ID c	
	B	C ₄ H ₆ O ₄	117.0193	0.5	Succinic acid	-	(Wang et al., 2017)
	C	C ₇ H ₁₀ O ₅	173.0454	0.0		α -pinene	(Chen et al., 2020) (Kleindienst et al., 2007)
	D	C ₄ H ₆ O ₅	133.0142	1.0	Malic acid	Isoprene	(Nguyen et al., 2010)
¹ IDs correspond to the labels illustrated in Figure 3.5-1 .							

3.5.2.2 Carbon oxidation states

To further characterize the background chemical composition of the aerosol, the average carbon oxidation state (OSC) was calculated for each detected molecular CHO formula. This metric was introduced by Kroll et al. (2011) and is a useful parameter to describe complex mixtures of organic aerosols. Various chemical and physicochemical processes in the atmosphere are determined by the oxidation state of the organic components. For example, highly oxidized molecules (HOM) with sufficiently low volatility can form clusters, which leads to the formation of new particles and subsequent particle growth, even of small particles (Bianchi et al., 2016; Molteni et al., 2018).

To give an impression of the position of the corresponding OSC values within the regular Van Krevelen plots, organic compounds with OSC = 0 are indicated by the dashed line in **Figure 3.5-2**. To the left are compounds with an OSC < 0 (not or less oxidized), to the right are compounds with OSC values > 0, e.g. the HOMs, which are defined as molecules with O/C $\geq$ 0.6 and/or OSC $\geq$ 0 (Tu, Hall, & Johnston, 2016). As shown in **Figure 3.5-1**, the samples from the 2018 dry season had the highest number of highly oxidized compounds, which accounted for about 30 % of the total number of compounds. The average molecular formula for the HOMs

in the 2018 dry season was C_{6.5}H_{8.6}O_{5.1} with C₄-C₁₀ backbones, which can be interpreted that isoprene and monoterpene precursors are also the main source of HOMs in the Amazon rainforest in the dry season. The 2019 dry season showed fewer oxidized molecules, with a mean molecular formula of C_{6.7}H_{10.2}O_{5.7}. The difference in HOM concentrations between the dry seasons of 2018 and 2019 may be related to differences in the chemical composition of OH reactivity during those periods. Pfannerstill et al. (2021) observed that while total OH reactivity was higher in September 2019 than in October 2018 ($29.1 \pm 10.8 \text{ s}^{-1}$ vs. $28.1 \pm 7.9 \text{ s}^{-1}$ at 80 m), this increase was not driven by monoterpenes, which are key precursors for HOM formation. The high OH reactivity in the dry season 2019 was rather dominated by oxidized VOCs, such as aldehydes and organic acids. This shift toward more oxidized and aged VOCs indicates a more photochemically processed air mass, potentially affected by biomass burning. Although NO_x was not measured (Figure S 11.1-8), the authors suggest that fire-related emissions may have altered the oxidation regime. Given that high NO_x levels can suppress RO₂ autoxidation and thereby inhibit HOM formation, and that monoterpene contributions to OH reactivity were not elevated in 2019, it is plausible that the observed reduction in HOMs was due to a combination of reduced precursor availability and a shift in chemical conditions unfavorable for HOM production.

However, it should be noted that the analysis of highly oxygenated compounds would benefit from the use of a more polar stationary phase of the LC column, as a more comprehensive analysis of analytes of the entire polarity range would be enabled. This would ensure that even the very polar species are not underestimated due to insufficient separation.

Figure 3.5-2 shows the OSC values as a function of carbon number for each CHO compound, with OSC values ranging from -1.5 to +1.2 in the dry seasons and from -1.1 to +1.0 in the wet seasons. This result is consistent with other studies in remote continental areas (Kourtchev et al., 2013; Kourtchev et al., 2016b). Molecules with an OSC between -0.5 and -1.5 and a carbon number greater than seven are considered biomass-burning organic aerosol (BBOA). The comparison between dry and wet seasons clearly shows the large number of compounds associated with BBOA and that these substances contribute substantially to the SOA load of the Amazon rainforest during dry seasons. Interestingly, the contribution of BBOA-related compounds was significantly higher in the 2019 wet season (Figure S 11.1-12), which is likely due to the increased number of active fires during this period. In contrast, molecules with an OSC between -0.5 and +1.0 and less than 13 carbon atoms are generally associated with semivolatile and low-volatility oxygenated organic aerosol (SV-OOA and LV-OOA) (Kroll et al., 2011; Wang et al., 2017b). These compounds are formed by multiple oxidation reactions and are commonly attributed to fresh and aged SOA, respectively (Jimenez et al., 2009; Zhang et al., 2007). The background chemical composition during the dry seasons also revealed numerous compounds attributed to LV-OOA indicating more aged SOA components compared to the wet seasons. Whether the lower precipitation in the dry season and the associated longer residence times of the OA in the atmosphere are the cause of these observations, or whether these compounds also have their source in biomass combustion processes, cannot be clearly determined here. In contrast, the majority of background compounds during rainy seasons are associated with SV-OOA, suggesting that local biogenic emissions are the main source of freshly formed SOA. Overall, **Figure 3.5-2** clearly shows that large differences in chemical composition exist between the two seasons in the Amazon rainforest.

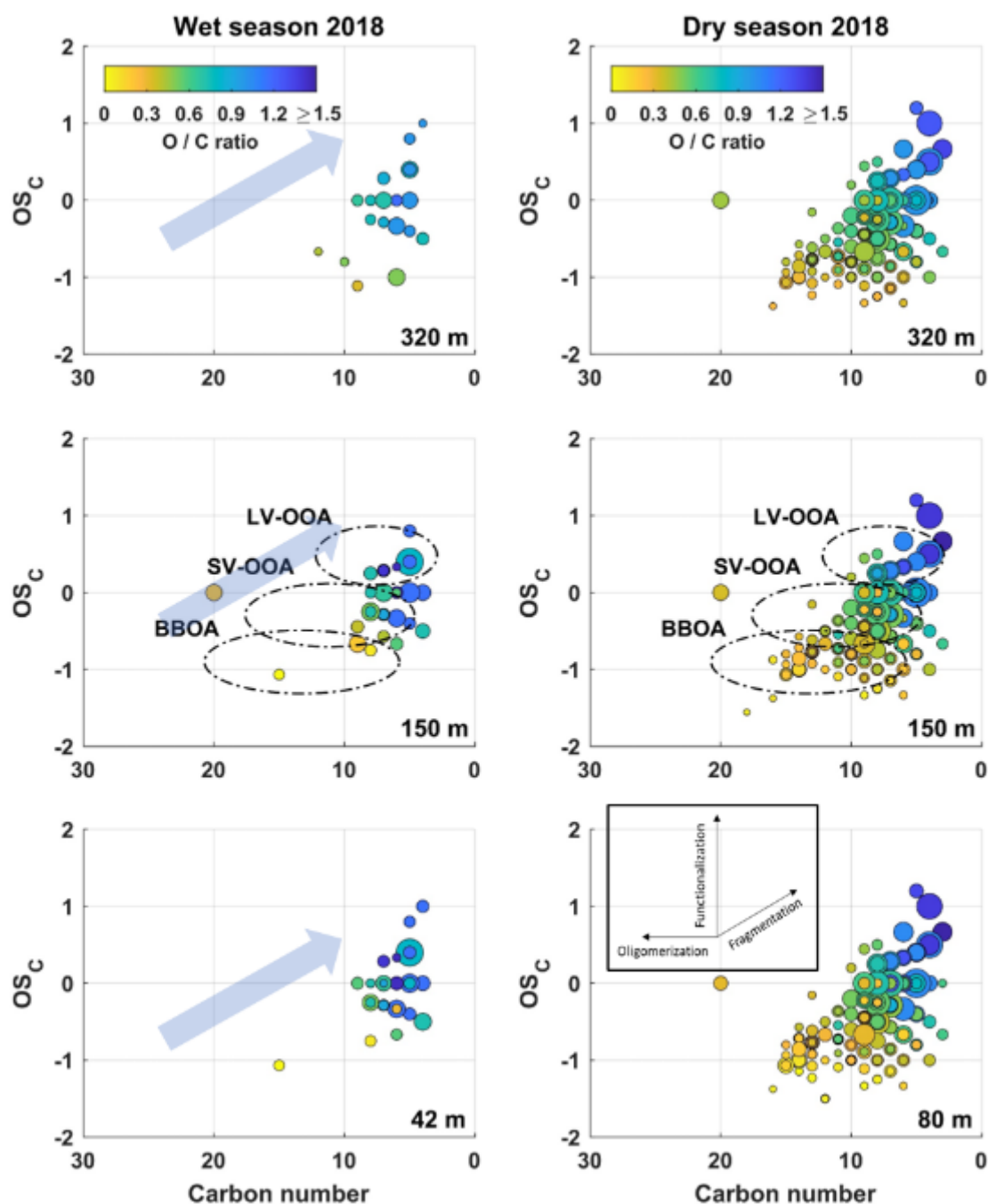


Figure 3.5-2: Carbon oxidation state (OSC) plots for all detected CHO species during the wet season 2018 (left) and dry season 2018 (right) at different sampling heights. Only background ions are included. The size of the data points represents the signal intensity of the corresponding peak. The color code illustrates the degree of oxygenation. The black dashed areas are related to low-volatility (LV-OOA) and semivolatile (SV-OOA) oxygenated organic aerosol and biomass-burning organic aerosol (BBOA). Insets: vectors corresponding to key classes of reactions of atmospheric organics: functionalization (addition of polar functional groups), fragmentation (cleavage of C–C bonds), and oligomerization (covalent association of two organic species). The combination of these reaction types leads to complex movement through (–the OSC–carbon number–) space; however, the inevitable increase in OSC with atmospheric oxidation implies that, given enough time, organics will generally move up and to the right (blue arrows). Insets based on Kroll et al., 2011.

3.5.2.3 Height-dependency of the background OA characteristics

The vertical profiles of the background organic aerosol (OA) composition exhibited only subtle variations across the sampled heights, with much smaller gradients than those observed between seasons. As illustrated in the van Krevelen diagrams **Figure 3.5-1** and summarized in **Table S11.1-2**, the background OA was dominated by CHO-type compounds at all heights and during all seasons, accounting for 82 % to 98 % of the detected molecular formulas. Nitrogen- and sulfur-containing species (CHON, CHOS, CHONS) contributed only minor fractions, with a slight increase in CHON and CHONS observed at 150 m during the wet season 2018 (CHON: 5 %, CHONS: 2 %). During the wet season 2019 CHON and CHONS species accounted for 0 % and 2 % at all sampling heights (80 m, 150 m, 320 m). The OSC of the background CHO species showed a weak increase with altitude during the wet season 2018 **Figure 3.5-2**. At 320 m, the mean OSC of CHO compounds was slightly higher (+0.04) compared to 150 m (−0.04) and 42 m (+0.03, **Table S11.1-2**), suggesting that the aerosol at higher altitudes had undergone marginally more extensive oxidation, likely due to longer atmospheric residence times or vertical transport from above the forest. Contrastingly, during the wet season 2019 the mean OSC of CHO compounds did not show significant variations at different sampling heights (around −0.5, **Table S11.1-2**). The magnitude of order for the OSC values for the wet season 2019 were comparable to the dry season 2018. Hereby should be noted that the sampling heights from the wet season 2019 and dry season 2018 (80 m, 150 m, 320 m) differed from the wet season 2018 (80 m instead of 42 m) and the dry season 2019 (0 m, 80 m, 320 m). Therefore, the chemical composition in the wet season 2018 could also include more local OA sources at the canopy level (sampling at 42 m) whereas the dry season 2018 and wet season 2019 probably reflect more regional sources that are well mixed. However, during the dry season 2018 and wet season 2019, vertical gradients nearly disappeared. The background CHO compounds at all heights exhibited similar OSC values (around −0.4 for the dry season 2018 and −0.5 for the wet season 2019, **Table S11.1-2**) with a significant lower number of signals in the wet season 2019 (51-60) than in the dry season 2018 (209-211). The compounds clustered closely in the SV-OOA and LV-OOA regions (**Figure 3.5-2**), suggesting the dominance of regionally aged aerosol, as well as pronounced BBOA signals originating from biomass burning and other long-range sources. The dry season 2019 exhibited a markedly lower contribution of biomass burning organic aerosol (BBOA) signals (**Figure S 11.1-12**) and a reduced number of detected molecular formulas (72-198, **Table S11.1-2**) compared to the dry season 2018 (209-211, **Table S11.1-2**). Despite similar average oxidation states (OSC ~ −0.4), the aerosol composition in the dry season 2019 was characterized by a lower contribution of aromatic compounds ($X_c = 0.3-0.5$) and sulfur-containing species (CHOS 1 % at 150 m). These differences suggest a shift in the dominant sources and atmospheric processes during this period. Interestingly, fire activity across the Amazon basin was in fact higher in 2019, with 19925 recorded fires (**Table S 11.1-3**), compared to previous years. However, the expected increase in biomass burning tracers at ATTO was not observed. This discrepancy suggests that the smoke plumes generated by these fires were either transported in other directions or did not reach the ATTO site efficiently. Possible explanations include altered large-scale atmospheric circulation patterns, such as changes in wind direction or vertical stability, which limited the transport of biomass burning emissions from southern and southwestern Amazonia towards the northeastern Amazon, where ATTO is located. In the reduced biomass burning influence, the aerosol composition at ATTO during the dry season 2019 was shaped predominantly by regional background air masses and local processes. The highest oxidation state of CHO-type compounds was observed below the canopy at 0 m sampling height (OSC: −0.367), along with the highest mean molecular weight (196 Da). This points to local oxidative processes near the forest floor, such

as the oxidation of biogenic emissions from soil and understory vegetation or nighttime nitrate radical chemistry. Limited vertical mixing during stable nighttime conditions may have allowed the accumulation of heavier, more oxidized compounds below the canopy.

In total, the observed vertical differences in the background composition are subtle and become significant only under low-turbulence wet season conditions like in the wet season 2018. Even then, the background aerosol remains compositionally similar across heights, reflecting the strong influence of regional air masses and long-range transport on the background aerosol burden at the ATTO site. These findings highlight that, while vertical gradients in the background aerosol composition are generally small when averaged over entire seasons, individual events or specific atmospheric conditions may exhibit much more pronounced vertical or temporal variability. Therefore, future studies will focus on single event-based analyses examining specific episodes of chemical stratification, nighttime oxidation, or pollution influence that could provide a more detailed understanding of the underlying processes.

3.5.3 Variable OA characteristics

The occurrence of variable component contributions to the chemical composition of OA is attributed to irregular atmospheric events, which are presumably caused by varying meteorological conditions, i.e. uncommon wind direction, long-range transported plumes or fires or anthropogenic pollution nearby. Compounds that were only detected once in the respective data set were excluded, as they were not considered representative. As already mentioned, the previously discussed background compounds were not taken into account for the group of variable compounds defined here. The remaining signals were assigned according to the sampling time during the day (7:00 - 17:00 local time, UTC-4 h) and night (17:00 - 7:00 local time, UTC-4 h). An additional sample in the morning (7:00 – 12:00 local time, UTC-4 h) was collected during the dry season 2019 only, while the daytime sample was collected between 12:00 and 17:00 local time, UTC-4 h. The results and trends for 2018 and 2019 are discussed in this chapter, but for clarity, the graphs for 2019 are shown in the supplement (Figure S 11.1-13, Figure S 11.1-14, Figure S 11.1-15, Figure S 11.1-16).

3.5.3.1 Molecular tracer compounds of individual events

In this section, Van Krevelen and OSC diagrams are discussed with the aim of identifying molecular tracer components that can be associated with individual meteorological or atmospheric chemical events. Representative VK diagrams for the seasons in 2018 are shown in Figure 3.5-3. The respective diagrams of the wet and dry season 2019 are shown in Figure S 11.1-13 and Figure S 11.1-14. For better understanding, the VK diagrams were divided into five areas: *I* for very highly oxidized organic compounds, *II* for highly oxidized compounds, *III* for intermediately oxidized compounds, *IV* for oxidized unsaturated organic compounds and *V* for highly unsaturated organic compounds. The five areas were defined according to Zhang et al., 2021.

(*I*) Very highly oxidized organic compounds: Area *I* shows very highly oxidized organic compounds, with isoprene oxidation products being a distinctive feature. Since less wet deposition of aerosol particles occurred due to less precipitation events during the dry season 2018, a greater number of compounds were identified during the dry season 2018 than during the wet season 2018. This result is consistent with the particle mass and number concentrations (Figure S 11.1-6, Figure S 11.1-7) observed during these campaigns. $C_5H_{12}O_4$ (m/z 136.0662) was detected in all samples from all seasons and identified as 2-methyltetrole, a prominent product of isoprene oxidation (Claeys et al., 2004a). A large number of CHOS

compounds were detected during the dry season 2018. More than 85 % of the CHOS molecules detected showed an O/S ratio ≥ 4 , indicating the presence of at least one sulfate functional group. Species with O/C ≥ 1 and H/C ≥ 2 with highly oxygenated C4 and C5 backbones were particularly prominent. Their structures emphasize that isoprene is the main precursor for S-containing OA at ATTO. $C_5H_{12}O_7S$ (m/z 215.0231, IEPOX-OS) and $C_5H_{10}O_7S$ (m/z 213.0075) were detected in filter samples from all four campaigns and showed the highest intensities. Both structures have already been identified as isoprene-derived OS and correlate with increased sulfate concentrations during dry periods. The latter can be attributed to the long-range transport of anthropogenic emissions (Andreae et al., 2015). It is well established that isoprene-derived organosulfates are primarily formed via photochemical oxidation mechanisms, involving reactive intermediates such as ISOPOOH and IEPOX under low-NO conditions, often leading to enhanced production during the daytime (Surratt et al., 2006b; Surratt et al., 2008). However, in our study, we observed consistently higher CHOS signal intensities at night across all seasons. While OS formation is photochemically driven, the nocturnal enhancement in signal intensities is likely not indicative of in situ nighttime production, but instead reflects more efficient partitioning into the particle phase during cooler nighttime conditions. This explanation is consistent with the findings of Gómez-González et al. (2012) and Kourtchev et al. (2014b), who also reported strong diurnal differences driven by temperature-dependent gas-particle partitioning.

Concerning the height-dependent analysis the wet season 2018 reveals that CHON and CHOS species in area I were more abundant at 42 m (slightly above canopy) during the day, whereas their number increased at 320 m during the night. CHO compounds, in contrast, showed a lower relative contribution at 320 m compared to 42 m in both, day and night samples (Figure 3.5-3). These observations suggest a vertical redistribution of specific compound classes influenced by boundary layer dynamics. The nocturnal increase in CHON and CHOS compounds aloft may be related to residual layer effects or long-range transport, whereas the canopy-level daytime maxima point to local, biogenic emissions and in-canopy photochemical processing. In the dry season 2018, no clear vertical trend was observed in area I, suggesting enhanced atmospheric mixing and a more homogeneous chemical distribution due to convective processes. These interpretations are supported by recent findings that showed that under very stable nocturnal conditions (assumed for wet season 2018), the boundary layer height can remain below 100 m, allowing upper levels (e.g., 320 m) to remain decoupled and enriched in aged or transported aerosol components. Furthermore, the prevalent southwesterly wind direction in the dry season 2018 is associated with higher surface roughness and increased turbulence, potentially leading to more uniform vertical distributions and mixing of aged, oxidized species (Mendonça et al., 2025).

(II) Highly oxidized organic compounds: In general, area II is characterized by highly oxidized organic species like late monoterpene oxidation products due to oxidative aging or higher generation oxidation products (Zhang et al., 2021). The dry season 2018 shows a higher number of compounds than the wet season 2018, indicating more aged organic aerosol. This is also underlined by an increased number of LV-OOA species in the OSC plots in Figure 3.5-4. An intense ion signal with m/z 203.0562 ($C_8H_{12}O_6$) could be assigned to 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) by comparison with an authentic standard (Table S 11.1-5). MBTCA is a well-established tracer compound for aged biogenic SOA formed by the photooxidation of α - and β -pinene (Szmigielski et al., 2007a; Zhang et al., 2010b). Similarly, two detected CHONS compounds at m/z 294.0654 ($C_{10}H_{17}O_7NS$) and m/z 296.0446 ($C_9H_{15}O_8NS$) were associated with aged SOA, which were previously identified as oxidation products of α -pinene, β -pinene and limonene (Surratt et al., 2008). The O/(N+S) ratio ≥ 3.5

allows for the presence of both $-\text{OSO}_3\text{H}$ and $-\text{ONO}_2$ functional groups and assignment as nitrooxy organosulfates (NOS). Similar to the higher concentrations of very highly oxidized CHOS species (*I*), highly oxidized (*II*) CHONS species also show increased concentrations in dry periods and high correlations with SO_2 levels, but also NO_x concentrations (increased NO_x and black carbon equivalent concentrations (BCe) in the dry season 2018; Figure S 11.1-8 and Figure S 11.1-17). This underlines the importance of anthropogenic emissions reaching the ATTO site by long-distance transport and changing the chemical composition of organic aerosols by mixing biogenic and anthropogenic sources.

The molecular assignment of two further ions, m/z 161.0455 ($\text{C}_6\text{H}_{10}\text{O}_5$) and m/z 129.0194 ($\text{C}_5\text{H}_6\text{O}_4$) with increased concentrations in the dry season clearly shows a connection with biomass burning activities. The overall burning activity in the basin was significantly lower in the wet season 2018 compared to the dry season 2018 (Table S 11.1-3). $\text{C}_6\text{H}_{10}\text{O}_5$ can be assigned to 1,6-anhydro- β -D-glucopyranose (Levogluconan) by comparison with authentic standard substances (Table S 11.1-5). Levogluconan is a generally recognized product of cellulose pyrolysis that is used as a marker compound for biomass burning activities (Nolte, Schauer, Cass, & Simoneit, 2001; Simoneit et al., 1999). However, $\text{C}_5\text{H}_6\text{O}_4$ can be explained less clearly. A compound with this molecular formula was found as an oxidation product of the reaction of 3-methylfuran with NO_3 radicals (Joo, Rivera-Rios, Takeuchi, Alvarado, & Ng, 2019), while furans themselves were detected as products of cellulose combustion (Mettler et al., 2012). The $\text{C}_5\text{H}_6\text{O}_4$ molecule observed here showed higher concentrations in dry season samples (higher number of fires) and in night samples (nitrate radical chemistry), supporting the hypothesis that the reaction of 3-methylfuran with NO_3 radicals is a source of this compound. However, the C5 backbone can also suggest isoprene as potential precursor, which can also form $\text{C}_5\text{H}_6\text{O}_4$ according to photooxidation experiments in chamber studies (Clark, Nakao, Asa-Awuku, Sato, & Cocker, David R., 2013; Nguyen, Roach, Laskin, Laskin, & Nizkorodov, 2011).

During the wet season 2018, the oxidized organic aerosol subtype LV-OOA showed its highest O/C ratios at 150 m during daytime (Figure 3.5-4), indicating a vertical gradient in oxidation state. While the oxidation state increased with height, the total number of LV-OOA species decreased at 320 m. This pattern is consistent with oxidative aging during vertical transport and lower precursor availability aloft. At night, this vertical pattern persisted, albeit with overall lower O/C ratios (Figure 3.5-4). CHON signals in area *II* were most abundant at 320 m, leading to the assumption that highly oxidized, aged CHON compounds reached the ATTO site by long-range transported aerosols.

(*III*) Intermediately oxidized organic compounds: Area *III* mostly consists of first-generation oxidation products of monoterpenes and sesquiterpenes that are intermediately oxidized (Zhang et al., 2021). Again, the dry season 2018 is characterized by a higher number and concentration of compounds than the wet season 2018 while no significant differences are observed between the daytime and nighttime samples. The compounds are characterized by aliphatic species that can be attributed to mixed anthropogenic and biogenic sources (Henze et al., 2008; Kourtchev et al., 2013). A prominent ion was observed at m/z 185.0819, which was assigned to the molecular formula $\text{C}_9\text{H}_{14}\text{O}_4$. The compounds with this molecular formula showed multiple signals in the LC-MS analysis, indicating the presence of several isomeric structures. One signal was identified as pinic acid (PA) from an authentic standard compound (Table S 11.1-5). The additional signals are likely to be oxidation products of other monoterpenes, such as β -pinene, limonene and Δ^3 -carene (Chen & Griffin, 2005; Hammes et al., 2019; Jenkin, 2004). In contrast to MBTCA, pinic acid is an oxidation product that is already

formed during the first oxidation steps of α -pinene and can therefore be used as a tracer for freshly formed SOA. Later generation products, such as MBTCA, were more concentrated in the dry seasons, indicating more processed SOA particles, while PA was predominant in the wet periods. The OSC analysis in Figure 3.5-4 shows that the dry season 2018 has pronounced signals at small numbers of C atoms with high O/C ratios, whereas the wet season 2018 is characterized by pronounced SV-OOA species, supporting the different seasonal variation of different generations.

During the wet season 2018, CHO and CHON species in area III were most abundant at 42 m during daytime, indicating a dominant contribution from local biogenic sources within or just above the canopy. CHO compounds decreased with height, while CHON compounds remained relatively constant (Figure 3.5-3). At night, however, CHON signals dropped at 42 m, possibly due to suppressed vertical mixing or altered chemical production pathways. This suggests that canopy dynamics and photochemical activity strongly influence the vertical distribution of first-generation monoterpene oxidation products. These trends are consistent with the findings of Mendonça et al. (2025), which indicate that under wet season conditions, when the wind predominantly arrives from the northeast (Figure S 11.1-5) and the surface roughness is relatively low, the nocturnal boundary layer is shallow (typically 80–120 m), limiting vertical exchange and favoring accumulation of semivolatile species near the canopy top.

(IV) Oxidized unsaturated organic compounds: This area is mainly characterized by unsaturated hydrocarbons with a low oxygen content. Most of these compounds are classified as CHON, CHOS and CHONS with $X_c \geq 2.5$, indicating aromatic molecular structures. The dry season 2018 shows a higher diversity of compounds whereas the wet season 2018 consists of a lower number of compounds mainly dominated by CHO species. However, the dry season of 2018 shows a higher presence of CHON species during nighttime compared to daytime samples. The most intense ion signals in the dry season 2018 m/z 154.0146 ($C_6H_5NO_4$, 4-nitrocatechol), m/z 168.0301 ($C_7H_7NO_4$, methyl-nitrocatechols) and m/z 185.0457 ($C_8H_9NO_4$, dimethyl-nitrocatechols) can be associated with nitroaromatic compounds, which are also considered markers for biomass burning OA (Claeys et al., 2012; Iinuma et al., 2010; Kahnt et al., 2013; Kitanovski, Grgić, Yasmeen, Claeys, & Čusak, 2012c; Siemens et al., 2023). Kourtchev and coworkers (Kourtchev et al., 2016b) also observed elevated concentrations of these compounds in the Amazon region during the period when numerous forest fires occurred. In contrast, no nitrocatechols were detected for the wet season 2018. However, $C_6H_5NO_4$ was the only compound identified as a background species during the dry season 2018 (**Figure 3.5-1**), suggesting a lower SOA contribution from $C_7H_7NO_4$ and $C_8H_9NO_4$ at ATTO.

Vertically resolved analysis of the wet season 2018 revealed that CHO signals in area IV were less abundant at 320 m compared to lower levels, similar as described in area III. No significant day-night differences were observed, indicating that these compounds may be governed more by long-range transport and vertical diffusion than by in situ photochemistry. The lack of clear diurnal variation points to a more persistent source, possibly influenced by combustion-related emissions or stabilized air masses.

(V) Highly unsaturated organic compounds: Area V is predominantly composed of highly unsaturated organic compounds that are combustion-related (Zhang et al., 2021). The number of compounds and the variety of species is enhanced for the dry season 2018 compared to the wet season 2018. This trend is also reflected in the BBOA areas in Figure 3.5-4. Furthermore, black carbon equivalent concentrations (BCe) were enhanced during the dry

season 2018 compared to the wet season 2018 (Figure S 11.1-17). No single dominant species was identified among the combustion-related highly unsaturated organic compounds, as their composition varied substantially between seasons. While the wet season 2018 shows mainly CHO species with a decreased number of compounds during nighttime, the dry season 2018 is dominated by CHOS and CHONS species and an increased number of CHON compounds during nighttime, suggesting enhanced particle-phase partitioning at lower temperatures.

During the wet season 2018, a greater number of highly unsaturated compounds were detected at 42 m compared to 320 m, both day and night. This points to a near-surface deposition and limited vertical mixing under stable boundary layer conditions, whereas no significant height resolved differences were observed for the dry season 2018.

The wet season of 2019 stands out due to individual pollution events that significantly influenced aerosol composition at the ATTO site. The number of components and their intensity increase across areas I–V for the wet season 2019 (Figure S 11.1-13), compared to the wet season 2018 (Figure 3.5-3) and the dry season of the same year (Figure S 11.1-14). The wet season 2019 also shows higher levels of CHON and CHO species relative to the 2019 dry season. The concentrations of OS related to isoprene remain comparable to those observed during the dry seasons of 2019 and 2018. In particular, area V in Figure S 11.1-13 and the BBOA area in Figure S 11.1-15 highlight the impact of biomass burning during this period. This is further supported by elevated BC_e concentrations (Figure S 11.1-17). While the background OA characterization still shows typical wet season features, such as low BBOA contributions, a dominance of early-stage monoterpene oxidation products, minimal aging effects (Figure S 11.1-12), and absent signals in area V (Figure S 11.1-9), it becomes evident that, with the inclusion of individual events, episodes of considerable pollution were present, temporarily altering the aerosol profile. These deviations likely reflect enhanced fire or combustion activity upwind or near the ATTO site during this period (Table S 11.1-3). Additionally, emissions from biomass burning in the Sahel savanna regions, transported across the Atlantic Ocean (Figure S 11.1-5), could have contributed to the observed aerosol characteristics (Holanda et al., 2020; Holanda et al., 2023).

In the wet season 2019, no significant vertical trends were observed across areas I–V, indicating a well-mixed atmosphere, possibly due to convective activity or large-scale transport. However, the dry season 2019, which included sampling at three different times and at sub-canopy level (0 m), revealed unique patterns. SV-OOA and CHOS compounds in areas I and II peaked at 80 m during nighttime, consistent with gas-particle partitioning favored by cooler, stable layers above the canopy. CHON compounds were most abundant at 0 m and 80 m in the morning but diminished at 320 m. These patterns underline the importance of both vertical stratification and local chemical processing in modulating aerosol composition at different heights and times of day. Mendonça et al. (2025) noted that dry season nights at ATTO, characterized by southwesterly winds and enhanced surface roughness, can exhibit deeper but more turbulent boundary layers, allowing complex layering and submesoscale motions to form, which could explain the varied height-dependent signals observed in this campaign. Moreover, the presence of the highest CHOS and SV-OOA signals at 80 m during nighttime suggests a zone of active condensation and SOA formation just above the canopy, where gas-particle partitioning is favored by cooler and more stable stratification. The fact that CHON species were relatively suppressed at 320 m both during morning and daytime indicates limited upward transport of nitrogen-containing precursors or their rapid transformation near the surface. The chemical differences between 0 m and 80 m, particularly for CHON and CHO

species in areas II and III, also suggest that in-canopy processes such as deposition, emissions, and light penetration significantly modulate chemical composition. Together, these observations highlight the sensitivity of nighttime aerosol chemistry to fine-scale vertical structure and suggest that sub-canopy and canopy-top levels may act as chemically distinct compartments in the nocturnal boundary layer during the dry season.

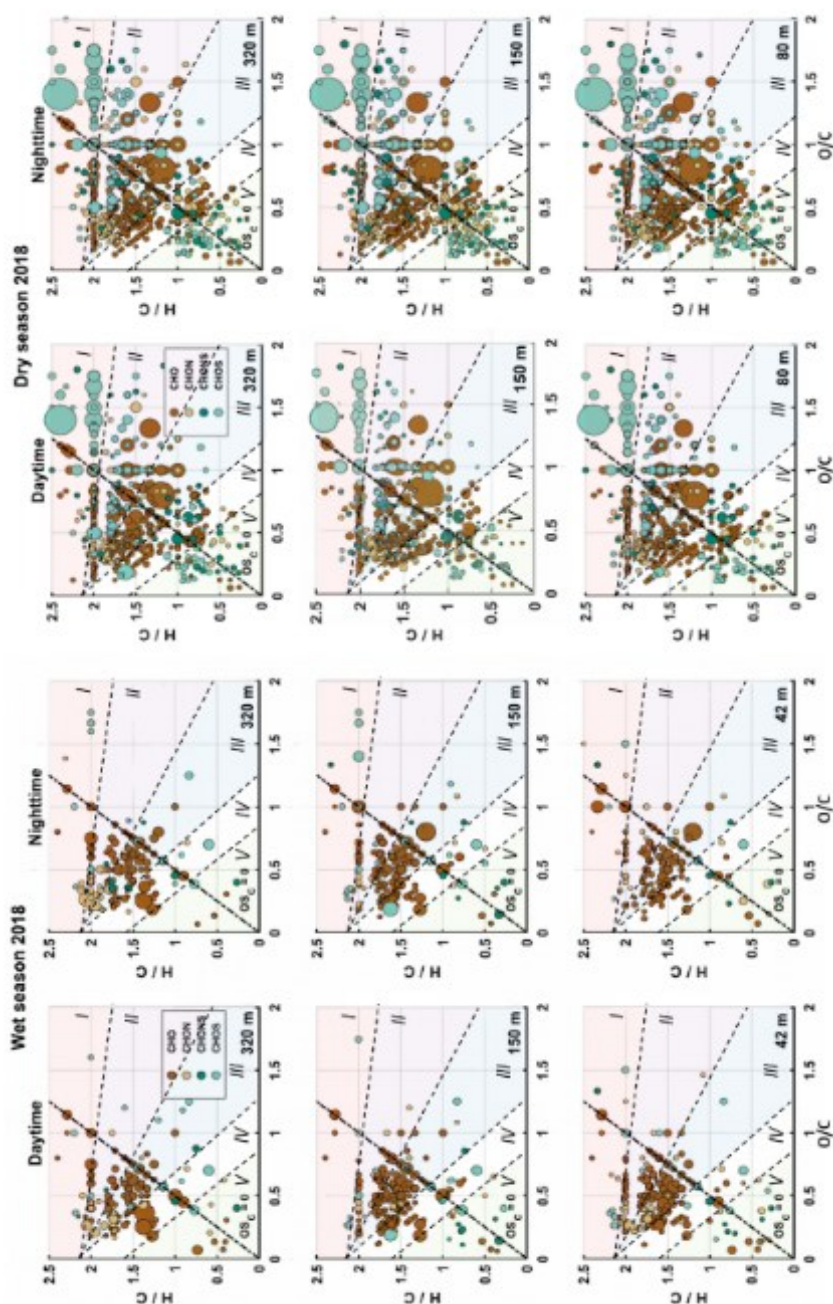


Figure 3.5-3: Van Krevelen plots from the wet season 2018 (left panel) and dry season 2018 (right panel) during daytime and nighttime at 42 m, 150 m, 320 m height and 320 m height and dry season 2018 (right panel) during daytime and nighttime at 80 m, 150 m, and 320 m height. Included are only molecular formulae that were present in more than one of the samples, respectively. The background signals are subtracted. The size of the data points represents the signal intensity of the corresponding peak. The four subgroups CHO, CHON, CHONS and CHOS are distinguished with different colors. Compounds located on the black dashed line have an average carbon oxidation state of 0 ($OSC = 0$). The VK diagram was divided into five areas: I for very highly oxidized organic compounds, II for highly oxidized compounds, III for intermediately oxidized compounds, IV for oxidized unsaturated organic compounds and V for highly unsaturated organic compounds. The five areas were defined according to Zhang et al., 2021.

Area (I) is mainly characterized by CHOS molecules with at least one sulfate functional group and C4 and C5 backbones. Area (II) is dominated by highly oxidized compounds representing aged OA and biomass burning products. Area (III) shows mainly aliphatic species. Area (IV) is dominated by unsaturated hydrocarbons with low oxygen content and aromatic structures while area (V) shows mainly combustion related species.

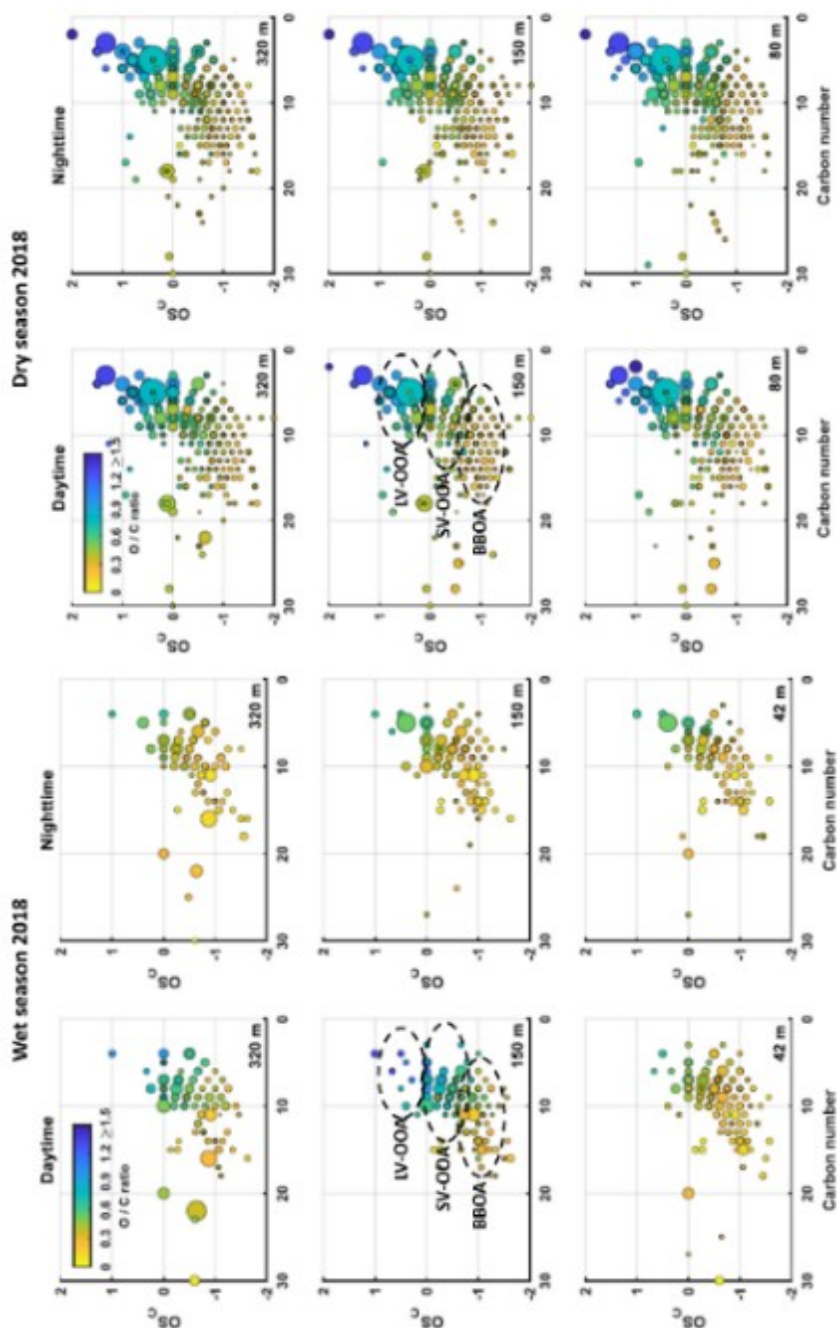


Figure 3.5-4: Carbon oxidation state (OSC) plots for all detected CHO species during the wet season 2018 at daytime and night time at 42 m, 150 m, 320 m and dry season 2018 (right) at daytime and nighttime at 80 m, 150 m and 320 m sampling height. Included are only molecular formulae that were present in more than one of the samples, respectively. The background signals are subtracted. The size of the data points represents the signal intensity of the corresponding peak. The color code illustrates the degree of oxygenation. The black dashed areas are related to low- volatility (LV-OOA), semivolatile (SV-OOA) oxygenated organic aerosol and biomass burning organic aerosol (BBOA).

3.5.3.2 Saturation vapor pressure

The saturation vapor pressure C^0 is an important thermodynamic property that regulates the gas-to-particle partitioning properties of organic molecules and enables their classification as VOCs, intermediate volatile organic compounds (IVOCs), semi-volatile OCs (SVOCs), low-volatility OCs (LVOCs) and extremely low-volatility OCs (ELVOCs) (Murphy, Donahue, Robinson, & Pandis, 2014; Odum et al., 1996; Pankow, 1994). The relationship between molecular weight, chemical composition and saturation vapor pressure has already been used to describe the chemical evolution of organic aerosols (Li et al., 2016; Shiraiwa, Berkemeier, Schilling-Fahnestock, Seinfeld, & Pöschl, 2014). A case study for organic species observed in the dry and wet season 2018 is presented in Figure 3.5-5 showing 2-D maps of molecular weight versus saturation vapor pressure. Nearly all CHONS compounds are located within the LVOC/ELVOC range, and it is clear that many of the additional compounds detected in the dry season exhibit very low volatility, indicated by high molecular weights, and a more oxidized (aged) character relative to the wet season composition. Increased nitrogen oxide and SO₂ concentrations and thus the formation of N- and S-functionalized oxidation products, but also a lower removal by precipitation and thus longer residence times in the atmosphere could explain these differences between wet and dry season. These factors suggest that the observed compounds reflect a regional burning signature in the dry season. Several high molecular weight compounds with C₈-C₁₀ or C₁₇-C₂₀ backbones have also been identified as LVOC/ELVOC, suggesting oligomeric structures derived from isoprene and monoterpene precursors. It is hypothesized that these products are low volatile due to the incorporation of additional functional groups and the increase in carbon number in the molecular structure (Daumit, Kessler, & Kroll, 2013; Kroll & Seinfeld, 2008). Two prominent ion signals at m/z 333.0859 (C₁₀H₂₂O₁₀S) and m/z 357.1557 (C₁₇H₂₆O₈) were previously reported in chamber studies with isoprene and α -pinene (Kristensen et al., 2013; Surratt et al., 2008). Most oligomers were detected in filter samples collected during the dry season, suggesting a stronger contribution of the oligomerization reaction to SOA under these conditions. In addition to structures derived from isoprene and monoterpene precursors, compounds with molecular formulae such as C₁₄₋₁₅H₂₂₋₂₄O₃₋₇ were detected in the dry season 2018 (i.e. C₁₄H₂₂O₇; C₁₅H₂₄O₄), contributing to the LVOC fraction. These signals are in line with oxidation products previously identified in chamber simulation experiments of β -caryophyllene ozonolysis (Gao et al., 2022) and could be assigned to β -caryophyllonic acid (C₁₅H₂₄O₃) as well as β -nocaryophyllonic acid and β -caryophyllinic acid (C₁₄H₂₂O₄) by comparison with authentic standard compounds (Table S 11.1-5). The authors investigated the formation of SOA under varying nitrogen oxide levels at different temperatures. At a temperature of 313 K and the absence of nitrogen oxides, monomers (mainly C₁₄₋₁₅H₂₂₋₂₄O₃₋₇) and dimers (mainly C₂₈₋₃₀H₄₄₋₄₈O₅₋₉) could be detected. In the presence of nitrogen oxides, which is more characteristic of the dry season conditions in 2018, most organonitrates were found as monomers with a C₁₅ skeleton and one nitrate group (C₁₅H₂₃₋₂₅O₇₋₉N). However, in the wet and dry season 2018 no significant contribution of C₂₈₋₃₀H₄₄₋₄₈O₅₋₉ or C₁₅H₂₃₋₂₅O₇₋₉N could be found. In case of CHON compounds with only one N atom, the dominant compound in the dry season 2018 was C₁₄H₂₇NO₇. This molecule has previously been identified as a product of toluene-derived SOA in chamber experiments (Zhang et al., 2020b). These findings imply that, in addition to biogenic precursors, aromatic anthropogenic emissions may also play a relevant role in shaping the low-volatility organic aerosol composition during the dry season.

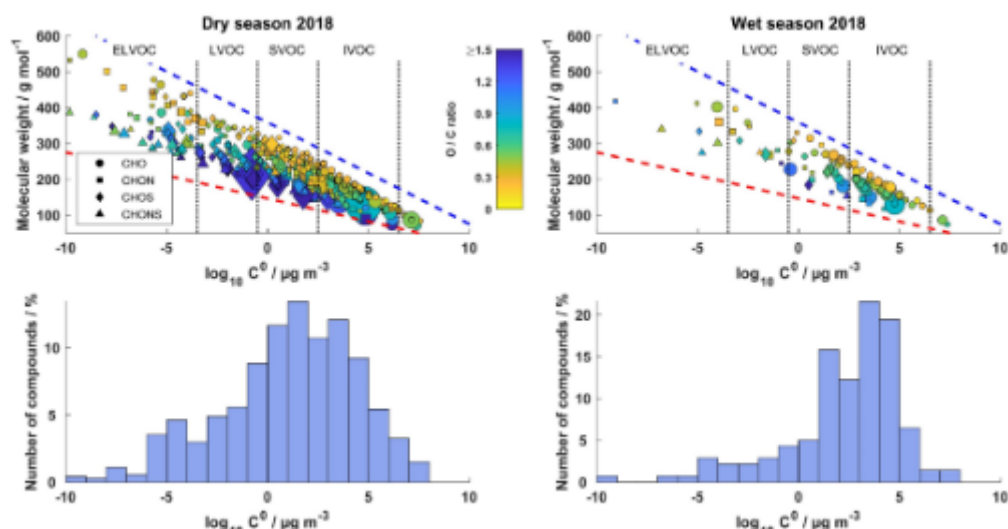


Figure 3.5-5: Molecular classification of organic species for the dry season 2018 (left) and the wet season 2018 (right) according to their saturation vapor pressure C^0 . The color code describes the degree of oxygenation. The blue dashed line indicates linear alkanes C_nH_{2n+2} , while the red dashed line represents sugar alcohols $C_nH_{2n+2}O_n$ according to Li et al. (2016). The lower panel shows the distribution of all detected compounds among the respective classes.

3.5.3.3 Kendrick mass analysis

Kendrick mass analysis is a valuable visualization tool for complex organic mixtures and was introduced by Kendrick (1963) and later refined by Hughey et al. (2001). This technique has already been used to characterize organic aerosol samples (Kourtchev et al., 2013; Lin et al., 2012; Rincón et al., 2012). It enables the assignment of all signals of a homologous series when the elemental composition of a compound has been identified (Nizkorodov et al., 2011). Figure 3.5-6 compares the KMD_{CH_2} diagrams (see eq. 2.5 and 2.6) for the dry and wet seasons in 2018. Compounds differing only in their number of CH_2 units have the same KMD values. Homologous series can be identified as horizontal lines in KMD plots.

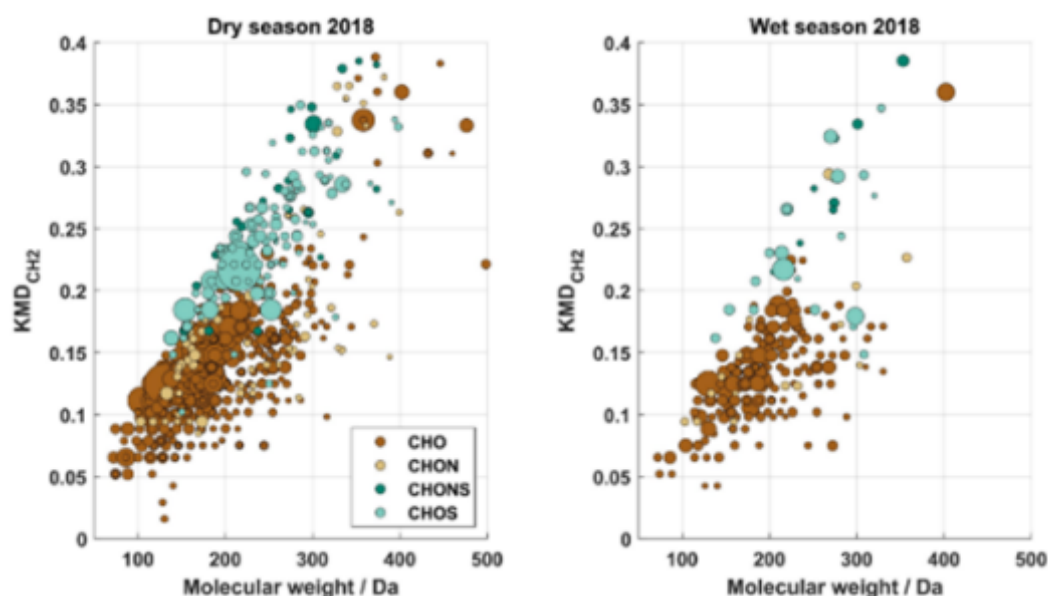


Figure 3.5-6: CH_2 -Kendrick diagrams for all signals detected at 150 m during the dry season 2018 (left) and the wet season 2018 (right), respectively. The size of the data points represents the signal intensity of the corresponding peak. The four subgroups are distinguished with different colors.

As mentioned above, the dry season was characterized by biomass burning and the occurrence of aged organic aerosol components, resulting in large-membered homologous series of CHO compounds with higher MW than in the wet season. Compounds with $\text{KMD}_{\text{CH}_2} \leq 0.11$ appear to be unsaturated carboxylic acids with the general molecular formulae $\text{C}_n\text{H}_{2n}\text{O}_2$, $\text{C}_n\text{H}_{2n}\text{O}_3$, $\text{C}_n\text{H}_{2n-2}\text{O}_2$ and $\text{C}_n\text{H}_{2n-2}\text{O}_4$. The elemental composition suggests fatty acids, which have been described in OA-related studies as essential compounds of marine and terrestrial vegetation (Kourtchev et al., 2014b; Rincón et al., 2012; Stephanou & Stratigakis, 1993). Thus, long-range transport of marine aerosols or BBOA could explain the greater abundance of fatty acids during the dry season (Oros & Simoneit, 2001; Tervahattu, Juhanoja, & Kupiainen, 2002). In addition, a large number of CHOS compounds with $\text{KMD}_{\text{CH}_2} \geq 0.21$ were detected exclusively during the dry season. Similar results were reported by Kourtchev et al. (2016b), who found a larger number of homologous series of CHOS compounds in aerosol samples affected by anthropogenic emissions. These species are presumably highly oxygenated organosulfates, which are probably formed by heterogeneous reactions on acidic sulfate particles.

Another interesting ion was detected at m/z 186.1135 ($\text{C}_9\text{H}_{17}\text{NO}_3$) with high signal intensities, especially during the dry season 2018. This compound has already been observed in biomass burning chamber experiments and field measurements in the Amazon rainforest (Kourtchev et al., 2016b; Laskin, Smith, & Laskin, 2009). In the present study, Kendrick mass analysis revealed evidence of a homologous series, which is shown in the KMD plot in Figure 3.5-7. The general molecular formula can be described as $\text{C}_n\text{H}_{2n-1}\text{NO}_3$, where n ranges from 3 to 17 depending on the filter sample. The elemental composition initially suggested a nitrooxy functional group ($-\text{ONO}_2$), but MS^2 experiments (Figure S 11.1-18) did not show the typical nitrate fragment. Instead, the observed fragments indicated the presence of a carbamate functional group ($\text{R}-\text{NH}-\text{COOH}$). Due to their zwitterionic structure, these species could be relevant for condensed phase chemistry in the atmosphere, similar to amino acids (Barbaro et al., 2011; McGregor & Anastasio, 2001; Milne & Zika, 1993; Mopper & Zika, 1987).

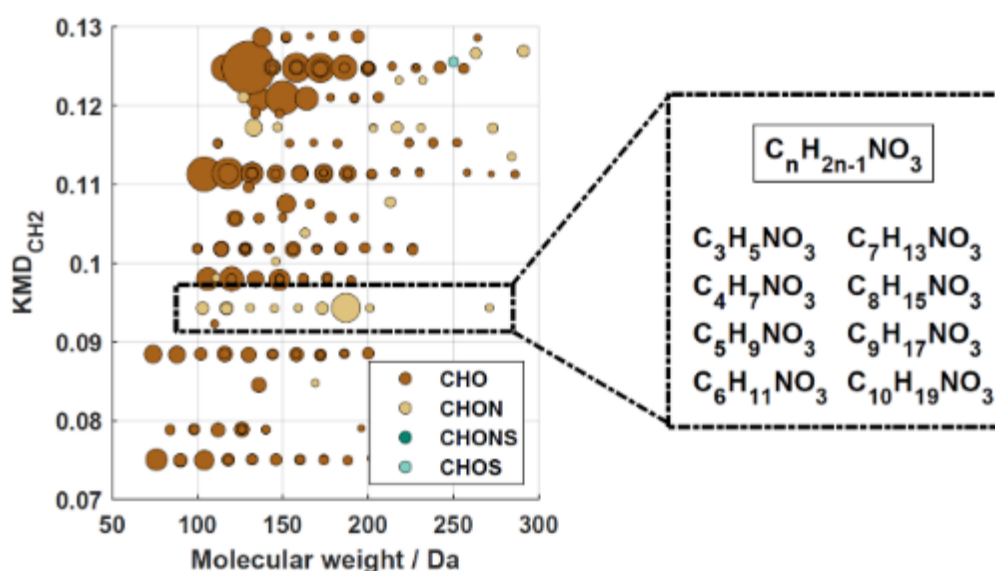


Figure 3.5-7: Kendrick mass defect diagram for the dry season 2018. The size of the data points represents the signal intensity of the corresponding peak. The four subgroups are distinguished with different colors. The dashed box highlights a homologous series of CHON compounds with a molecular formula of $\text{C}_n\text{H}_{2n-1}\text{NO}_3$ with $n = (3 - 17)$, potentially related to biomass burning emissions.

3.6 Conclusion

The organic chemical composition of atmospheric OA particles from the Amazon rainforest was investigated at the ATTO station using high-resolution MS in combination with an UHPLC system. Between 2018 and 2019, a total of four measurement campaigns were carried out, including two dry and wet seasons, with one "clean" wet period, one wet period influenced by biomass burning and combustion activities and two "polluted" dry periods. This allows conclusions to be drawn about seasonal influences in a unique ecosystem that is characterized by the complex interaction of numerous emission sources. In this analysis, a distinction was made between background compounds with a relatively low variability over time, and compounds with a much higher variability in their concentrations.

The results show a high fraction of isomeric structures in each data set, highlighting the need to use chromatographic separation methods for molecular identification of the aerosol components. Such an approach allows the reliable identification and quantification of a number of important marker compounds if reference compounds are available. However, the semi-quantitative determination of other compound classes is also possible, particularly by reducing ion suppression. The majority of compounds measured in both seasons had molecular weights (MW) below 250 Da. In addition, the analysis of the dry season samples showed signals in the oligomeric range between 300 and 450 Da with lower intensities. In general, the background molecular composition of organic aerosols at ATTO showed a clear seasonality with large differences between the dry and wet seasons. A considerable number of suitable marker compounds for different SOA sources were identified. The most important sources of background SOA at ATTO were the oxidation of isoprene and monoterpenes at both, high and low NO_x concentrations and the formation of organosulfates. The results show that isoprene is the main precursor for S-containing SOA components at ATTO. The formation of isoprene OS probably occurs through the reactive uptake of IEPOX on acidic sulfate particles. It is assumed that in the wet season the sulfate particles reach the ATTO station mainly by long-range transport of marine aerosol, while in the dry season direct anthropogenic sources are also likely to be present. Furthermore, earlier studies showed that organic sulfur emissions from soils increase with higher soil water content which indicates a stronger organosulfur soil source from the forest itself in the wet seasons. Isoprene organosulfates can have both, purely biogenic and anthropogenic sources, whereby the biogenic sources appear to have a greater influence if the background OA composition is taken into account. This is further supported by the observation that the CHOS subgroup accounted for $(8 \pm 7) \%$ in the wet season compared to only $(3 \pm 2) \%$ in the dry season. Other dominant SOA groups that characterized the background were aromatic compounds whose source was most likely biomass burning. Thus, various oxygenated and nitrated hydrocarbons and oxidized polycyclic compounds showed significantly higher concentrations during the dry seasons. The evaluation of carbon oxidation states shows that LV-OOA and BBOA were the predominant and highly concentrated species in the dry seasons, while SV-OOA dominated in the wet seasons. We assume that a significant proportion of LV-OOA is formed by the aging and chemical processing of SOA components.

High signal intensities of nitroxyorganosulfates were observed in the dry seasons 2018 and 2019 as well as in the wet season 2019, whereby these were particularly derived from monoterpene precursors and correlated with the increased occurrence of fires and the SO₂ and NO_x concentrations. Noteworthy are the low vapor pressures of the CHONS compounds, which therefore make a significant contribution to ELVOCs. In addition, we find evidence of oligomeric structures of biogenic SOA components, as well as dimers of sesquiterpene oxidation products, which could also contribute to the ELVOC fraction. At the same time, a

large fraction of BBOA contributes to the total OA, as shown by the high X_c values. Consequently, unsaturated and aromatic compounds such as nitrocatechols and nitrophenols were mainly attributed to deforestation fires, which occurred mainly during the dry periods. Interestingly, the chemical composition of OA particles from the 2019 wet season revealed a similar OA composition as in the dry season, suggesting that combustion emissions played a larger role in the wet season 2019. Fossil fuel combustion in Europe or strong biomass burning in the Sahel savanna regions could be responsible via long-distance transportation across the Atlantic. Follow up studies to address these different long-range transport scenarios in dedicated case studies, providing a more detailed understanding of their respective contributions are in preparation.

Data availability

The data sets are available at upon registration at <https://www.attodata.org> (last access: 25 January 2022), and more information can be given by Thorsten Hoffmann (t.hoffmann@uni-mainz.de).

Author contributions

DL and SH contributed equally. DL, SH and TH planned and designed the study. DL conducted the aerosol sampling, the sample preparation and analysis, the evaluation and wrote the manuscript. SH conducted the method validation of sample preparation and analysis, the evaluation and wrote the manuscript. NZ helped to collect the aerosol samples and revised the manuscript. LK, BH, JW, CP, and SW provided the SMPS and trace gas data. The meteorological data was provided by MS. MCS and UP provided scientific input and revised the manuscript. All authors contributed to the discussion of the results as well as the finalization of the manuscript.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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4 The role of size resolution in the molecular characterization of primary and secondary organic aerosols in the Amazon rainforest

This chapter is a reprint of the manuscript in preparation for *Atmospheric Chemistry and Physics*:

Summary

This chapter provides a size- and height-resolved molecular characterization of primary and secondary organic aerosols (OA) at the Amazon Tall Tower Observatory (ATTO) using targeted ultra-high-performance liquid chromatography coupled to high-resolution Orbitrap mass spectrometry (UHPLC–HR-Orbitrap-MS). The study analyzes 32 molecular marker compounds across a particle size range of 10 nm to 10 μm , collected at 60 m and 320 m heights during wet, transition, and dry seasons under varying atmospheric conditions (clean, mixed, and polluted). The results reveal systematic variations in molecular composition with particle size, season, and atmospheric state, elucidating distinct formation and aging pathways.

Oxidation products of isoprene, monoterpenes, and sesquiterpenes dominate sub-50 nm particles, indicating their role in new particle formation and early growth. Primary biological markers, such as sugar alcohols and amino acids, contribute significantly to the smallest size fractions, while aged monoterpene secondary organic aerosol (SOA) markers peak in the accumulation mode. Organosulfates increase with particle size and altitude, highlighting the importance of multiphase processing and long-range transport. Biomass burning and anthropogenic tracers are enhanced under polluted conditions, further influencing the molecular fingerprint of Amazonian aerosols. This chapter contributes to a deeper understanding of the size-resolved molecular composition of OA in the Amazon, demonstrating how primary emissions, secondary formation, and atmospheric processing interact across particle sizes and seasons. The findings underscore the necessity of size-resolved molecular observations to constrain aerosol–cloud–climate interactions in tropical ecosystems.

I am the first author of this manuscript. I developed and validated a UHPLC–HR-Orbitrap-MS method for 32 molecular markers, collected and processed all aerosol samples at two heights across three seasonal campaigns, and conducted evaluations to identify size-dependent compositional patterns. I authored the manuscript and incorporated the co-authors' inputs into the final version.

Size-resolved molecular characterization of primary and secondary organic aerosols in the Amazon rainforest

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4.1 Abstract

Organic aerosols (OA) in the Amazon rainforest are strongly influenced by biogenic emissions, long-range transport, and biomass burning, yet their molecular composition and formation pathways, which vary with particle size, remain poorly constrained. Here, we present a size- and height-resolved molecular characterization of primary and secondary OA at the Amazon Tall Tower Observatory (ATTO) based on targeted ultra-high performance liquid chromatography high-resolution Orbitrap mass spectrometry (UHPLC–HR-Orbitrap-MS) analysis of 32 molecular marker compounds in aerosol particles from 10 nm to 10 μm . Samples were collected at 60 m and 320 m in height during the wet, transition, and dry seasons and classified into clean, mixed, and polluted atmospheric conditions.

The molecular composition varies systematically with particle size, season, and atmospheric conditions, revealing distinct formation and aging pathways. Oxidation products of isoprene, monoterpenes, and sesquiterpenes contribute substantially to sub-50 nm particles, indicating a role in new particle formation and early growth. In addition, primary biological markers, including sugar alcohols and amino acids, show pronounced contributions to the smallest size fractions, demonstrating that primary organic aerosol can directly contribute to ultrafine particle populations. Aged monoterpene SOA markers peak in the accumulation mode, while organosulfates increase with particle size and altitude, highlighting the importance of multiphase processing and long-range transport. Biomass burning emissions exhibit strong size- and height-dependent variability in organic aerosol composition, with ultrafine particles dominated by fresh, nearby sources and accumulation-mode aerosols reflecting aged, long-range transported smoke. These patterns persist even during the wet season, indicating a continuous background influence from biomass burning alongside biogenic sources. The size-resolved distribution highlights how different emission regimes and atmospheric processing shape organic aerosol properties in the Amazon.

4.2 Introduction

Organic aerosols (OAs) are a dominant component of atmospheric particles worldwide, accounting for up to 90 % of total aerosol mass (Jimenez et al., 2009; Kanakidou et al., 2005; Kroll & Seinfeld, 2008). OA consist of primary organic aerosols (POA), which are emitted directly into the atmosphere through processes such as biomass combustion and biological activity, and secondary organic aerosols (SOA), which form when volatile organic compounds (VOCs) undergo oxidation and subsequently undergo nucleation and/or condensation (Seinfeld & Pankow, 2003). Due to their abundance, complex composition, and interactions with radiation, clouds, and organisms, OA play a central role in atmospheric chemistry and the climate system (Hallquist et al., 2009; Pöschl, 2005b). However, the molecular composition of OA, especially its formation and growth processes, is poorly understood in many natural environments.

In this context, the Amazon basin is one of the most atmospherically significant yet least understood regions on Earth. With approximately 40 % of the world's tropical forest area, the Amazon rainforest significantly influences the climate system through its role in the global

carbon and water cycles, as well as through the radiative effects of its extensive cloud systems (Artaxo et al., 2013a; Baccini et al., 2012; Goulding et al., 2003). The atmosphere above the Amazon rainforest is characterized by exceptionally high emissions of biogenic volatile organic compounds (BVOCs) from vegetation. These emissions are dominated by isoprene, with mono- and sesquiterpenes as supplements (Guenther et al., 2012). They serve as a basis for intensive secondary aerosol formation and therefore contribute significantly to the global inventory of aerosols and cloud condensation nuclei (CCN). Concurrently, the region is subject to pronounced seasonal variations, ranging from virtually pristine conditions in the wet seasons to strongly anthropogenically influenced conditions in the dry seasons, particularly due to biomass burning and long-range transport (Holanda et al., 2023; Pöhlker et al., 2019).

A central and yet unresolved question concerns the formation of ultrafine aerosol particles (UAPs, < 100 nm) and their growth to climatically relevant sizes. Although UAPs themselves interact only weakly with radiation, they represent a major source of larger particles that scatter or absorb solar radiation, thereby directly affecting Earth's radiation balance (Kulmala, 2025). Moreover, particles formed via new particle formation (NPF) are estimated to contribute up to 50 % of global CCN, thereby exerting a substantial indirect climatic effect through aerosol–cloud interactions (Gordon et al., 2017; Merikanto, Spracklen, Mann, Pickering, & Carslaw, 2009; Wang & Penner, 2009; Westervelt et al., 2013). In boreal forest ecosystems, NPF and subsequent particle growth have been intensively studied, resulting in a comparatively robust conceptual understanding. In these environments, NPF frequently occurs within the near-surface boundary layer and is commonly driven by sulfuric acid, ammonia, and highly oxygenated organic molecules (HOMs) formed from the oxidation of monoterpenes (Ehn et al., 2014; Kulmala et al., 2004). These insights form the basis of many current parameterizations of aerosol formation in regional and global atmospheric models.

In the Amazon region, however, particle formation processes appear to differ fundamentally from those observed in boreal forests. Despite comparable or even higher BVOC emissions, NPF near the surface is rarely observed (Martin et al., 2010). Instead, ultrafine particles occur episodically and often without evidence of continuous growth (Varanda Rizzo et al., 2018). A growing body of evidence suggests that intense NPF in Amazonia predominantly takes place in the free troposphere, where lower temperatures and distinct chemical conditions favour nucleation (Fan et al., 2018; Wang et al., 2016b). Newly formed particles can subsequently be transported into the planetary boundary layer by convective downdrafts, where they may continue to grow through the condensation of organic vapours (Andreae et al., 2018; Ekman et al., 2008). These pronounced differences in particle formation pathways imply that mechanisms and parameterizations derived from boreal forest studies cannot be directly transferred to tropical rainforest systems.

An additional layer of complexity in the Amazon arises from the dominant role of isoprene. Under low- NO_x conditions, isoprene oxidation has been shown to suppress the formation of highly oxygenated organic molecules, potentially inhibiting early particle growth. At the same time, isoprene substantially contributes to organic aerosol mass and ozone chemistry through the formation of IEPOX-derived organosulfates (Glasius et al., 2018b; Isaacman-VanWertz & Aumont, 2021). Whether these products contribute to nucleation and early growth of ultrafine particles, or predominantly to mass accumulation in larger particles, remains largely unresolved. A key limitation in addressing these questions is the lack of size-resolved molecular measurements, particularly in the ultrafine particle size range where nucleation and initial growth processes occur.

Beyond secondary aerosol formation, primary biological aerosol particles, including fungal spores, pollen fragments, and other biogenic debris, constitute an important component of the Amazonian aerosol population across both fine and coarse size ranges (Barbosa et al., 2022; Prass et al., 2021). These primary emissions interact with secondary processes and may influence particle growth, aging, and CCN activity (Ariya et al., 2009; Sun & ARIYA, 2006). Furthermore, anthropogenic perturbations such as urban emissions from Manaus, biomass burning during the dry season, and long-range transport of marine and aged continental aerosol modify the chemical environment and affect organic aerosol formation and growth pathways (Glicker et al., 2019; Sá et al., 2019). Disentangling these interacting influences requires a detailed understanding of aerosol chemical composition across particle sizes. Given the immense chemical complexity of organic aerosol, encompassing thousands of compounds with diverse functionalities, polarities, and volatilities (Goldstein & Galbally, 2007), bulk measurements alone are insufficient to resolve the processes governing particle formation and evolution.

Many of the compounds most relevant for nucleation and early particle growth occur at ultra-trace concentrations and differ only subtly in elemental composition (Nozière et al., 2015b), rendering them inaccessible to low-resolution approaches. High-resolution mass spectrometry (HR-MS), which offers high mass accuracy and resolving power, is therefore essential for discriminating isobaric and near-isobaric species (Burgay et al., 2023; Nozière et al., 2015b; Xie & Laskin, 2024). When combined with soft ionization techniques such as electrospray ionization (ESI), HR-MS enables a molecular-level characterization of organic aerosol (Hildmann & Hoffmann, 2024; Nizkorodov et al., 2011). Furthermore, size-resolved aerosol sampling is a prerequisite for disentangling the processes governing particle formation, growth, and atmospheric aging. Particle size directly reflects the dominant physical and chemical processes acting on aerosols, ranging from nucleation and early growth in the ultrafine size range to condensational growth, cloud processing, and long-range transport in larger particles. Because aerosol chemical composition varies systematically with particle size, bulk measurements obscure size-dependent molecular signatures and prevent the attribution of specific compounds to distinct formation pathways or source processes. Therefore, combining molecular-level characterization with particle-size-dependent analysis is essential to address these questions.

In this study, targeted liquid chromatography–high-resolution mass spectrometry (LC-HR-MS) analyses were applied to size-resolved aerosol samples collected at the Amazon Tall Tower Observatory (ATTO) during different seasons. The objective of this study is to characterize the molecular composition of organic aerosols as a function of particle size, altitude, and seasonal conditions, and to quantify the relative contributions of different atmospheric sources and processes. This size- and molecularly resolved perspective aims to fill key knowledge gaps in our understanding of aerosol chemistry in the tropical rainforest and to provide an improved basis for representing aerosol–cloud–climate interactions in atmospheric and climate models, particularly for an ecosystem that is both globally significant and undergoing rapid change.

4.3 Experimental section

4.3.1 Terminology

For the population of submicron particles from the Amazon region with multimodal size distribution, the widely accepted terms Aitken mode (50–100 nm) and accumulation mode (100–1000 nm) are used (Machado et al., 2021; Pöhlker et al., 2016). Since the particles

analyzed here, with a diameter less than 50 nm, have already undergone initial aging and growth to a diameter between 10 nm and 50 nm, the term “nucleation mode”, which usually refers to particles smaller than 25 nm, refers to an aerosol population relatively shortly after nucleation (Kulmala et al., 2012; Nieminen et al., 2018), could be misleading. Therefore, the term “sub-50 nm mode” is used for particles between 10 and 50 nm (Franco et al., 2021).

4.3.2 Aerosol sampling

Ambient size resolved aerosol samples were collected in the Amazon rainforest at the Amazon Tall Tower Observatory (ATTO). In total, five measurement campaigns were performed to investigate seasonal variations of OA composition. The sampling time covered the wet season 2022 (April/May 2022), the dry season 2022 (September/October 2022), the transition season 2022/23 (December 2022/January 2023), the wet season 2023 (April/May 2023) and the dry season 2023 (September/October 2023). The research site allows height-resolved measurements on a 325 m tall tower in the central Amazon basin (coordinates: 2°8.752' S 59°0.335' W) and is described in detail by (Andreae et al., 2015). Briefly, the nearest urban region is Manaus which is located approximately 150 km southwest of ATTO. The station is part of the Uatumã Sustainable Development Reserve (UDSR) and is reached via the roughly 12 km distant Uatumã river. The tower is located at about 120 m above sea level on a plateau that is embedded in a dense, non-flooded forest (terra firme) with adjacent floodplain forests and white-sand soil savannas (campinas) and forests (campinaranas). The area at ATTO is characterized by a canopy height of about 35 m. The meteorological conditions at ATTO depend on the location of the Intertropical Convergence Zone (ITCZ) providing clean and rainy circumstances from February until May and polluted and drier conditions from August to November with strong contributions from anthropogenic deforestation and land-use change (Pöhlker et al., 2019). Relevant meteorological parameters were constantly measured and are shown in the Supplement. The corresponding wind profiles and backward trajectories were generated by the HYSPLIT Trajectory Model (Rolph et al., 2017; Stein et al., 2015).

Two micro-orifice uniform deposit impactor samplers were connected to an aerosol inlet at 325 m (MSP, Model 122-R) and 60 m (MSP, Model 125-R) height at the tall tower (coordinates 2°08.756' S, 59° 00.335' W) to collect aerosol particles according to their aerodynamic diameter. Thirteen stages, equipped with pre-baked quartz filters (Whatman, QM-A), enabled sampling of particles covering diameters between 10 nm to 10 µm at a constant flow of 30 L min⁻¹ and 10 L min⁻¹, respectively. The actual flows were measured before each sampling period by using a TSI flow meter (model 4045) with a HEPA filter (PALL 12144, HEPA capsule filter) connected in between the flow meter and the inlet of the MOUDI. A critical Stokes number determines the cut-off diameter of each MOUDI stage and depends on the jet velocity in the impaction nozzles (Marple, Rubow, & Behm, 1991). As the nozzle geometry is fixed, the jet velocity is proportional to the volumetric flow rate f , and the 50% cut-off diameter scales with the inverse square root of the flow rate ($d_{50} \propto f^{-1/2}$). Therefore, deviations of the actual sampling flow from the nominal value led to a shift in the effective cut-off diameters of the MOUDI stages that was estimated by the following equation:

$$d_{50, \text{cor.}} = d_{50} \cdot \left(\frac{f_0}{f}\right) \quad \text{Equation 4.3-1}$$

where $d_{50, \text{cor.}}$ is the corrected 50 % cut-off diameter of a given MOUDI stage, d_{50} is the nominal cut-off diameter specified by the manufacturer for the nominal flow rate f_0 (10 L min⁻¹ and 30 L min⁻¹), and f is the actual volumetric flow rate during sampling. This relationship

follows from the dependence of the impaction cut-off on a constant critical Stokes number, implying $d_{50} \propto f^{-1/2}$.

Blank filters were collected according to the mentioned procedures but with a HEPA filter (PALL 12144, HEPA capsule filter) connected in between the aerosol inlet and the inlet of the MOUDI. In total, 16 MOUDI runs (eight at 60 m and 8 at 320 m height) from 2022 and 2023 were chosen to be analyzed according to their atmospheric conditions during the corresponding sampling periods. Sampling periods are shown in **Table S 11.2-1**.

4.3.3 Sample preparation and analysis

4.3.3.1 Chemicals

Levogluconan (>99 %) and *p*-hydroxybenzoic acid (99 %), hydroxymethylfurfural (98 %), were purchased from Acros Organics (Geel, Belgium). Acetonitrile (LC-MS grade), methanol (LC-MS grade), water (LC-MS grade), D(+)-arabitol (99 %) and D(-)-glutamine (98 %) were purchased from Fisher Scientific (Darmstadt, Germany). Ammonium acetate (98%), D/L-malic acid ($\geq 99.5\%$), and 2,6-dimethyl-4-nitrophenol (98 %) were purchased from Merck (Darmstadt, Germany). Salicylic acid (99%), camphorsulfonic acid (98%), *cis*-pinonic acid (98%), pimelic acid (96%), terebic acid, *cis,trans*-pinic acid, ammonium hydroxide solution (25 %), *meso*-erythritol (>99 %), mannitol ($\geq 98\%$), methanesulfonic acid (99 %), xylitol ($\geq 99\%$), fumaric acid ($\geq 99\%$), succinic acid ($\geq 99\%$), D/L-threitol (97 %), 4-hydroxybenzaldehyde ($\geq 97.5\%$), 3,4-dinitrophenol ($\geq 97\%$), 2-methyl-4-nitrophenol (97 %), and 2-C-methyl-D-erythritol ($\geq 90\%$) were purchased from Sigma-Aldrich (Steinheim, Germany). D/L-aspartic acid (98 %), D/L-glutamic acid (92 %) were purchased from TCI (Eschborn, Germany). 4-Nitrophenol (99 %) and 4-methyl-3-nitrophenol (98 %) was obtained from Alfa Aesar (Karlsruhe, Germany). Formic acid (LC-MS, 99 %) was delivered by VWR International GmbH (Darmstadt, Germany). Ultrapure water with 18.2 M Ω resistance was produced by a Milli-Q water system from Merck Millipore (Darmstadt, Germany). 3-Methyl-1,2,3-butanetricarboxylic acid, β -caryophyllinic acid, β -caryophyllonic acid, nocaryophyllonic acid and ((2*R*,3*S*)/(2*S*,3*R*)- and (2*S*,3*S*)/(2*R*,3*R*)-2,3,4-trihydroxy-3-methylbutyl sulfates (3-methyltetrol sulfate ester) were synthesized in-house according to Szmigielski et al., 2007b, van Eijck et al., 2013 and Bondy et al., 2018.

4.3.3.2 Filter extraction

A part of each filter sample (1/2) was extracted three times by adding 1.5 mL of a 9:1 (v:v) mixture of methanol and water (Fisher Scientific, Optima™ grade). The samples were subsequently agitated for 30 min on a laboratory shaker. The combined liquid phases were evaporated by a stream of N₂ (0.5 L min⁻¹) using a Turbopap LV (Biotage) to approximated to 100 μ L. The residue was then filled up to 0.2 mL with a 1:1 (v:v) mixture of water and acetonitrile (Fisher Scientific, Optima™ grade). The extracts were sonicated for 10 min and filtered through a 0.2 μ m PTFE syringe filter (Carl Roth, Rotilabo® KC 94.1). Five microliters of a 3500 ppb solution of campher-10-sulfonic acid (Sigma Aldrich, 98 %) in a 1:1 (v:v) mixture of water and acetonitrile (Fisher Scientific, Optima™ grade) were added as internal standard to correct the volume uncertainty.

4.3.3.3 UHPLC-HESI-HR-Orbitrap-MS analysis

Ten microliters of each sample were analyzed three times by ultra-high-performance liquid chromatography (UHPLC) (Thermo Fisher Scientific, UltiMate 3000) coupled to a high-

resolution Orbitrap mass spectrometer (MS) (Thermo Fisher Scientific, Q Exactive™). A heated ESI (HESI) source was installed and operated in the negative ionization mode. The instrument was externally calibrated with a calibration solution (Fisher Scientific, Pierce™) and a 2 mM sodium acetate aqueous solution providing mass accuracies below 1 ppm. The ESI probe was heated to 150 °C (HESI) to enhance solvent evaporation, the capillary temperature was set to 320 °C, sheath gas pressure to 60 psi, auxiliary gas pressure to 20 psi, and the spray voltage to –3.5 kV. The mass spectrometer was operated in full scan mode (m/z 80–500), with a mass resolution of 140,000. The UHPLC system was operated with an Acquity UPLC CSH Fluoro-Phenyl column (100x2.1 mm, 1.7 μ m) from Waters (Milford, USA), and the mobile phase A (water with 2 % acetonitrile and 0.04 % formic acid) and mobile phase B (acetonitrile with 2 % water). The conditions for gradient elution were as follows: 0 – 11 min 10 % B, 11 – 12 min linear increase to 99 % B, 12 – 12.5 min linear decrease to 10 % B, 12.5 – 13 min 10% B at a constant flow rate of 500 μ L min⁻¹. The column temperature was maintained at 30 °C. For highly polar compounds, the UHPLC system was operated with an iHILIC-Fusion(+) column (100 × 2.1 mm, 1.8 μ m) from HILICON AB (Umeå, Sweden), heated at 30 °C during separation. The injection volume was 10 μ L, and the flow rate was set to 0.4 mL/min. For HILIC separation a buffer solution of ammonium acetate (5 mM, pH 6.0) (A) and pure ACN (B) were used as the mobile phase with the following conditions for gradient elution: 0 - 0.5 min 97 % B, 0.5 - 12 min linear decrease to 50 % B, 12 - 14 min 50 % B, 14 - 14.5 min linear increase to 97 % and 14.5 - 22 min constant flow with 97 % B.. Additionally, to enhance ionization a post-column flow (PCF) of a methanolic NH₄OH (50 mM) solution was introduced by a T-piece between the column and the mass spectrometer with a constant flow rate of 0.1 mL/min. Data were recorded from 0 to 14 min, and the column was then re-equilibrated for 8 min to the starting conditions for the next run.

To ensure the identification of the different target analytes, fourteen-point calibration curves were generated with concentrations ranging from 0.5 ng mL⁻¹ to 500 ng mL⁻¹. All coefficients of determination were $R^2 \geq 95$ %. All reported values were normalized to the internal standard and field-blank-corrected. For the determination of the concentrations of mannitol, arabitol/xylitol, D-aspartic acid, D-glutamic acid, fumaric acid, D-(-)-glutamine, erythritol, threitol, pinonic acid, malic acid, levoglucosan, hydroxymethylfurfural, 2-C-M-D-erythritol and ((2*R*,3*S*)/(2*S*,3*R*)- and (2*S*,3*S*)/(2*R*,3*R*)-2,3,4-trihydroxy-3-methylbutyl sulfates, the results of the UHPLC measurements operated with the HLIC column were used, whereas the results of the reversed phase LC (RPLC) measurements operated with the PFP column were used.

The concentrations and the corresponding concentration uncertainties of the 32 individual compounds analyzed were calculated by the following equations:

$$c = 2 \cdot 0.2 \text{ mL} \left(\frac{\left(\frac{\overline{Area}_S}{\overline{Area}_{IS,S}} - \frac{\overline{Area}_{FB}}{\overline{Area}_{IS,FB}} \right) - b}{m} \right) \cdot \frac{1}{V_{MOUDI}} \quad \text{Equation 4.3-2}$$

$$\Delta c = 2 \cdot 0.2 \text{ mL} \cdot \frac{1}{V_{MOUDI}} \cdot \quad \text{Equation 4.3-3}$$

$$\sqrt{\left(\frac{\Delta \overline{Area}_S}{\overline{Area}_{IS,S} \cdot m} \right)^2 + \left(\frac{\Delta \overline{Area}_{FB}}{\overline{Area}_{IS,FB} \cdot m} \right)^2 + \left(\frac{\overline{Area}_S \cdot \Delta \overline{Area}_{IS,S}}{\overline{Area}_{IS,S}^2 \cdot m} \right)^2 + \left(\frac{\overline{Area}_{FB} \cdot \Delta \overline{Area}_{IS,FB}}{\overline{Area}_{IS,FB}^2 \cdot m} \right)^2 + \left(\frac{\overline{Area}_{FB} \cdot \Delta m}{\overline{Area}_{IS,FB} \cdot m^2} - \frac{\overline{Area}_S \cdot \Delta m}{\overline{Area}_{IS,S} \cdot m^2} + \frac{b \cdot \Delta m}{m^2} \right)^2 + \left(\frac{\Delta b}{m} \right)^2}$$

Where c is the concentration of the individual compound in [ng/m³] air, $\overline{Area}_S$ is the average of the areas of the integrated peak of the compound of interest in the sample vial S , $\overline{Area}_{FB}$ is the average of the areas of the integrated peak of the compound of interest in the field blank vial FB , $\overline{Area}_{IS,S}$ is the average of the areas of the integrated peak of the internal standard IS , campher-10-sulfonic acid, in the sample vial, $\overline{Area}_{IS,FB}$ is the average of the areas of the integrated peak of campher-10-sulfonic acid in the field blank vial and m and b are the slope and the intercept of the calibration curve of the compound of interest. The averages of the areas were calculated between the triple measurements of each sample and the individual MOUDI runs corresponding to one atmospheric case (2 runs for clean conditions, 3 runs for mixed conditions and 3 runs for polluted conditions) at the specific height (60 m or 320 m) and specific particle size (10 nm ≤; 18 nm ≤; 32nm ≤; 56 nm≤; 100 nm≤; 320 nm≤; 560 nm≤; 1000 nm≤; 3200 nm≤; 5600 nm≤; 10000 nm≤).

Furthermore, a correction for inlet transmission-related losses was applied. Therefore, mass concentrations of the individual compounds determined by filter sampling, UHPLC-ESI-HR-Orbitrap-MS analysis, and calculated with Equation 4.3-2, were multiplied with particle loss correction factors, shown in **Table S 11.2-4**. Concentration uncertainties were calculated using Gaussian error propagation.

Relative amounts were determined by dividing the amount of the individual compound on the individual filter by the calculated sum of the 32 compounds on the individual filter and averaged between the triple measurements of each sample and the individual MOUDI runs corresponding to one atmospheric case (2 runs for clean conditions, 3 runs for mixed conditions and 3 runs for polluted conditions) at the specific height (60 m or 320 m) and specific particle size. The uncertainty in the relative amounts was calculated using Gaussian error propagation.

4.3.4 Particle number size distributions

4.3.4.1 SMPS measurements

To choose the MOUDI runs to be analyzed for this study, meteorological conditions were systematically classified into representative atmospheric cases, and samples were chosen accordingly.

For this purpose, particle number size distributions (PNSDs) ranging from 10-300 nm were obtained from two scanning mobility particle sizers (SMPS) models 3080 and 3081 (TSI Inc., Shoreview, USA) using CPC, model 3772 (TSI Inc., Shoreview, USA) with an inlet located at 60 m and 320 m above ground. The detailed setup, methodology, and quality assurance are described elsewhere (Franco et al., 2021). Briefly, the 60 m inlet used to sample the aerosols is installed on an 80 m high tower (02°08.602' S, 59°00.033' W; 130 m a.s.l.), whereas the 320 m inlet used is installed on the tall tower (coordinates 2°08.756' S, 59° 00.335' W) at the ATTO site. The SMPS measurements cover the particle size range from 10 to 400 nm and yield a temporal resolution of 5 min. The SMPS data used in this study have been normalized to standard conditions (STP) and corrected for inlet transmission-related losses. Furthermore, a subsequent correction was implemented to mitigate artifacts in the small size range, particularly to reduce the unrealistically high particle counts observed at very small diameters.

The analysis of the MOUDI sample time intervals involved extracting SMSP data from the designated time windows and then performing a subsequent visual assessment. Periods

during which the device malfunctioned were meticulously documented and subsequently filtered out. All subsequent evaluations and calculations are based exclusively on the filtered SMPS data. For each designated measurement period, the median PNSD and the 10th and 90th percentiles were calculated. For each distinct case, the mean PNSD was calculated across all associated samples. Therefore, a uniform weighting method was implemented, regardless of missing values or duration.

4.3.4.2 OPS measurements

Particle number size distributions ranging from 300 to 10000 nm were obtained from an optical particle sizer (OPS, model 3330, TSI Inc. Shoreview, MN, USA) with an inlet located 60 m above ground. The detailed setup, methodology and quality assurance is described elsewhere (Moran-Zuloaga et al., 2018). Briefly, a 25 mm stainless steel inlet line with a total suspended matter (TSP) inlet head at 60 m a.g.l. and 30 m above canopy height, is installed on an 80 m high tower (02°08.602' S, 59°00.033' W; 130 m a.s.l.) at the ATTO site. The sampling intervals and thus the time resolution of the measurements were set to 5 min. The OPS data used in this study have been normalized to standard conditions (STP) and corrected for inlet transmission-related losses. OPS data were filtered to match the MOUDI sampling periods. The raw counts were converted into number concentrations per logarithmic particle diameter. Mass concentration was calculated by integrating logarithmically over the bin boundaries, assuming spherical particles with a density of 1 g/cm³. For each designated MOUDI run, the median PNSD and the 10th and 90th percentiles were calculated. Furthermore, the mean distribution per case was calculated across all associated samples, not as the mean of the medians.

4.3.5 Black carbon measurements

Furthermore, equivalent black carbon mass concentrations (eBC) were obtained from a Multi-Angle Absorption Photometer (MAAP, model 5012, Thermo Electron Group), which is part of the long-term aerosol monitoring program at the ATTO site (Pöhlker et al., 2018b; Saturno et al., 2018a). Black carbon equivalent concentrations were determined by default measuring the light absorption and converting it to eBC using the default mass absorption efficiency of 11.4 m²/g (637 nm) for wet season and 12.3 m²/g (637 nm) for dry season periods according to the findings of (Saturno et al., 2018b). The data were normalized to standard temperature and pressure (STP).

4.3.6 Estimation of total aerosol mass collected

To estimate the particle size-dependent significance of the selected molecular markers in relation to the total aerosol mass, the proportion of the 32 analyzed compounds in the total aerosol mass was estimated using OPS mass concentrations at 60 m shown in **Table S 11.2-2** and **Table S 11.2-3**. Only particle size ranges greater than 320 nm were considered for this purpose. For particles smaller than approximately 300 nm, particle mass concentrations derived from SMPS and OPS measurements are associated with large uncertainties. SMPS-based mass estimates rely on assumptions of spherical shape and constant effective density, which are often violated for sub-300 nm organic-rich particles, leading to substantial errors in number-to-mass conversion. In addition, uncertainties in charging efficiency and diffusion losses increase with decreasing size (Wiedensohler et al., 2012). OPS-derived mass is further limited by a low, composition-dependent light-scattering efficiency below 300 nm, resulting in poor sizing accuracy and a systematic low bias. Consequently, particle mass concentrations

derived from SMPS and OPS below 300 nm should be considered qualitative and are not directly comparable to filter-based chemical mass measurements.

OPS bin boundaries were first corrected for particle refractive index using the TSI AIM software. Refractive indices of $1.33 - 0.006i$ were applied for cases 1 and 2 (wet-season conditions; Franco et al., 2024), and $1.41 - 0.013i$ for Case 3 (biomass burning conditions; Guyon et al., 2003 Guyon). Following this correction, the optical particle diameter measured by the OPS was treated as equivalent to the particle's volume-equivalent (geometric) diameter.

Mass concentrations were calculated by logarithmic integration across bin boundaries, assuming spherical particles with densities $\rho = 1.47 \text{ g cm}^{-3}$. The optical particle diameter measured by the OPS was treated as equivalent to the volume-equivalent (geometric) diameter of the particles (Peters, Ott, & O'Shaughnessy, 2006). To ensure comparability with MOUDI measurements, the geometric diameters d_p were converted to aerodynamic diameters d_a using the following formula (Kulkarni, 2011):

$$d_a = d_p \cdot \sqrt{\frac{\rho_p}{\rho_0}} \quad \text{Equation 4.3-4}$$

where $\rho_0 = 1 \text{ g cm}^{-3}$ and $\rho_p = 1.47 \text{ g cm}^{-3}$, respectively. The mass concentrations within the size ranges corresponding to the MOUDI stages were determined using partial bin integration. Absolute masses for each time interval were obtained by multiplying by the MOUDI-sampled air volume per OPS time interval. Total mass over the entire measurement period is calculated by summing all time intervals.

Nevertheless, these calculations have limitations. OPS sizing is calibrated using polystyrene latex (PSL) spheres and applies refractive-index corrections that represent a bulk aerosol average. Particles with optical properties that differ from the refractive indices used for correction may therefore be mis-sized.

Comparisons with physical and aerodynamic sizing show that optical methods systematically overestimate particle size, particularly in the coarse mode, and produce broader size distributions. Additional uncertainties stem from assumptions of particle sphericity, constant density, and uniform refractive index, which can bias mass estimates and affect comparability with impactor-based measurements (Moran-Zuloaga et al., 2018).

Nevertheless, previous studies showed that the sampled aerosol mass using impactors and the calculated mass via OPS mass concentrations had comparable dimensions for the coarse mode fraction (Moran-Zuloaga et al., 2018).

4.4 Results and Discussion

4.4.1 Classification of different atmospheric conditions at ATTO

The meteorological conditions at ATTO depend on the location of the Intertropical Convergence Zone (ITCZ) providing clean and rainy circumstances from February until May and polluted and drier conditions from August to November with strong contributions from anthropogenic deforestation and land-use change (Pöhlker et al., 2019). The periods between December and January and between June and July represent transition seasons (Pöhlker et al., 2016). Within the respective seasons, individual meteorological events can occur, resulting

in more polluted conditions during the wet seasons or cleaner conditions during the dry seasons. The chemical composition of organic aerosols is subject to variation based on factors such as particle size and the specific season under consideration. The primary sources of aerosols can be categorized into two distinct categories: natural biogenic aerosols, which are prevalent during the wet seasons, and biomass burning aerosols, which are prominent during the dry seasons. Furthermore, from February to May, the ITCZ allows also transport of Saharan dust to the Amazon (Ben-Ami et al., 2010; Moran-Zuloaga et al., 2018) or urban pollution from Manaus, Belem, or Santarem with regional effects (Martin et al., 2010; Mouchel-Vallon et al., 2020). Recently, the long-range transport of biomass burning and volcanic emissions from Africa to the central Amazon has also been documented (Holanda et al., 2020; Saturno et al., 2018a).

For this study, samples obtained under analogous meteorological conditions were systematically classified into atmospheric cases. Three cases were identified: (1) clean conditions, (2) mixed conditions, and (3) polluted conditions. Aerosol sampling with the MOUDIs was conducted over several days to ensure sufficient aerosol mass at the lowest MOUDI stages, specifically for the smallest particles. Additionally, the two MOUDIs were running in parallel at heights of 320 m and 60 m at the tall tower. To differentiate between the various scenarios, the backward trajectories of the air masses arriving at ATTO during the collection period were mapped and examined using HYSPLITT (Stein et al., 2015). Furthermore, the particle number size distribution and concentration of the individual MOUDI runs and the black carbon (BC) concentration during the respective collection period were analyzed.

4.4.1.1 Case 1 – Clean conditions

The 11d backward trajectories of two MOUDI sampling runs, e.g., sub-case 1_1 and sub-case 1_2, (April 19-23, 2022, and May 16-20, 2023) showed that comparatively clean air masses with a prevailing wind direction from NE reached the ATTO site. The origin of the air masses was mainly in the Atlantic. Nevertheless, both sub-cases 1_1 and 1_2 were also influenced by air masses arriving from the West Sahara, where biomass burning and combustion activities have occurred, with a wind direction of E, and fires in the vicinity of the ATTO site (Figure S 11.2-1). Looking at the particle concentrations and particle size distribution of typical clean wet seasons at ATTO, these are characterized by low particle concentrations in the range of 100-400 $1/\text{cm}^3$ (Andreae et al., 2015). The selected MOUDI runs sub-case 1_1 and sub-case 1_2 met these criteria both at 60 m with particle concentrations between 50 $1/\text{cm}^3$ and 700 $1/\text{cm}^3$, as well as at 320 m with concentrations between 100 $1/\text{cm}^3$ and 700 $1/\text{cm}^3$ for particle sizes between 10 nm and 300 nm (Figure S 11.2-12 , Figure S 11.2-13). The particle concentrations of particles between 300 nm and 1 μm in size ranged between 1 $1/\text{cm}^3$ and 10 $1/\text{cm}^3$ (Figure S 11.2-4 , Figure S 11.2-5). In addition to low particle concentrations, the average BC mass concentrations were also low, with values between 0.003–0.008 $\mu\text{g m}^{-3}$ at 60 m and 0.013–0.016 $\mu\text{g m}^{-3}$ at 320 m (Table S 11.2-5). This is consistent with observations from previous studies (Stern et al., 2025; Valiati et al., 2025). Furthermore, previous studies have shown that particle size distributions (PNSD) exhibit a characteristic "wet season shape," which is characterized by a 3-modal shape with a pronounced Aitken mode at a maximum of ~ 70 nm, a separate accumulation mode with a maximum at ~ 150 nm, (Andreae et al., 2018; Varanda Rizzo et al., 2018); Varanda Rizzo et al., 2018) and a significant coarse mode. In Figure 4.4-1 , the number concentrations per logarithmic particle diameter are plotted against particle diameter. The PNSDs have the shape typical of clean wet seasons. This is the case

for both heights, with sub-case 1_1 at 320 m showing a greater contribution from aged aerosol. However, since both the low particle concentration and the low mean BCo concentration of $0.003 \mu\text{g m}^{-3}$ indicate clean conditions, sub-case 1_1 at 320 m was nevertheless considered representative of clean conditions and included in the further evaluation.

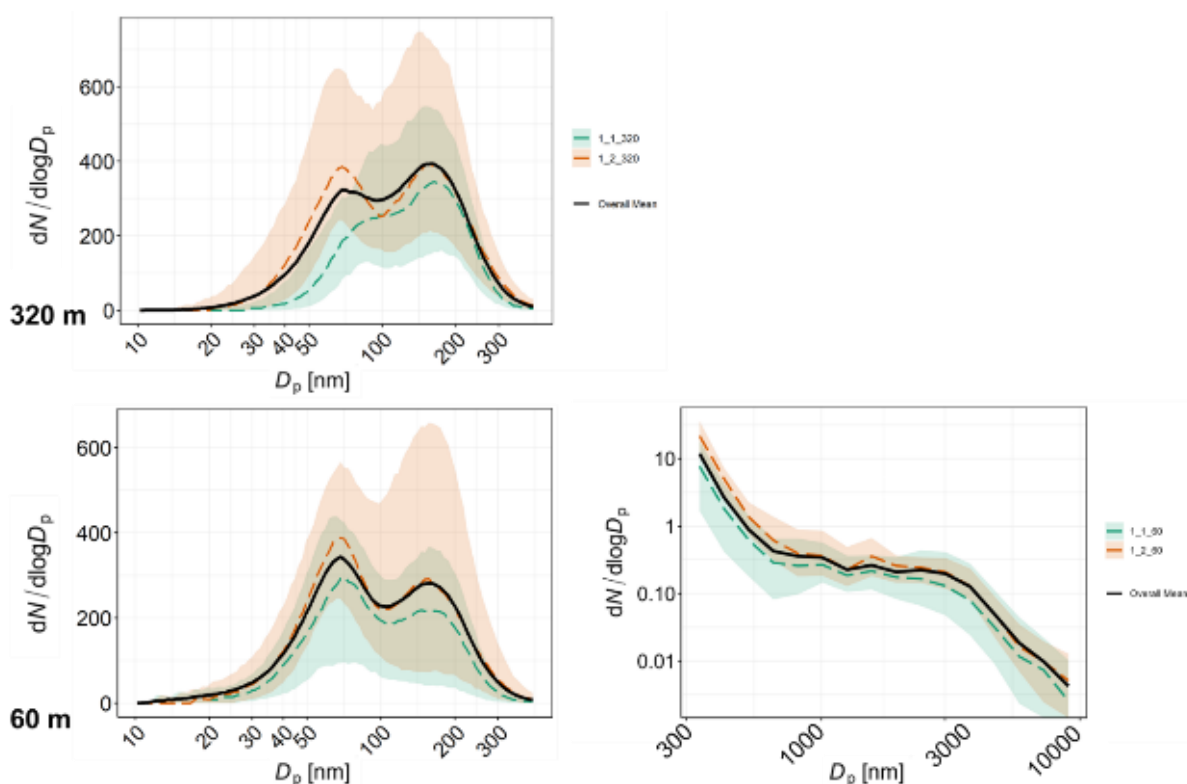


Figure 4.4-1: The median PNSD value in $dN/d\log D_p$ for each individual sub-case is shown as a colored dashed line (sub-case 1_1 and sub-case 1_2), with the percentile bands (p10–p90) shown as a band. The solid black line represents the mean distribution per case (case 1), which was calculated across all associated samples and not as the mean of the medians. The median PNSD value for particle sizes in the range from 10 nm to 300 nm was determined using SMPS data, while OPS data were used for particle sizes in the range from 300 nm to 10000 nm.

4.4.1.2 Case 2 – Mixed conditions

The 11d backward trajectories of three MOUDI sampling runs, e.g., sub-case 2_1, sub-case 2_2, and sub-case 2_3 (May 21, 2022–May 24, 2022, December 8, 2022–December 12, 2022, and May 11, 2023–May 15, 2023) show mixed air mass origins (Figure S 11.2-2). Sub-case 2_1 has a prevailing wind direction of S, whereas sub-cases 2_2 and 2_3 have two prevailing wind directions, namely NE and SE. In all three sub-cases, the air masses not only pass over the Atlantic Ocean but also over urban regions and regions with frequent fire activities. The air masses of sub-case 2_2 also pass over the Sahel savanna region with strongly enhanced fire activities. Sub-case 2_1 also passes through urban regions such as Belém, Santarém, and Manaus. Particle concentrations range from 200–1500 $1/\text{cm}^3$ to 150–2500 $1/\text{cm}^3$ for particle sizes between 10 nm and 300 nm at heights of 60 m and 320 m (Figure S 11.2-14, Figure S 11.2-15, Figure S 11.2-16) and between 1–30 $1/\text{cm}^3$ for particle sizes between 300 nm and 1 μm at a height of 60 m (Figure S 11.2-6, Figure S 11.2-7, Figure S 11.2-8). The average black carbon concentrations range between 0.021 $\mu\text{g m}^{-3}$ and 0.135 $\mu\text{g m}^{-3}$ at a height of 60 m and between 0.026 $\mu\text{g m}^{-3}$ and 0.130 $\mu\text{g m}^{-3}$ at 320 m (Table S 11.2-5). Sub-case 2_3 has the lowest BC concentration, which corresponds to the air mass origin based on the HYSPLIT backward trajectories, namely a predominantly NE wind direction and no passage through

large urban regions (Valiati et al., 2025). Regarding PSND, previous studies have shown significant changes when long-range-transported aerosols are present, regardless of season. Typically, particle concentrations in the accumulation mode and coarse mode are significantly increased. The Aitken mode can be viewed only as a shoulder of the accumulation mode (Andreae et al., 2015). This also corresponds with our observations (Figure 4.4-2). In addition to the Aitken and accumulation modes, the coarse mode is also strongly pronounced, with a maximum at 3000 nm. The PSNDs of all three sub-cases are comparable at both altitudes. However, the sub-cases differ significantly in particle concentration (sub-case 2_1 has more than three times the particle concentration in accumulation mode than sub-case 2_3). However, since the mean black carbon concentration of sub-case 2_3 is significantly higher than that of the clean (case 1) MOUDI runs, it is assigned to the mixed conditions in the following discussion.

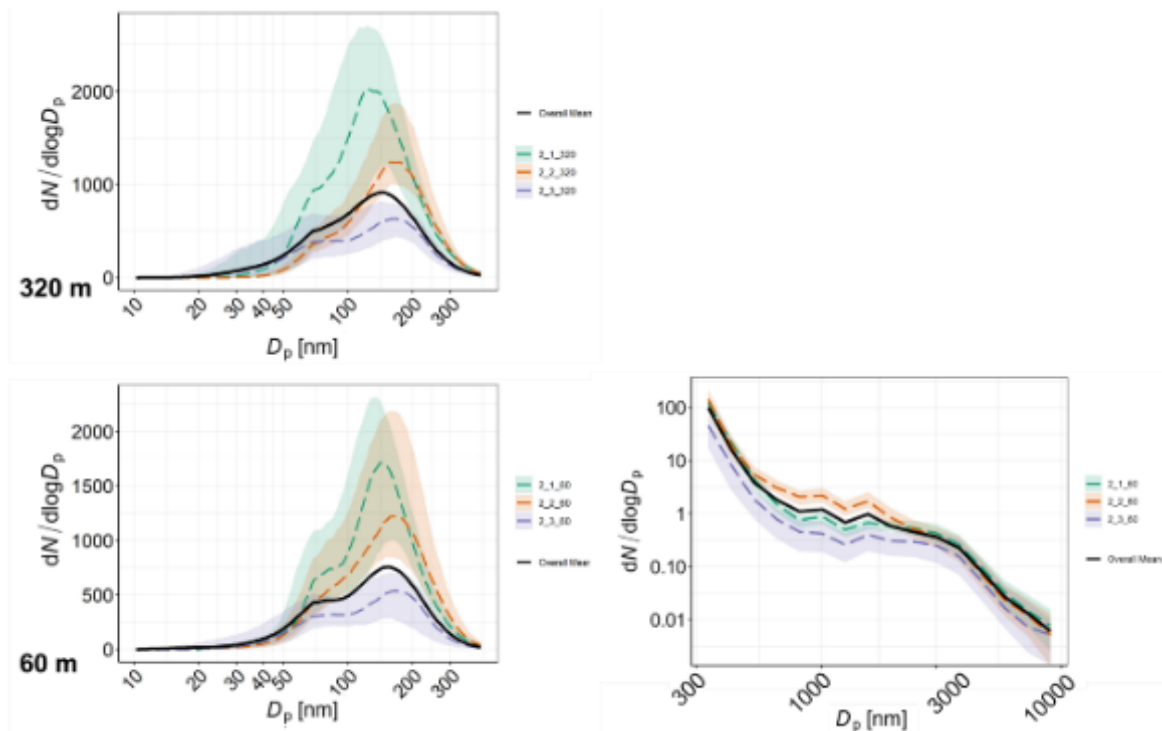


Figure 4.4-2: The median PSND value in $dN/d\log D_p$ for each individual sub-case is shown as a colored dashed line (sub-case 2_1, sub-case 2_2, and sub-case 2_3), with the percentile bands (p10–p90) shown as a band. The solid black line represents the mean distribution per case (case 2), which was calculated across all associated samples and not as the mean of the medians. The median PSND value for particle sizes in the range from 10 nm to 300 nm was determined using SMPS data, while OPS data were used for particle sizes in the range from 300 nm to 10000 nm.

4.4.1.3 Case 3 – Polluted conditions

The 11d backward trajectories of three MOUDI sampling runs, e.g., sub-case 3_1, sub-case 3_2, and sub-case 3_3 (September 24, 2022–September 27, 2022, October 1, 2022–October 4, 2022, and September 30, 2023–October 2, 2023) show air mass origins from E and SE (Figure S 11.2-3). The air masses passed through large urban regions such as Belem, Santarem, and Manaus, as well as the Sahel savanna region and the Western Sahara, with strongly enhanced biomass burning and combustion activities.

Particle concentrations range between 500-12,000 $1/\text{cm}^3$ and 1000-8000 $1/\text{cm}^3$ for particle sizes between 10 nm and 300 nm at heights of 60 m and 320 m (Figure S 11.2-17 ,Figure S 11.2-18 ,Figure S 11.2-19) and between 10-500 $1/\text{cm}^3$ for particle sizes between 300 nm and 1 μm at a height of 60 m (Figure S 11.2-9 ,Figure S 11.2-10 ,Figure S 11.2-11). Typical particle concentrations in the dry season are between 500 and 2000 $1/\text{cm}^3$ (Andreae et al., 2015), which shows that heavily polluted conditions are considered in case 3. The average black carbon concentrations range between 0.264 $\mu\text{g m}^{-3}$ and 1.067 $\mu\text{g m}^{-3}$ at an altitude of 60 m and between 0.307 $\mu\text{g m}^{-3}$ and 0.897 $\mu\text{g m}^{-3}$ at 320 m (Table S 11.2-5), and are thus significantly elevated, indicating an influence of biomass burning and combustion processes, corresponding to typical dry season values at ATTO (Holanda et al., 2020; Holanda et al., 2023; Saturno et al., 2018a; Valiati et al., 2025) . The PSND shows a clear difference from the previous cases 1 and 2. The Aitken mode was completely “swallowed up” by the sharply increased accumulation mode (Figure 4.4-3). The particle concentrations in the accumulation mode maximum differ significantly between the individual sub-cases. Sub-case 3_3 has the highest concentration at approximately 7500 $1/\text{cm}^3$, whereas the maximum of sub-case 3_2 is 1500 $1/\text{cm}^3$ at a height of 60 m. In addition, the coarse mode in all three sub-cases has a mean particle concentration that is almost one order of magnitude higher, and there is no significant difference in particle concentration between them. The coarse mode peak at 3000 nm is pronounced in all three cases 1, 2, and 3, with a significantly higher frequency in the dry season, accounting for a large proportion of the aerosol mass. In the absence of long-range transported aerosols, primary biogenic aerosol particles are assumed to be the dominant coarse mode source (Després et al., 2022; Pöschl et al., 2010).

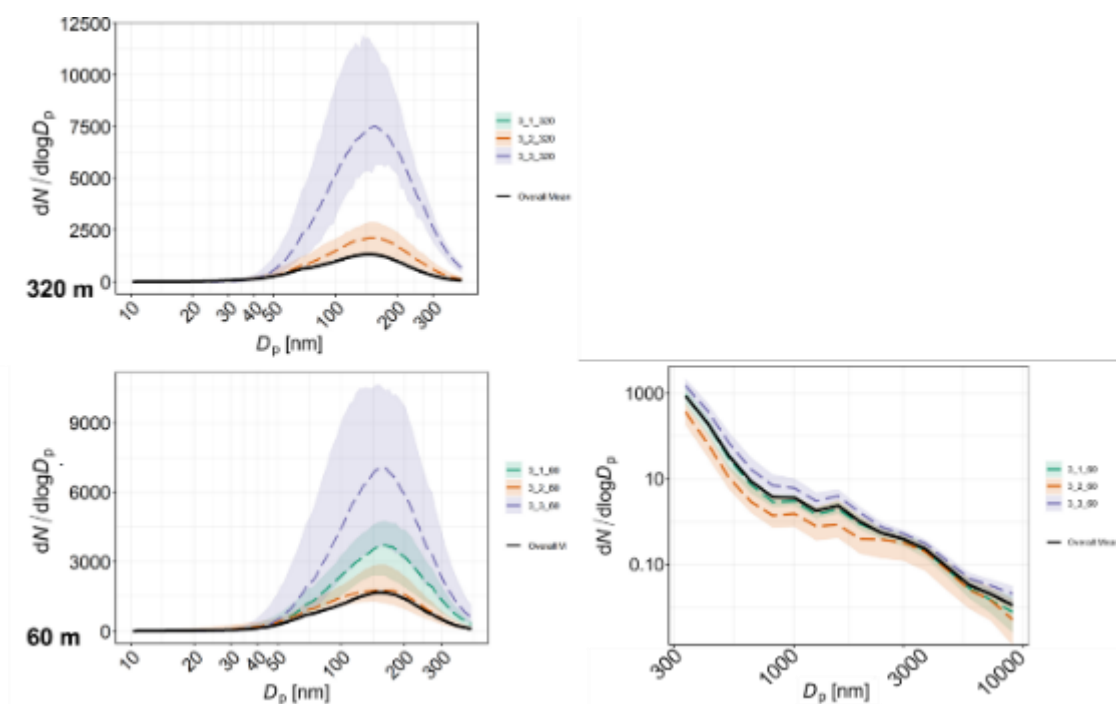


Figure 4.4-3: The median PNSD value in $dN/d\log D_p$ for each individual sub-case is shown as a colored dashed line (sub-case 3_1, sub-case 3_2, and sub-case 3_3), with the percentile bands (p10–p90) shown as a band. The solid black line represents the mean distribution per case (case 3), which was calculated across all associated samples and not as the mean of the medians. The median PNSD value for particle sizes in the range from 10 nm to 300 nm was determined using SMPS data, while OPS data was used for particle sizes in the range from 300 nm to 10000 nm. Sub-case 3_1 could not be taken into account at 320 m because the SMPS system malfunctioned.

4.4.2 Size- and height-resolved molecular patterns of different OA marker species

Mass spectrometric analyses of molecular marker compounds are a valuable tool for studying primary and secondary organic aerosols. These analyses have demonstrated significant utility in investigating atmospheric processes. The marker substances are selected based on their relevance to atmospheric chemistry or their uniqueness and studied in a targeted approach. Their quantification provides information on their contribution to the actual aerosol mass, if an authentic standard is available. In this study, 32 marker compounds were analyzed and evaluated. To obtain representative relative contributions for clean, mixed, and polluted atmospheric conditions in the Amazon region, the individual compounds were quantified per MOUDI stage and sampling height across all eight sub-cases (1_1; 1_2; 2_1; 2_2; 2_3; 3_1; 3_2; 3_3), then averaged. The relative contribution was determined based on aerosol mass, calculated as the sum of the 32 compounds. A graphical representation of the relative contributions is shown in Figure 1.4-- 4. The relative contributions of the 32 compounds to the total aerosol mass collected are estimated from OPS data and shown in Figure 1.4-- 5. Furthermore, the mean concentration of the individual compounds in PM_{10} , PM_1 , and $PM_{0.056}$ was determined for each atmospheric case. For the latter, the absolute concentrations were averaged across the sub-cases for each particle size range and corrected for particle loss during sampling. The results are shown in Table 4.4-1.

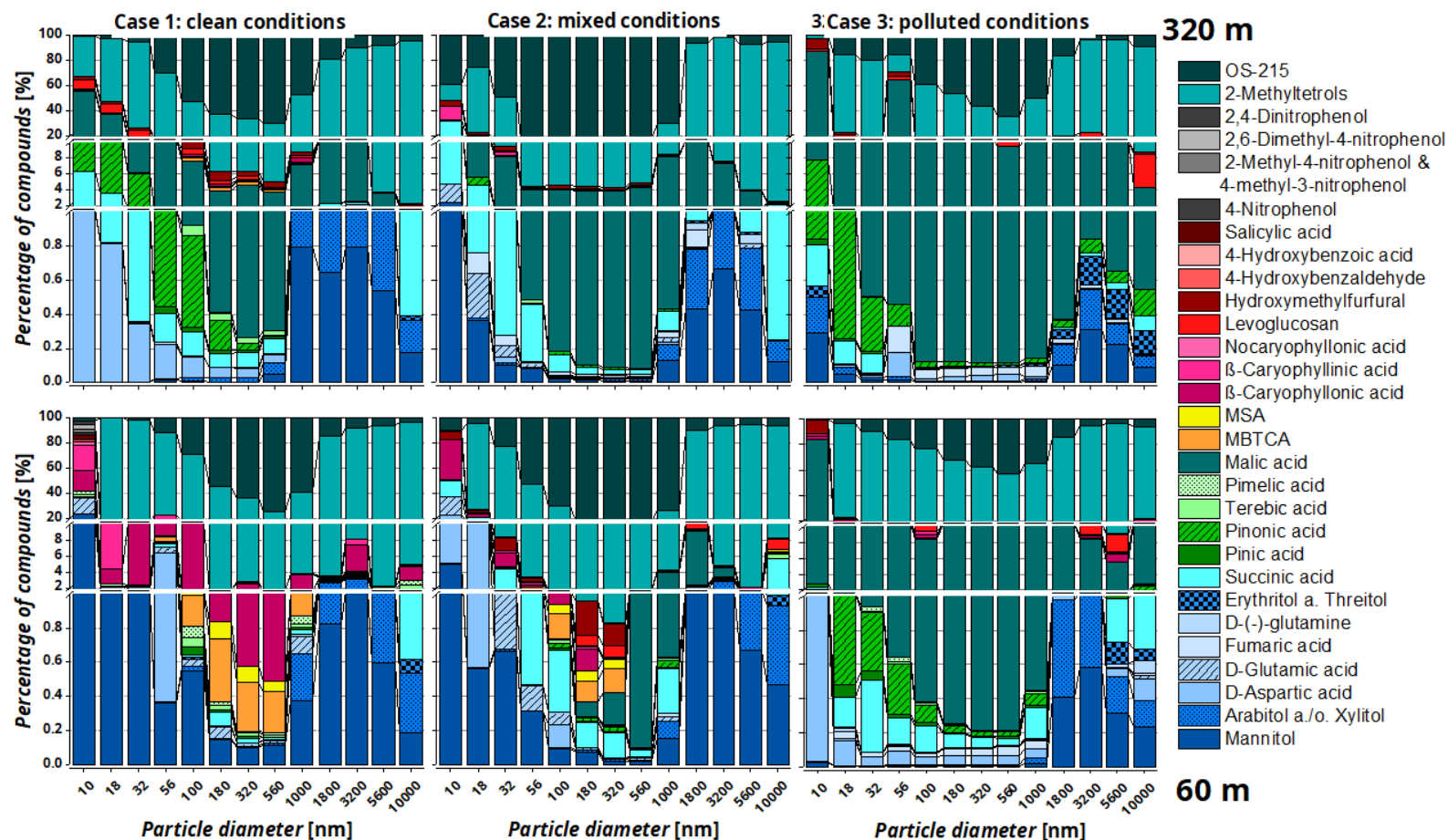


Figure 4.4-4: Relative amounts of 32 selected molecular marker species determined with RPLC and HILIC-ESI-HR-Orbitrap-MS. All values are field blank corrected. 100 % correspond to the sum of the 32 quantified compounds. An estimate of the contribution to the total aerosol mass is shown in Figure 1.4-- 5. OS-215 corresponds to the sum of six isomers quantified with the response factor of an isomeric mixture of 3-methyltetrol sulfate ester (Figure S 11.2-20). Arabitol/xylitol and erythritol/threitol co-eluted and therefore can represent both regioisomers. 2-methyl-4-nitrophenol and 4-methyl-3-nitrophenol could not be baseline separated and, therefore, are addressed as a sum concentration. It should be noted that case 1 at 60 m was contaminated by diesel combustion plumes by the ATTO site, and anthropogenic marker species should not be considered as a real atmospheric event (see discussion).

4.4.2.1 Isoprene oxidation products

The Amazon rainforest is the world's largest source of atmospheric isoprene emissions. Under conditions of low nitrogen monoxide (NO) content, isoprene reacts rapidly with hydroxyl radicals ($\text{OH}^\bullet$) to form isoprene-derived peroxy radicals ($\text{ISOPOO}^\bullet$), which subsequently react with the hydroperoxyl radical ($\text{HO}_2^\bullet$) to form isoprene epoxydiols (IEPOX). The semi-volatile IEPOX compounds are efficient precursors for the formation of SOA (Langford et al., 2022). IEPOX can be hydrolyzed with water under slightly acidic conditions and react to form 2-methyltetrols or react further with sulfuric acid to form isoprene organosulfates (Claeys & Maenhaut, 2021). 2-Methyltetrols are a molecular marker for isoprene oxidation products from $\text{OH}^\bullet$ chemistry under low NO concentrations (Clements & Seinfeld, 2007; Surratt et al., 2006c; Surratt et al., 2010). They occur in two diastereomers, namely 2-methyl-erythritol and 2-methyl-threitol, each with two enantiomers, namely (2R,3R)-2-methylthreitol and (2S,3S)-2-methylthreitol, as well as (2S,3R)-2-methyl-erythritol and (2R,3S)-2-methyl-erythritol. Authentic standards are required for accurate quantification, but are only available for a few isoprene OA markers. In this study, the response factor of 2D-2C-methylerythritol and HILIC chromatography was employed to quantify the sum of all four isomers. Consequently, the values displayed herein correspond to the sum concentration of all four isomers. As illustrated in Figure 1.4-5, 2-methyltetrols show a trimodal distribution, evident in both height and all three cases. Nevertheless, semitargeted quantifications have been performed in the extant literature using the response factors of threitol and erythritol (Claeys et al., 2010a; Clements & Seinfeld, 2007), which is likely to have led to a significant underestimation of the concentrations. In this study, the response factors of the mixture of threitol and erythritol ($m = (0.00159 \pm 0.00005) \text{ mL ng}^{-1}$; $b = 0.001 \pm 0.002$; $R^2 = 0.996$) differed from those of 2D-2C-methylerythritol ($m = (0.000042 \pm 0.000003) \text{ mL ng}^{-1}$; $b = 105 \pm 55$; $R^2 = 0.987$) by 97 %, resulting in a change in concentration of two orders of magnitude. The sum of the areas of erythritol and threitol was considered in this study, as these could not be separated at the baseline either.

2-methyltetrols show a trimodal distribution in all three cases considered and at both heights (**Figure 4.4-4**). This trimodal structure suggests distinct formation mechanisms: condensation of freshly formed SOA in the Aitken mode, growth through multiphase reactions in the accumulation mode, and potential primary contributions in the coarse mode. It is noteworthy that 2-methyltetrols also contribute substantially to sub-50 nm particles (case 1 60 m 18 nm: 11.39 %; case 2 60 m 18 nm: 2.36 %; case 3 60 m 18 nm: 8.57 %). Contrary to the prevailing hypothesis that isoprene oxidation products inhibit the formation of new particles, this study's results demonstrate an opposing trend. Machado et al., 2024 demonstrated that precipitation consistently results in nanoparticle bursts within the nucleation size range in the Amazon rainforest. This phenomenon could be attributed to the washout of larger particles induced by precipitation, which subsequently reduces the condensation sink. Additionally, ozone injection into the forest canopy has been observed to increase the oxidation of biogenic VOCs, particularly terpenes, thereby promoting the formation of new particles. The authors found that isoprene concentration decreased significantly as ozone levels in the forest canopy increased. In this study, the mean total precipitation in a 10 km radius was 126 ± 34 mm for case 1, 21 ± 25 mm for case 2, and 42 ± 71 mm for case 3 (emerge data processed with Earth Engine), which substantiates the indicated dependency of 2-methyltetrol contribution to sub-50 nm particles on the amount of rain.

2-methyltetrols show a maximum relative contribution in the accumulation mode, which is consistent with IEPOX-driven reactive uptake onto pre-existing acidic particles. However, they

contribute significantly to the coarse-mode aerosol mass, suggesting a possible primary source of 2-methyltetrols. A study by González et al., 2014 investigated the stereoisomers of 2-methylerythritol and 2-methylthreitol in the Amazon rainforest using chiral gas chromatography-mass spectrometry (GC-MS) analysis. The study demonstrated that both diastereomers exhibited enantiomeric excesses of 60-72% in a subset of samples. This enantiomeric excess corresponded to compounds of entirely biological origin. Subsequent analyses revealed that racemic fractions of 2-methyl-erythritol and 2-methyl-threitol, representing both enantiomers in a 1:1 ratio, were also of biological origin. This finding led to the conclusion that a fraction of 2-methyltetrols from primary aerosol sources accounted for 69% of PM₁₀. The implementation of chiral, size-selective analyses could facilitate the estimation of the influence of primary emissions in fine particles.

In recent years, the field of atmospheric science has seen a marked increase in attention to organosulfates (OS). This trend is evidenced by an increase in studies reporting the presence of various OS species in ambient aerosols (Brüggemann et al., 2020b). Organosulfates, especially isoprene epoxydiol organosulfate ester (IEPOX-OS), have been shown to account for a significant proportion of the chemical diversity of organic aerosols in the Amazon basin (Kourtchev et al., 2016b; Leppla et al., 2025). The present study examined methyltetrol sulfate esters ($MW\ 216$, $[M-H]^- = m/z\ 215$), which will henceforth be abbreviated as OS-215. These compounds can be formed under low-NO_x conditions via the IEPOX reaction pathway, via acid hydrolysis and subsequent reaction with the sulfate anion, SO₄²⁻ (Surratt et al., 2010). Sulfate concentrations during the wet seasons are primarily attributed to biogenic and marine sources (Andreae et al., 2015), whereas elevated levels during dry seasons are associated with combustion activities (Pöhlker et al., 2018a). Sulfur compounds can also be emitted from soils, with higher emissions occurring at higher soil moisture (Pugliese et al., 2023), resulting in a significant organic sulfur source from the forest itself. These findings indicate that IEPOX-OS are pertinent SOA compounds irrespective of the prevailing season, thereby corroborating the concept of a combination of anthropogenic and biogenic sources. Methyltetrol sulfate esters occur as a complex mixture of isomers resulting from four stereoisomeric 2-methyltetrol backbones (two diastereomers, each with two enantiomers) and two possible regioisomers corresponding to sulfation at one of the two terminal hydroxyl groups, resulting in a total of eight isomeric forms. In conventional reverse-phase LC, these isomers cannot be completely resolved and typically elute as a few composite peaks. The application of HILIC separation has been demonstrated to enhance the resolution of regio- and diastereomeric forms (Cui et al., 2018a). However, it should be noted that enantiomeric separation remains unattainable without using chiral stationary phases. Consequently, quantitative analyses are generally based on the summed signal of all methyltetrol sulfate esters. Recently, Cui et al., 2018a achieved the characterization of OS-215 derived from the sulfation of IEPOX, separating their six possible isomeric forms, i.e., three positional isomers, each occurring as diastereomeric pairs. Furthermore, the developed HILIC method enabled the simultaneous analysis of 2-methyltetrols. The findings revealed that conventional GC/EI-MS analyses overestimated 2-methyltetrols by up to 188%, a phenomenon partly attributable to the degradation of methyltetrol-organosulfates. In recent years, semiquantitative methods have been employed to quantify OS-215 by utilizing the response factors of camphorsulfonic acid (Kristensen & Glasius, 2011), methanesulfonic acid, octyl sulfates (Brüggemann et al., 2019), or butadiene dihydroxy epoxide (BEPOX) (Worton et al., 2011). However, earlier studies have already demonstrated that the absolute concentrations of OS-215 were underestimated by a factor of 5 to 10 compared to determinations using OS from BEPOX, which is structurally related to OS-215 (Worton et al., 2011). Nevertheless, semi-quantitative methods for the determination

of organosulfates can provide important information on variation in levels and time trends and remain useful for marker-based source apportionment. Nevertheless, recent progress has facilitated the generation of authentic standards of OS-215 (Bondy et al., 2018). Here, HILIC separation with the response factor of the in-house synthesized OS-215 standard 3-methyltetrol sulfate ($m = (0.0090 \pm 0.0001) \text{ mL ng}^{-1}$, $b = -0.006 \pm 0.004$, $R^2 = 0.999$) was chosen to facilitate precise quantifications. The chromatographic separation of six isomers was achieved, and the sum of the signal areas for all six isomers was considered. A comparison of the response factor of the synthesized 3-methyltetrol sulfate esters with that of camphersulfonic acid ($m = (0.6907 \pm 0.0002) \text{ mL ng}^{-1}$, $b = 22.89 \pm 0.03$, $R^2 = 0.989$) indicated that 3-methyltetrol sulfate esters are underestimated by two orders of magnitude when semiquantitative methods are employed. In this experiment, 3-methyltetrol sulfate esters were synthesized according to Bondy et al. (2018). The reaction product was a mixture of isomers, with 3-methyltetrol sulfate esters as the predominant component. In addition, a mixture of isomers of 2-methyltetrol sulfate esters was observed to be a by-product (**Figure S 11.2-20**). For external calibration, the four signals obtained from the corresponding isomers of the synthesized standard were integrated to emulate the integration across six isomers in the authentic samples (**Figure S 11.2-20**). It is crucial to be aware that regioisomers and diastereoisomers can exhibit significantly different ionization efficiencies under ESI. Therefore, the values given here are only estimated. This can lead to both over- and underdetermination, since the ratios of isomers in the reference standard are different from those in the real samples.

As illustrated in **Figure 4.4-4**, an upward trend for OS-215 is evident in all three cases. At 320 m, the relative proportions for all particle size ranges are higher than at an altitude of 60 meters (i.e. case 1 at 60 m/ 320 m: 56 nm: 1.31 %/ 5.13 %; 560 nm: 22.54 %/ 27.28 %; 5600 nm: 0.035 %/ 0.056 %). Since OS-215 is a late isoprene oxidation product, this phenomenon could be explained by an increased frequency of aged or atmospherically processed aerosols at 320 meters. Recent studies also stated higher mass fractions for sulfates in PM₁ at 320 m underlining the results shown here (Valiati et al., 2025). Given the seasonal influence of OS-215 and 2-methyltetrols, it is essential to evaluate their ratio. The relative contribution of 2-methyltetrols in accumulation mode is lowest for mixed conditions and highest for polluted conditions (case 2 60 m/320 m: 320 nm: 8.23%/ 6.28%; case 3 60 m/320 m: 320 nm: 34.36%/ 28.85%), whereas the relative contribution of OS-215 in accumulation mode is highest for mixed conditions and lowest for polluted conditions (case 2 60 m/320 m: 320 nm: 46.50%/ 53.11%; case 3 60 m/320 m: 320 nm: 27.34%/ 52.98%). This phenomenon can be attributed to competitive reactions at elevated NO concentrations. At high NO levels, isoprenitroxyorganosulfates rather than pure isoprenorganosulfates can be formed. Isoprene SOA-related nitrooxy organosulfates (NOS) have been detected in smog chamber experiments in the presence of NO_x and in ambient PM (Gómez-González et al., 2008; Nestorowicz et al., 2018; Surratt et al., 2008). It has been proposed that the formation of these nitrooxy organosulfates is associated with the gas-phase nitration of isoprene followed by particle-phase sulfation (Surratt et al., 2008). In the presence of elevated NO concentrations within the particle phase, various reaction products have been observed to compete with OS-215. These include 2-methylglyceric acid (2-MG) and its organosulfates and organonitrates (particle phase), which are formed via methacrolein (MACR), methacryloyl peroxyxynitrate (MPAN), and methacrylic acid epoxide (MAE) (gas phase) (Lin et al., 2013). This seasonal trend is confirmed by the findings of Leppla et al. (2025), which showed a significant increase in CHONS compounds during dry seasons compared to wet seasons (Leppla et al., 2025). The maximum relative contributions of OS-215 under mixed conditions in accumulation mode

can also be explained chemically. In comparison with clean conditions, elevated levels of SO₂ resulting from the long-distance transport of anthropogenic emissions have the potential to reach the ATTO site. A recent study by Valiati et al., 2025 also showed that the mass fraction of sulfates in PM₁ is the highest at wet seasons influenced by long-range transport, which are comparable conditions to the mixed conditions shown here. This increase in SO₂ has been shown to stimulate the formation of SOA from isoprene (Glasius et al., 2018). Consequently, IEPOX can react with these same seeds to form isoprene OS. However, due to the low NO concentrations, there are fewer competing reactions to form isoprene NOS.

4.4.2.2 Monoterpene oxidation products

Monoterpenes are the most abundant biogenic hydrocarbons in the troposphere, and these compounds affect the oxidising capacity of the atmosphere (Kanakidou, Tsigaridis, Dentener, & Crutzen, 2000). Even if isoprene is the major biogenic BVOC in the Amazon, previous studies showed that the monoterpene oxidation product concentrations in the central Amazonian Basin are even in close agreement with the concentrations measured during summertime in the Boreal forest, where the pinene skeleton (α - and β -pinene) is the most abundant monoterpene (Andreae et al., 2015; Vestenius et al., 2014). α -pinene reacts rapidly with ozone (O₃), nitrate radicals (NO₃[•]) and hydroxyl radicals ([•]OH), with significant first-generation products including pinonaldehyde. Pinonaldehyde contains carbonyl groups, and is highly reactive toward [•]OH and NO₃[•] radicals, leading to the formation of second-generation products such as the carboxylic acids pinonic acid, pinic acid (Kahnt et al., 2014; Yasmeen et al., 2011) and third-generation products such as 3-methyl-1,2,3-butanetricarboxyl acid (MBTCA) (Witkowski et al., 2023), as well as lactone-ring-containing compounds like terebic acid (Florou et al., 2024; Sato et al., 2016). A marker that has received particular attention is 3-methyl-1,2,3-butanetricarboxylic acid, which is established as a suitable marker for aged α -pinene SOA. MBTCA is formed by successive generations of gas-phase and particle-phase oxidation of α -pinene (Müller et al., 2012; Szmigielski et al., 2007a). Its formation involves reactions with [•]OH and ozone, followed by further functionalization and fragmentation in the particle phase, and therefore requires multiple oxidation steps. Consequently, MBTCA is generally interpreted as a molecular marker for enhanced oxidative aging of biogenic SOA rather than for fresh aerosol formation.

Pinic acid, pinonic acid, and terebic acid show their highest relative contribution at sub-50 nm particles in case 1 and case 3, with the highest relative contribution of 2.50% pinonic acid at ≤ 32 nm particles at 320 m at clean conditions. The seasonality trend is in alignment with 2-methyltetrols in sub-50 nm particles. This could be explained with the precipitation rates that were the highest for cases 1 and 3 (126 $\pm$ 34 mm for case 1, 21 $\pm$ 25 mm for case 2, and 42 $\pm$ 71 mm for case 3 (emerge data processed with Earth Engine), correlating with ozone injections into the forest canopy leading to NPF due to terpene oxidation as stated from Machado et al. 2024. Furthermore, elevated relative contributions of pinonic acid ($\sim$ 0.02-0.04) % and smaller but pronounced concentrations of pinic acid are observed in the coarse mode at both heights in case 3. The coarse-mode distribution of pinonic and pinic acids may be related to the condensation of organic species from the gas phase on the surface of preexisting atmospheric aerosol particles, since these species are semivolatile and can exist at considerable concentration levels in the gas phase (Feltracco et al., 2018; Kavouras & Stephanou, 2002; Pöhlker et al., 2012; Wang, Bi, Sheng, & Fu, 2009; Zangrando et al., 2013). The size distribution profile reported for pinonic acid in the present study shows that this compound may present some contributions to the Aitken mode and sub-50 nm mode. As

proposed by Feltracco et al. (2018), pinonic acid can undergo photo-oxidation processes in nucleation mode, causing the formation of pinic acid that leads to the growth of aerosols, which could also explain the presence of pinic acid in coarse mode during the warm period (Amarandei, Olariu, & Arsene, 2023). MBTCA shows the highest relative contributions in the accumulation modes. Interestingly, the highest contributions are found in clean periods and the lowest ones in the polluted periods (accumulation mode 60 m/320 m: 1.39 %/0.79 % case 1; 0.45 %/ 0.50 % case 2; 0.31 %/0.01 % case 3). Studies showed that the SOA yield of monoterpenes decreases with increased NO_x concentrations (Ng et al., 2007). Under low-NO_x conditions, RO₂ autoxidation and peroxy radical self-reactions favour the formation of highly functionalized low-volatility products, thereby promoting MBTCA formation. In contrast, elevated NO_x shifts the dominant reaction pathway toward RO₂ + NO, enhancing the formation of organonitrates and fragmentation products and limiting further functionalization (Pullinen et al., 2020). Consequently, high-NO_x conditions are expected to suppress MBTCA production relative to low-NO_x environments, consistent with the reduced abundance of highly oxidized SOA components reported in chamber and field studies. This behaviour highlights the potential of MBTCA as an indicator of oxidative aging under biogenically dominated, low-NO_x regimes rather than as a universal tracer for α -pinene SOA.

4.4.2.3 Sesquiterpene oxidation products

In the last decade, studies showed that sesquiterpenes also play an important role in the formation of secondary organic aerosol (Hallquist et al., 2009). The total global sesquiterpene emission is estimated to be about 14.8 Tg per year (Henze et al., 2008) and they are emitted in large quantities by tropical vegetation such as the Amazon rainforest (Bourtsoukidis et al., 2018). Especially high temperatures seem to increase the emission (Duhl, Helmig, & Guenther, 2008; Hakola et al., 2006). β -Caryophyllene is found to be one of the most abundant sesquiterpenes in the atmosphere (Hakola et al., 2006; Helmig et al., 2007). Furthermore, sesquiterpenes show a high reactivity towards O₃ (Kesselmeier & Staudt, 1999; Shu & Atkinson, 1995) and produce especially low-volatile oxygenated products (Jaoui, Leungsakul, & Kamens, 2003; Lee et al., 2006; Nguyen et al., 2009). Sesquiterpene oxidation products, including β -caryophyllonic acid, β -caryophyllinic acid, and nocaryophyllonic acid, are established molecular markers for the formation of SOA from biogenic sesquiterpenes (van Eijck et al., 2013) and are formed by atmospheric oxidation of sesquiterpenes, predominantly β -caryophyllene, via $\cdot$ OH radicals, ozone, and nitrate- chemical reactions. Quantifying these sesquiterpene oxidation products has been challenging due to the limited availability of authentic chemical standards. Early studies often relied on semiquantitative calibrations using structurally related compounds or estimated response factors, which could lead to uncertainties in absolute concentrations (Jaoui et al., 2003). More recent work has used synthesized authentic standards, enabling more accurate quantification by HPLC-MS (van Eijck et al., 2013). Here, the corresponding authentic standards were synthesized, and an accurate, targeted quantification was applied.

The sesquiterpene OA analyzed here show unique trends in size, vertical distribution, and seasonality. They make up to ~45 % at 60 m in case 1, ~32 % in case 2 and ~5 % in case 3 for sub-18 nm particles. In the accumulation mode, they only reach relative contributions below 1 %, except in case 1 at 60 m, with ~11 %. In the coarse mode, concentrations are slightly higher than in the accumulation mode. At 320 m the sesquiterpene OA contributions are below 1 %. Sesquiterpene OA are highly nucleating compounds forming highly polar species via dimerization (Gao et al., 2022). Their reaction products are low-volatile, and other studies

observed sesquiterpene OA peaks in the fine mode (Kanellopoulos, Chrysoschou, Koukoulakis, & Bakeas, 2021). Therefore, their substantial contribution to the sub-50 nm aerosol mass can be expected. In contrast to the isoprene and monoterpene OA studied here, β -caryophyllonic acid, β -caryophyllinic acid, and nocaryophyllonic acid do not show a similar trend concerning seasonality and therefore do not seem to correlate with the precipitation amount. Nevertheless, it should be noted that these compounds are early generation oxidation products of β -caryophyllene oxidation and therefore, do not serve as a marker for further sesquiterpene-related reactions, e.g., via nitrate or sulfate chemistry. Recent studies showed that the chemical composition of β -caryophyllene ozonolysis changes with varying NO_x concentrations and temperature (Gao et al., 2022). While high NO_x concentrations decrease the SOA yield of isoprene and monoterpenes, they increase the SOA yield of sesquiterpenes, forming low-volatility organic nitrates, and/or isomerization of alkoxy radicals leads to less volatile products. The authors even conclude that the formation of SOA from sesquiterpenes may be more efficient in polluted air (Ng et al., 2007). Therefore, different mechanisms for NPF at the ATTO site might be expected in dry, polluted seasons compared to clean periods. Furthermore, a recent study synthesized α -hydroxy-organosulfates from β -caryophyllene and quantified considerable amounts in ambient samples (Wang et al., 2019b). Therefore, under dry season conditions, other oxidation products might be expected, influenced by NO_x chemistry and chemical aging. A recent study showed that first-generation sesquiterpene oxidation products, such as β -nocaryophyllonic acid, become progressively more oxidized, reacting with $\bullet$ OH to form later-generation oxidation products. Since older OA are expected at 320 m compared to 60 m on average, the insignificant amount of β -caryophyllonic acid, β -caryophyllinic acid, and nocaryophyllonic acid can be explained. Sesquiterpene OAs have been insufficiently studied to date, and therefore more detailed chemical transformations and trends will be addressed in future work.

4.4.2.4 MSA

Methane sulfonic acid (MSA) is a widely recognized molecular marker for sulfur oxidation in the atmosphere, originating primarily from the biogenic precursor dimethyl sulfide (DMS), which is emitted by vegetation, microbial activity, and oceanic sources (Andreae & Crutzen, 1997; Charlson, Lovelock, Andreae, & Warren, 1987; Stefels, Steinke, Turner, Malin, & Belviso, 2007). Extensive work on the atmospheric photooxidation of DMS has shown that the main oxidant of DMS is $\bullet$ OH, leading to the production of SO₂ and lesser amounts of MSA, dimethyl sulfoxide, and dimethyl sulfone. Furthermore, studies showed that DMS reactions with NO₃ were the most important loss mechanism of NO₃, suppressing MSA formation (Koga & Tanaka, 1996).

In this study, the relative MSA contributions do not seem to follow a specific trend. Interestingly, the highest contribution was found for sub-50 nm particles at clean conditions and at 320 m height (1.92 %), and at 60 m height for polluted conditions (0.57 %), whereas the lowest contribution (0 %) was found at 60 m height at clean conditions. The highest relative contribution to the accumulation mode was observed during clean periods at 320 m (0.71 %). Long-range-transported aerosols from the Atlantic Ocean are an expected source of elevated relative amounts of MSA in the accumulation mode. The higher amounts of MSA found at 320 m in clean and mixed conditions, compared to 60 m, underline the influence of long-range-transported sulfur-containing aerosols. Nevertheless, under polluted conditions, the relative amount of MSA was 10 times lower at 320 m than at 60 m in the accumulation mode (0.03 % and 0.33 %, respectively). Jardine et al., 2015a investigated DMS mixing ratios in the Amazon

rainforest and observed highly variable DMS mixing ratios within the canopy, showing clear evidence of a net ecosystem source to the atmosphere during day and night in both the dry and wet seasons. Daytime gradients showed mixing ratios (up to 80 ppt) peaking near the top of the canopy as well as near the ground following a rain event. Furthermore, Amazonian soils were confirmed to be one DMS source as a function of temperature and soil moisture, and light- and temperature-dependent DMS emissions were measured from seven tropical tree species. A recent study by Pugliese et al., 2023 also showed that Amazonian soils show different emissions as a function of soil moisture and rain, showing increased reduced sulfur emissions at rainy conditions after long periods of drought. Furthermore, chamber studies showed that the mass fraction of MSA increased with increasing NO_x concentrations (van Rooy et al., 2021). Altogether, MSA is a product of complex DMS (and other reduced sulfur-containing compounds) emissions, being dependent on moisture, light, and temperature. Furthermore, MSA has different terrestrial and regional sources, and its formation is also affected by varying NO_x concentrations. Therefore, the missing trend in particle size, season, and altitude is a product of these complex overlying atmospheric mechanisms and a topic for upcoming studies. Nevertheless, the fact that MSA shows its maximal relative contributions in sub-50 nm particles in some cases is remarkably interesting and warrants further investigation regarding MSA's involvement in NPF events under tropical conditions.

4.4.2.5 Sugar alcohols, amino acids and low-molecular-weight dicarboxylic acids

Sugar alcohols are a common energy reserve material in fungi and are produced in large amounts by many fungi. Thus, sugar alcohols, especially arabitol and mannitol, may constitute an important fraction of the dry weight of fungi (Carlile and Watkinson 1994). While four sugar alcohols (arabitol, mannitol, erythritol, and glycerol) are commonly found in fungi, arabitol and mannitol are particularly widespread (Carlile & Watkinson, 1994). Although other sources of sugar alcohols in airborne PM cannot be excluded, such as plants and algae, arabitol and mannitol have been mostly associated with fungal spores (Graham et al., 2003; LEWIS & SMITH, 1967; Zhang et al., 2010a). Mannitol is the most widely distributed sugar alcohol in nature, and was proposed as a molecular tracer for actively wet-discharged basidiospores (Elbert et al., 2007). In addition to mannitol, arabitol has also been proposed as a suitable marker for fungal spores (Bauer et al., 2008). Moreover, Bauer and co-workers have determined a conversion factor that can be used to estimate the contributions of fungal spores to PM₁₀ mass by microscopically counting the spores (Bauer et al., 2002). In this study, mannitol, arabitol, xylitol, erythritol, threitol, D-aspartic acid, D-glutamic acid, D-(–)-glutamine, fumaric acid, and succinic acid were separated with HILIC chromatography and accurately quantified with authentic standards. Unfortunately, xylitol and arabitol as well as threitol and erythritol could not be differentiated since they are co-eluted. Therefore, the values for arabitol and erythritol presented here could also include amounts of xylitol and threitol, respectively.

Mannitol and arabitol show their highest relative contributions in the coarse mode at 60 m for all three cases (0.5–4.9 %). This is in accordance with theoretical expectations since they are known to be a marker compound for fungal spore emissions that are expected in the coarse-fraction. Nevertheless, mannitol also shows significant relative contributions to sub-50 nm particles (up to 20 % for case 1, 60 m for particles ≤18 nm), suggesting its involvement in NPF or early particle growth mechanisms in the Amazon. A recent study by Brill and co-workers (2025) showed that Ascomycota species co-emit liquid droplets in the submicron size range during spore emission. These liquid droplets represent a new source of submicron primary aerosols and contain substantial amounts of organic matter. Furthermore, the liquid droplets

contained mannitol, arabinol, D-aspartic acid, D-glutamic acid, D-(–)-glutamine, fumaric acid, and succinic acid. These compounds contribute significantly to the sub-50 nm particle aerosol mass (up to ~20 % for D-glutamic acid at 60 m, cases 1 and 2, $d \leq 18$ nm) and show the same size- and height-resolved signature as mannitol.

However, it should be noted that there are other possible sources for these compounds. Besides fungal emissions, biological emissions can also include the release of amino acids from plants, bacteria, fungi, and animals (coarse mode) (Xu, Xiao, Xiao, & Xiao, 2025). Furthermore, amino acids, in fine aerosol particles, can also be derived from anthropogenic sources (Abe, Akutsu, & Kagemoto, 2016; Cape, Cornell, Jickells, & Nemitz, 2011). The presence of amino acid and amine compounds in aerosols is also influenced by biomass burning (e.g., wildfires and agricultural burning) and fossil fuel combustion (e.g., from vehicles and power plants) (Song et al., 2017). Lastly, in addition to direct emissions, amino acids can be formed secondarily in the atmosphere through abiotic and biological processes, contributing to secondary organic nitrogen compound formation (Xu et al., 2025).

Furthermore, succinic acid and fumaric acid are not source-specific biological tracers, but rather low-molecular-weight dicarboxylic acids that are produced by extensive oxidative processing of a variety of organic precursors, including isoprene, monoterpene, and aromatic SOA, such as toluene and naphthalene (Bikkina, Kawamura, Sakamoto, & Hirokawa, 2021; Kawamura & Bikkina, 2016; Röhl & Lammel, 2002). Chamber studies showed that trace levels of maleic acid and fumaric acid were detected during the photooxidation of naphthalene. A trace amount of succinic acid was detected in the SOA produced from the oxidation of isoprene (Sato et al., 2021).

Erythritol and/or threitol showed their highest relative contributions in the coarse mode at 60 m and 320 m in case 3, but lower than 1 %. Previous studies also showed elevated concentrations of erythritol in the coarse fraction of Amazonian aerosols and dry season samples (Graham et al., 2002; Graham et al., 2003). The authors present evidence that, due to the general lack of correlation with various biomass-burning indicators, these particles may have formed part of the natural background aerosol. The higher coarse-fraction concentrations suggested a likely association with the primary biogenic aerosol, consistent with observations in the present study.

Malic acid is not clearly linked to a single precursor or oxidation pathway. Instead, it is formed as a low-molecular-weight dicarboxylic acid through extensive oxidative fragmentation of a variety of organic aerosol compounds, including products from isoprene, monoterpenes, and aromatic hydrocarbons (Röhl & Lammel, 2002; Sato et al., 2021). Therefore, it can be either anthropogenic or biogenic. Its formation is favoured under conditions of high oxidation capacity and is often associated with multiphase oxidation in the aqueous aerosol phase or in cloud droplets. Therefore, malic acid is generally considered a non-specific tracer for photochemical aging and oxidative processing of organic aerosols rather than a source-specific marker. Malic acid shows significantly higher relative contributions across all particle sizes, with a clear trend in height: higher concentrations at 320 m than at 60 m. The highest contributions are in the accumulation mode, with relative contributions around 10 % for each accumulation mode size fraction. However, increased contributions to sub-50 nm particles at 320 m can reach up to 60 % in all three cases. The trend in size- and height-resolution seems to follow the same pattern for sub-50 nm particles as for the monoterpene oxidation products discussed above,

underscoring the predominant role of monoterpene oxidation in new particle formation and early particle growth processes in the Amazon.

4.4.2.6 Biomass burning and anthropogenic emissions

Biomass combustion represents a dominant source of primary organic aerosol (POA), emitting a complex mixture of partially oxidized organic compounds formed during the thermal decomposition of lignocellulosic material, where levoglucosan, an anhydrous sugar derived almost exclusively from the pyrolysis of cellulose and hemicellulose at temperatures exceeding 300 °C, serves as the most specific molecular tracer for biomass burning due to its near-quantitative formation under combustion conditions and minimal interference from other sources (Simoneit et al., 1999; Simoneit, 2002). Alongside levoglucosan, hydroxymethylfurfural (HMF), produced from the thermal degradation of hexose sugars, is emitted in both gas and particle phases and remains closely associated with fresh smoke plumes, while 4-hydroxybenzaldehyde and 4-hydroxybenzoic acid, originating from lignin pyrolysis, reflect emissions from woody biomass, either through direct particle-phase release or rapid oxidation of volatile lignin-derived precursors (Coggon et al., 2019; Romanias et al., 2024; Simoneit, 2002). Salicylic acid, in contrast, acts as a mixed marker, indicating both primary biomass-burning emissions and secondary oxidation of phenolic combustion products, thereby signaling partially aged smoke aerosols (Hopstock et al., 2024; Li et al., 2023).

The observed size-resolved distribution of biomass burning tracers at the ATTO site reveals distinct patterns between 60 m and 320 m, suggesting differential emission sources, atmospheric processing, and local contamination. In case 1, at 320 m, the substantial contribution of levoglucosan (21 %) and hydroxymethylfurfural (HMF, 8 %) to sub-50 nm particles contrasts sharply with their minimal presence in the accumulation and coarse modes (<2 % and <1 %, respectively). This pattern may reflect primary fresh biomass-burning smoke plumes arriving at the ATTO site (Carrico et al., 2016; Hosseini et al., 2010; Louchouart, Kuo, Wade, & Schantz, 2009). Looking at the backtrajectories in **Figure S 11.2-1**, air masses nearby may have passed over areas with fire activities, resulting in fresh smoke arriving during MOUDI sampling. A similar trend is observed for 4-hydroxybenzaldehyde and 4-hydroxybenzoic acid, with contributions in the sub-50 nm range and lower contributions in the accumulation and coarse mode. This co-variance between lignin-derived markers and levoglucosan underscores the presence of proximity emissions. At 60 m, the enhanced sub-50 nm contributions of 4-hydroxybenzaldehyde (2 %) and 4-hydroxybenzoic acid (0.5 %) alongside elevated nitrophenol levels (2–4 %) strongly indicate local biomass combustion and diesel generator emissions, respectively. The SMPS plot in **Figure S 11.2-12** also shows quite specific spikes in small particle concentrations at 60 m that were already observed as fresh generator plumes. The absence of nitrophenols at 320 m confirms their ground-level source. The negligible contribution of salicylic acid across all sizes aligns with its secondary formation pathway, predominantly occurring in aged aerosols from anthropogenic sources. Collectively, these findings suggest that 320 m measurements reflect regional transport, whereas 60 m data are contaminated by local emissions, likely from the ATTO site's own diesel combustion.

In case 2, levoglucosan shows a different trend in particle-size contribution. The highest levoglucosan contribution is found in the coarse mode at both heights, with 2 % at 60 m and 0.3 % at 320 m. The contributions to the accumulation mode are ~0.3% at both heights and negligible (<0.3%) for sub-50-nm particles. Case 3 shows the highest relative contributions of all cases for levoglucosan in the accumulation and coarse modes (~15 % and 12 % at both heights), as well as significant contributions in the sub-50 nm fraction with 5 % at 60 m and

8 % at 320 m. These findings underscore the complexity of biomass burning activities in shaping the chemical composition of OA. The contributions in the accumulation mode reflect the influence of long-range-transported biomass-burning plumes arriving at the ATTO site (Franco et al., 2024; Valiati et al., 2025), and the contributions in the coarse mode underscore the primary emissions from fire activities as a significant OA source. Nevertheless, the high abundance of biomass-burning markers in the sub-50 nm particle fraction shows how individual events, such as fresh smoke, affect the overall chemical composition of submicrometer organic aerosols. The influence of such individual atmospheric events was also shown by a recent study by Leppla et al. (2025), which showed that the chemical composition changes significantly when they are considered. Furthermore, the study found that even under wet-season conditions, biomass-burning aerosols cannot be neglected in the background OA at the ATTO site. HMF shows the highest relative contributions in the sub-50 nm fraction, around 10 %, supporting fresh smoke events as a major source of HMF and shaping the ultrafine OA fraction. 4-hydroxybenzaldehyde and 4-hydroxybenzoic acid contribute <5 % each, and nitrophenols contribute <0.25 % each, in cases 1 and 2, indicating that urban anthropogenic emissions (traffic, industry) still do not have a significant effect on chemical speciation in remote areas of the Amazon rainforest. Furthermore, vertical gradients under mixed and dry season conditions are very subtle, underlying the strong vertical mixing (Mendonça et al., 2025).

However, while it was previously thought that particle composition during the dry period is dominated by biomass burning (Sá et al., 2019), the relative contributions shown here exhibit a larger influence from BVOCs due to decreased wet deposition, resulting in positive feedbacks on oxidants and emissions. Seasonal variations in isoprene, sesquiterpenes, and monoterpenes have been measured in previous studies, reflecting higher mixing ratios in the dry season (Alves et al., 2016). Additionally, with the lack of rainfall, in-basin pollution may be more prevalent, especially in areas downwind of cities and settlements (Glicker et al., 2019; Martin et al., 2010).

4.4.2.7 Estimation of the proportion of characterized aerosol mass relative to the size-resolved total aerosol mass collected

The relative proportion of the compounds examined, based on the aerosol mass impacted on the filter of the corresponding MOUDI stage, is shown in **Figure 4.4-5**, selected by size.

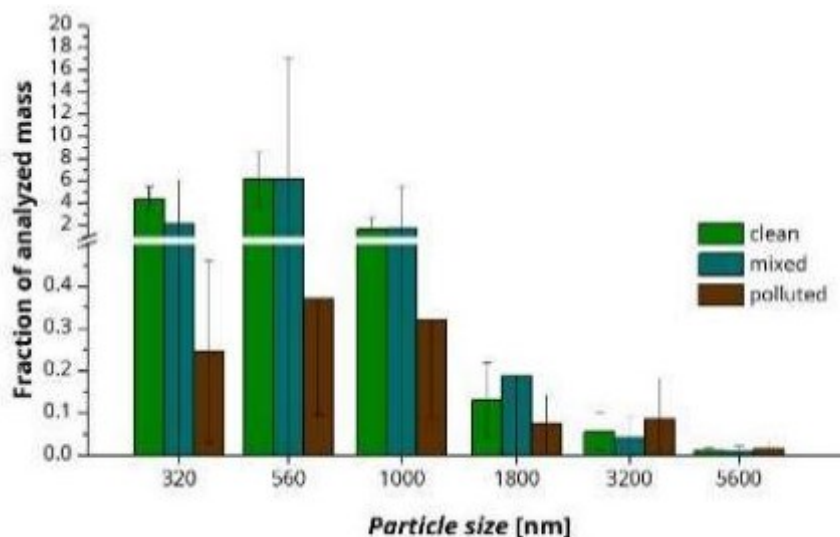


Figure 4.4-5: Particle size-selective fraction of OA mass of 32 quantified compounds in the total OA mass at 60 m. The total OA mass was estimated using OPS mass concentrations applying refractive indices of $1.33 - 0.006i$ for cases 1 and 2 (wet-season conditions; Franco et al., 2024), and $1.41 - 0.013i$ for Case 3 (biomass burning conditions; Guyon et al., 2003), assuming spherical particles and a density of 1.47 g/cm^3 . The optical particle diameter measured by the OPS was treated as equivalent to the particle's volume-equivalent (geometric) diameter.

Figure 4.4-5 shows good agreement between chemically derived organic aerosol mass and OPS-inferred mass for polluted air masses, whereas in clean and mixed conditions, the ratios are well above unity, particularly for particles in the Aitken and lower accumulation modes. Values larger than one are physically implausible and therefore indicate methodological rather than atmospheric effects. Under polluted conditions, particles are typically larger and more internally mixed, leading to more stable effective densities and refractive indices and thus improved optical sizing and number-to-mass conversion (Hand & Kreidenweis, 2002; Quinn et al., 2004).

In contrast, clean and mixed air masses are dominated by smaller, organic-rich particles ($<300\text{--}500 \text{ nm}$), for which OPS detection efficiency and optical sizing accuracy decrease strongly, and mass is systematically underestimated (Wiedensohler et al., 2012). At the same time, positive filter artifacts such as adsorption of semi-volatile organic vapours and enhanced gas–particle partitioning under low-loading conditions can bias chemically reconstructed mass upward (especially since the majority of compounds analyzed here are semi-volatile) and were found to be in the range of 21.7% and 48.0% for $\text{PM}_{2.5}$ and $\text{PM}_{0.1}$ on quartz filters in previous studies, respectively (Zhu, Tsai, Chen, Cao, & Roam, 2012).

Additional uncertainty arises from the MOUDI's size classification. The aerodynamic cut-off diameters of each stage depend on the sampling flow (Equation 1.3-- 1), such that systematically lower operating flows shift the effective cut-offs to larger diameters and cause partial misclassification of upper-accumulation-mode particles into smaller nominal-size bins. Furthermore, the particle cutoff characteristics (collection efficiency curves) of each stage and

interstage losses were determined using monodisperse aerosols during the development of MOUDI samplers and therefore can differ for ambient OA (Marple et al., 1991). This effect is expected to be strongest in the 320–1000 nm range, where particle mass increases steeply with size, thereby amplifying discrepancies between clean and mixed conditions. The overlap of the error bars indicates that a substantial fraction of the observed differences lies within the combined uncertainty of OPS-based mass estimation, MOUDI size cut-offs, and filter-related artifacts.

Nevertheless, the 32 selected marker compounds represent established oxidation products of biogenic and aged organic aerosol and thus provide a chemically meaningful subset of the organic fraction, mainly dominated by isoprene OA, monoterpene OA, and sesquiterpene OA, but also containing considerable amounts of primary biogenic aerosol particles, including sugar alcohols, especially mannitol. However, this marker-based reconstruction does not capture the full complexity of the organic matrix, and the polluted regime likely represents the most robust comparison case, whereas the elevated ratios under clean and mixed conditions should be interpreted as upper-limit biases rather than true mass enhancements.

4.4.3 Representative absolute concentrations under clean, mixed, and polluted conditions for PM₁₀, PM₁, and PM_{0.056}

The size- and height-resolved molecular characterization of organic aerosols at the Amazon Tall Tower Observatory (ATTO) reveals pronounced dependencies of marker compound distributions on particle size, atmospheric conditions, and altitude, offering critical insights into the sources, transformation pathways, and regional transport of organic aerosol (OA) in the central Amazon. By quantifying 32 molecular markers across three size fractions (PM₁₀, PM₁, PM_{0.056}) at 60 m and 320 m under clean, mixed, and polluted conditions, this study demonstrates how particle size resolves fundamental differences in emission regimes, atmospheric processing, and the vertical structure of aerosol composition. Nevertheless, it should be noted that long sampling times, necessary to ensure sufficient aerosol mass for molecular analysis of the smallest particle size fractions, might lead to sampling artifacts, especially for semi-volatile organic aerosols with efficient gas-to-particle conversion.

Primary biological markers, including sugar alcohols such as mannitol and arabitol, exhibit a clear dominance in the coarse-mode fraction (PM₁₀) across all air mass types, with concentrations ranging from 4 to 38 ng m⁻³. These values are consistent with previous observations in the Amazon basin, where mannitol and arabitol concentrations typically range from 5 to 50 ng m⁻³, reflecting their association with fungal spores and primary biological aerosol material (Samaké et al., 2019; Zhang et al., 2015). The minimal contributions of these compounds to the ultrafine fraction (PM_{0.056}) underscore their primary emission as coarse particles, a pattern similarly observed in boreal and temperate forest environments where biological aerosols are predominantly found in supermicron particles (Bauer et al., 2008). The slight decrease in mannitol concentrations with altitude under clean conditions is contrasted by a sharp increase under polluted conditions, particularly at 320 m. The unexpectedly elevated mannitol concentrations at 320 m during the dry season (up to 35 ng m⁻³) suggest that pyroconvective processes associated with intense biomass burning may play a critical role in vertically redistributing coarse biological particles, such as fungal spores, to altitudes well above the canopy. This hypothesis is supported by the co-occurrence of mannitol with biomass burning tracers (e.g., levoglucosan and HMF) at 320 m (3910 ng m⁻³), indicating that spores could be entrained in smoke plumes and lofted by strong updrafts generated during fire events or thunderstorms (Andreae et al., 2015; Barbosa et al., 2022; Moran-Zuloaga et al., 2018). The

extreme drought conditions in 2023, characterized by record-low precipitation and high temperatures (Espinoza et al., 2024), likely exacerbated this effect by intensifying fire activity and reducing wet deposition, thereby prolonging particle residence times in the atmosphere. However, alternative mechanisms, such as long-range transport of spores from distant sources or enhanced local emissions due to drought stress, cannot be ruled out without further analysis.

Amino acids such as D-aspartic acid exhibit a more differentiated size dependence. In clean air, PM₁₀ concentrations decrease slightly with altitude (2.2 ng m⁻³ at 60 m and 1.7 ng m⁻³ at 320 m), whereas in polluted air they increase sharply from 7 ng m⁻³ to 42 ng m⁻³. PM₁ closely mirrors PM₁₀ (39.367 ng m⁻³ in polluted air at 320 m), while PM_{0.056} remains lower (7 ng m⁻³). These concentrations are comparable with boreal forest environments (Helin et al., 2017), but the strong enhancement under polluted conditions suggests an additional contribution from aged biomass burning aerosol and secondary nitrogen-containing organic aerosol (Abe et al., 2016; Song et al., 2017; Xu et al., 2025). However, the vertical trend shows higher concentrations at 60 m than at 320 m, and PM_{0.056} concentrations are even higher than those of mannitol, highlighting a predominant local UAP source within the forest.

Dicarboxylic acids and oxidized organic acids exhibit particularly strong size and air-mass dependencies. Malic acid in polluted PM₁₀ increases from 1200 ng m⁻³ at 60 m to 18506 ng m⁻³ at 320 m, while PM_{0.056} remains lower (3740 ng m⁻³). These concentrations exceed by one to two orders of magnitude those reported for continental background and marine-influenced environments (typically 10–200 ng m⁻³; (Hsieh, Kuo, Chen, & Tsai, 2007; Röhl & Lammel, 2002) indicating exceptionally strong secondary processing and likely contributions from gas–particle partitioning and in-filter artifacts under high precursor loadings. Succinic acid and fumaric acid are dominated by PM₁₀ (1–12 ng m⁻³) and show comparable concentrations to rural and urban sites during the dry season (Hsieh et al., 2007; Röhl & Lammel, 2002). The vertical trend shows higher fumaric acid concentrations during the dry seasons at 320 m, suggesting long-range transport as a significant source. During the wet and transition seasons, missing trends in vertical distribution are consistent with local biogenic sources.

Monoterpene secondary organic aerosol (SOA) markers, including pinic and pinonic acid, reveal concentrations comparable to those observed in other forested environments. Pinic and pinonic acid, tracers of α - and β -pinene oxidation, show elevated concentrations under polluted conditions (pinonic acid PM₁₀ = 56 ng m⁻³ and PM_{0.056} = 22 ng m⁻³ at 320 m). These values fall within the range reported for tropical and boreal forests (1–50 ng m⁻³), confirming the ubiquitous role of monoterpene oxidation in SOA formation across different ecosystems (Kavouras, Mihalopoulos, & Stephanou, 1998; Vestenius et al., 2014; Ye et al., 2021). The enrichment of these markers in the ultrafine fraction (PM_{0.056}) under polluted conditions suggests efficient nucleation of monoterpene SOA, particularly when oxidant levels are elevated. The accumulation-mode peak of MBTCA further supports the role of atmospheric aging in redistributing semi-volatile oxidation products to larger particles (Szmigielski et al., 2007a). Sesquiterpene SOA markers, for example, β -caryophyllonic and β -caryophyllinic acid, also increase strongly in the dry season (up to 188 ng m⁻³ in PM₁₀ and 180 ng m⁻³ in PM₁), which is comparable during the wet and transitions seasons to but slightly above values reported for forested environments for the dry seasons (0.1–50 ng m⁻³) (Jaoui, Lewandowski, Kleindienst, Offenbergl, & Edney, 2007; Vestenius et al., 2014), indicating efficient oxidation of sesquiterpenes under elevated oxidant levels. Together, a larger influence from BVOCs due to decreased wet deposition, resulting in positive feedback on oxidants and emissions, is reflected in the monoterpene and sesquiterpene OA concentrations. Previous studies support

these findings by reporting seasonal variations in isoprene, sesquiterpenes, and monoterpenes, with higher mixing ratios in the dry season (Alves et al., 2016).

Isoprene oxidation products, including 2-methyltetrols and OS-215, show a strong dependence on particle size and air mass. PM_{10} concentrations of 2-methyltetrols in polluted air reach 49683 ng m^{-3} at 320 m, PM_1 36271 ng m^{-3} , and $PM_{0.056}$ 1893 ng m^{-3} , while OS-215 reaches 63895 ng m^{-3} in PM_{10} . These concentrations exceed typical literature values for isoprene SOA tracers ($100\text{--}2000 \text{ ng m}^{-3}$) (González et al., 2014; Yee et al., 2020) by one to two orders of magnitude, indicating exceptionally strong secondary aerosol production under polluted conditions. However, it should be noted that in this study, synthesized OS-215 was used for external calibration and a comparison of the response factor of the synthesized 3-methyltetrol sulfate esters with that of camphersulfonic acid ($m = (0.6907 \pm 0.0002) \text{ mL ng}^{-1}$, $b = 22.89 \pm 0.03$, $R^2 = 0.989$) indicated that 3-methyltetrol sulfate esters are underestimated by two orders of magnitude when semiquantitative methods are employed. However, it is important to note that the quantification of sulfate esters in this study may be subject to over- or underestimation due to calibration limitations, as the response factors of individual isomers can vary significantly. Future work employing stereochemical analysis would be essential to improve the accuracy of these measurements. The accumulation-mode dominance of OS-215 reflects gas–particle partitioning of low-volatility oxidation products and condensation onto pre-existing particles.

Biomass combustion tracers, including levoglucosan and hydroxymethylfurfural, show extreme enhancement under polluted conditions. PM_{10} levoglucosan reaches 3910 ng m^{-3} at 320 m (PM_1 3227 ng m^{-3} , $PM_{0.056}$ $= 167168 \text{ ng m}^{-3}$), while HMF reaches 1081 ng m^{-3} . These values are at the upper end of concentrations reported for Amazonian dry-season biomass burning plumes ($200\text{--}3000 \text{ ng m}^{-3}$) (Oliveira Alves et al., 2015), highlighting the dominant influence of fire emissions and efficient vertical transport of aged smoke aerosol. Especially sub-case 3_3, in Oct 2023, showed extremely high BC and particle number concentrations (**Table S 11.2-5**, **Figure S 11.2-19**). In 2023, record-dry-hot conditions in Amazonia occurred with extreme droughts and warmth (Espinoza et al., 2024; Ferreira, Buras, Zscheischler, Mahecha, & Rammig, 2025). Furthermore, the ATTO site was strongly affected by nearby biomass-burning plumes (**Figure S 11.2-3**). Biomass burning tracers, particularly levoglucosan and hydroxymethylfurfural (HMF), exhibit extreme enrichment under polluted conditions, with levoglucosan concentrations in the ultrafine fraction ($PM_{0.056}$) reaching values that far exceed those typically observed in other ecosystems. This extraordinary ultrafine enrichment, which contrasts with the accumulation-mode dominance observed in most other regions, suggests that Amazonian biomass burning plumes may undergo rapid vertical lofting and efficient nucleation onto biogenic seeds, processes that are less pronounced in temperate or polluted environments (Pöhlker et al., 2018a). The record dry and hot conditions in 2023, which were associated with extreme droughts and widespread fires across Amazonia, likely amplified these effects, as evidenced by the strong correlation between levoglucosan concentrations and black carbon measurements reported in Table S 12.2-5.

Nitrophenols contribute only marginally ($<1 \text{ ng m}^{-3}$ mainly in PM_{10}), consistent with photochemical formation and minor anthropogenic input (Kitanovski et al., 2021; Wang et al., 2020a).

Methanesulfonic acid, a marker of biogenic sulfur oxidation, was detected primarily in PM_{10} and PM_1 . Concentrations in clean air increased from 0.9 ng m^{-3} at 60 m to 3 ng m^{-3} at 320 m, suggesting efficient vertical transport and in situ formation from DMS oxidation. In polluted air, concentrations were highest near the ground (8 ng m^{-3} at 60 m) and decreased moderately

with altitude (7 ng m^{-3} at 320 m), indicating additional contributions from biomass burning and anthropogenic sulfur sources. PM_1 closely follows PM_{10} (7 ng m^{-3} at 60 m), while $\text{PM}_{0.056}$ remains negligible ($< 0.5 \text{ ng m}^{-3}$), confirming that MSA predominantly occurs in fine aerosol.

Overall, PM_{10} dominates primary biological material, biomass burning tracers and part of the terpene SOA, whereas PM_1 is particularly relevant for secondary oxidation products under polluted conditions. $\text{PM}_{0.056}$ contributes only minimally, except for highly oxidized SOA compounds. Altitude exerts the strongest influence during polluted conditions, reflecting efficient vertical mixing and regional transport of aged aerosol, whereas in clean air, vertical gradients are minor and local biogenic emissions dominate.

Table 4.4-1: Absolute concentrations of 32 selected molecular marker compounds at clean, mixed and polluted conditions in PM₁₀, PM₁ and PM_{0.056} determined with RPLC and HILIC-ESI-HR-Orbitrap-MS. All values are field-blank-corrected and corrected for particle loss. OS-215 corresponds to the sum of six isomers quantified with the response factor of a isomeric mixture of 3-methyltetrol sulfate ester. Arabitol/xylitol and erythritol/threitol co-eluted and therefore can represent both regioisomers. 2-methyl-4-nitrophenol and 4-methyl-3-nitrophenol could not be baseline separated and therefore, are addressed as a sum concentration.

		Clean 60 m		Clean 320 m		Mixed 60 m		Mixed 320 m		Polluted 60 m		Polluted 320 m	
Compound		c [ng m ⁻³]	Δc [ng m ⁻³]	c [ng m ⁻³]	Δc [ng m ⁻³]	c [ng m ⁻³]	Δc [ng m ⁻³]	c [ng m ⁻³]	Δc [ng m ⁻³]	c [ng m ⁻³]	Δc [ng m ⁻³]	c [ng m ⁻³]	Δc [ng m ⁻³]
Mannitol	PM ₁₀	4.214	0.311	3.824	0.272	9.118	0.639	4.139	0.523	8.132	0.556	35.847	2.365
	PM ₁	2.182	0.074	2.393	0.050	2.363	0.211	0.915	0.020	0.322	0.040	3.941	0.010
	PM _{0.056}	0.724	0.074	0.010	0.011	0.613	0.171	0.221	0.010	0.010	0.024	1.367	0.010
Arabitol a.o. Xylitol	PM ₁₀	4.014	0.452	4.383	0.312	6.376	0.426	2.658	0.200	10.348	0.747	37.654	2.485
	PM ₁	0.473	0.080	2.433	0.040	0.664	0.070	0.573	0.020	1.317	0.050	11.410	0.020
	PM _{0.056}	0.000	0.039	0.000	0.008	0.010	0.040	0.010	0.010	0.040	0.020	1.830	0.010
D-Aspartic acid	PM ₁₀	2.212	3.036	1.780	0.500	2.616	2.831	0.294	0.307	7.176	0.883	42.329	2.822
	PM ₁	2.111	2.894	1.699	0.462	2.503	2.266	0.251	0.293	5.308	0.623	39.367	0.392

	PM_{0.05}₆	2.111	2.894	0.724	0.302	2.202	2.079	0.020	0.168	0.553	0.251	7.852	0.080
D-Glutamic acid	PM₁₀	0.885	0.405	0.084	0.043	2.027	0.721	0.410	0.068	0.189	0.137	0.116	0.043
	PM₁	0.794	0.382	0.040	0.038	1.699	0.674	0.302	0.060	0.040	0.111	0.060	0.030
	PM_{0.05}₆	0.483	0.312	<LOQ	-	1.166	0.643	0.141	0.040	0.020	0.070	0.000	0.020
Fumaric acid	PM₁₀	0.032	0.098	0.116	0.043	0.431	0.136	0.903	0.158	5.158	0.936	63.761	4.225
	PM₁	0.030	0.094	0.070	0.030	0.171	0.082	0.483	0.111	4.061	0.764	57.683	0.352
	PM_{0.05}₆	0.030	0.094	0.010	0.020	<LOQ	-	0.070	0.070	0.201	0.141	8.063	0.050
D-(-)-glutamine	PM₁₀	0.295	0.054	0.348	0.038	0.725	0.072	0.378	0.049	0.861	0.119	0.396	0.033
	PM₁	0.020	0.035	0.131	0.024	0.010	0.046	0.020	0.007	0.101	0.050	0.015	0.013
	PM_{0.05}₆	<LOQ	-	0.004	0.020	0.010	0.033	<LOQ	-	0.070	0.030	0.001	0.011
Erythritol Threitol	a./o. PM₁₀	0.158	0.137	0.063	0.039	0.326	0.138	0.168	0.026	1.734	0.142	31.686	2.090
	PM₁	0.030	0.131	0.020	0.036	0.070	0.131	0.030	0.019	0.704	0.060	11.792	0.020

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	PM_{0.05}₆	0.000	0.080	<LOQ	-	0.010	0.080	<LOQ	-	0.010	0.040	0.151	0.010
Succinic acid	PM₁₀	0.980	0.244	4.930	1.554	9.496	0.776	4.433	1.088	12.807	3.783	11.672	2.929
	PM₁	0.372	0.177	3.790	1.448	7.470	0.422	3.117	1.005	8.716	2.875	7.389	2.684
	PM_{0.05}₆	0.131	0.074	2.333	0.080	2.875	0.231	1.880	0.090	1.297	1.096	2.483	1.216
Pinic acid	PM₁₀	0.190	0.054	0.348	1.781	0.399	0.232	0.084	1.218	1.744	0.195	0.641	3.184
	PM₁	0.161	0.040	0.292	1.689	0.271	0.161	0.060	1.166	1.247	0.141	0.503	3.046
	PM_{0.05}₆	0.050	0.030	0.040	0.010	0.060	0.060	0.030	0.020	0.241	0.030	0.171	1.367
Pinonic acid	PM₁₀	<LOQ	-	8.175	0.677	1.071	5.121	0.756	0.214	8.972	0.732	56.491	3.726
	PM₁	<LOQ	-	7.792	0.362	0.674	4.900	0.583	0.195	5.559	0.342	43.830	0.121
	PM_{0.05}₆	<LOQ	-	6.153	0.261	0.090	4.485	0.292	0.148	2.001	0.171	22.138	0.090
Terebic acid	PM₁₀	0.548	0.074	0.832	0.259	0.830	0.237	0.158	0.168	1.240	0.159	0.462	0.442
	PM₁	0.221	0.060	0.724	0.231	0.362	0.171	0.080	0.161	0.794	0.121	0.332	0.422

	PM_{0.05}₆	0.060	0.040	0.201	0.020	0.040	0.060	0.040	0.020	0.070	0.010	0.060	0.191
Pimelic acid	PM₁₀	0.611	0.133	0.095	0.232	0.305	0.242	0.021	0.055	1.040	0.153	0.294	0.305
	PM₁	0.261	0.121	0.070	0.171	0.191	0.181	0.020	0.017	0.493	0.111	0.221	0.292
	PM_{0.05}₆	0.101	0.070	0.040	0.040	0.070	0.070	0.020	0.020	0.141	0.050	0.111	0.131
Malic acid	PM₁₀	<LOQ	-	111.196	224.028	59.506	290.699	175.882	175.108	1200.906	1377.404	18506.964	1745.002
	PM₁	<LOQ	-	93.824	211.949	36.474	260.471	123.950	154.782	1010.471	1249.468	15253.427	1155.876
	PM_{0.05}₆	<LOQ	-	25.738	120.025	<LOQ	-	9.109	40.263	74.456	215.032	3740.862	199.289
MBTCA	PM₁₀	2.971	0.281	7.164	0.627	4.632	0.497	3.172	0.292	8.027	1.514	4.076	0.464
	PM₁	2.584	0.184	6.626	0.362	4.132	0.352	2.855	0.201	7.047	1.357	3.529	0.342
	PM_{0.05}₆	0.241	0.040	0.302	0.030	0.121	0.070	0.221	0.020	0.342	0.040	0.342	0.151
MSA	PM₁₀	0.927	0.093	3.066	0.235	2.447	0.288	1.513	0.135	8.857	1.102	7.270	1.457

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	PM₁	0.734	0.064	2.745	0.101	1.981	0.182	1.287	0.090	7.680	0.885	6.363	1.317
	PM_{0.056}	0.050	0.024	0.503	0.010	0.040	0.046	0.101	0.020	0.422	0.050	0.292	0.090
β-Caryophyllonic acid	PM₁₀	25.400	4.760	4.309	1.605	3.571	2.420	0.357	1.058	26.160	12.329	<LOQ	-
	PM₁	20.953	3.278	4.112	1.506	3.147	1.953	0.342	1.013	18.356	9.339	<LOQ	-
	PM_{0.056}	5.972	1.041	0.010	1.448	1.890	0.505	0.000	1.004	6.866	3.690	<LOQ	-
β-Caryophyllinic acid	PM₁₀	3.729	6.932	0.411	2.085	1.954	4.844	0.609	0.555	16.778	7.759	2.563	188.342
	PM₁	2.755	6.602	0.392	1.990	1.066	4.625	0.583	0.530	14.014	7.188	1.759	180.217
	PM_{0.056}	2.705	6.027	0.392	1.990	0.503	2.886	0.583	0.530	0.875	0.875	0.895	80.598
Nocaryophyllonic acid	PM₁₀	0.284	1.591	0.084	0.290	0.305	1.198	0.063	0.249	1.030	2.648	0.557	0.642
	PM₁	0.171	1.267	0.080	0.277	0.221	0.945	0.060	0.198	0.684	2.232	0.392	0.513
	PM_{0.056}	0.070	0.845	0.020	0.179	0.070	0.623	0.040	0.130	0.221	1.367	0.151	0.342

Levoglucozan	PM ₁₀	<LOQ	-	12.073	0.841	4.884	0.348	2.731	0.274	356.544	24.306	3910.913	257.808
	PM ₁	<LOQ	-	11.522	0.141	2.312	0.141	1.729	0.061	284.526	5.660	3227.796	2.671
	PM _{0.056}	<LOQ	-	6.435	0.111	0.020	0.046	0.111	0.031	9.772	0.392	168.103	0.261
Hydroxymethylfurfural	PM ₁₀	0.643	0.221	15.528	1.202	7.048	0.811	9.496	1.342	43.043	4.409	1081.704	71.379
	PM ₁	0.613	0.207	14.598	0.533	6.605	0.645	8.163	1.136	38.844	3.219	961.132	3.157
	PM _{0.056}	<LOQ	-	2.514	0.251	1.206	0.445	0.744	0.372	2.905	0.430	234.546	0.473
4-Hydroxybenzaldehyde	PM ₁₀	0.116	0.043	0.032	0.084	0.011	0.196	<LOQ	-	0.074	0.032	0.002	0.116
	PM ₁	0.111	0.040	0.030	0.080	0.010	0.161	<LOQ	-	0.050	0.020	0.001	0.111
	PM _{0.056}	0.060	0.030	0.030	0.005	0.010	0.060	<LOQ	-	0.020	0.010	0.001	0.001
4-Hydroxybenzoic acid	PM ₁₀	0.116	6.574	0.506	0.131	0.284	0.253	0.011	0.030	1.712	0.276	0.504	0.161
	PM ₁	0.090	6.274	0.462	0.111	0.171	0.201	0.002	0.027	0.895	0.141	0.322	0.151
	PM _{0.056}	0.030	4.464	0.151	0.060	0.050	0.060	<LOQ	-	0.211	0.050	0.070	0.070

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Salicylic acid	PM₁₀	0.242	0.101	0.105	0.348	0.095	0.201	0.021	0.231	0.851	0.187	0.189	0.599
	PM₁	0.231	0.090	0.101	0.332	0.080	0.166	0.020	0.221	0.694	0.171	0.161	0.573
	PM_{0.05}₆	0.090	0.060	0.000	0.010	0.050	0.063	<LOQ	-	0.020	0.040	0.000	0.261
4-Nitrophenol	PM₁₀	0.095	0.074	0.042	0.053	0.021	0.202	0.002	0.020	0.168	0.033	0.032	0.095
	PM₁	0.090	0.070	0.040	0.050	0.020	0.061	0.001	0.016	0.020	0.020	0.020	0.090
	PM_{0.05}₆	0.050	0.040	0.020	0.010	0.020	0.060	0.001	0.016	0.000	0.010	0.010	0.040
2-Methyl-4-nitrophenol a. 4-Methyl-3-nitrophenol	PM₁₀	0.200	0.075	0.005	0.186	<LOQ	-	<LOQ	-	0.007	0.039	0.003	0.431
	PM₁	0.191	0.070	0.005	0.177	<LOQ	-	<LOQ	-	0.002	0.031	0.002	0.412
	PM_{0.05}₆	0.080	0.050	0.005	0.004	<LOQ	-	<LOQ	-	<LOQ	-	<LOQ	-
2,6-Dimethyl-4-nitrophenol	PM₁₀	0.232	0.075	0.003	0.124	<LOQ	-	<LOQ	-	0.002	0.011	<LOQ	-
	PM₁	0.221	0.070	0.003	0.118	<LOQ	-	<LOQ	-	<LOQ	-	<LOQ	-
	PM_{0.05}₆	0.101	0.050	0.002	0.002	<LOQ	-	<LOQ	-	<LOQ	-	<LOQ	-

2,4-Dinitrophenol	PM₁₀	0.211	0.055	0.158	0.064	0.002	0.196	0.001	0.014	0.016	0.012	0.019	0.082
	PM₁	0.201	0.050	0.151	0.060	0.001	0.161	0.001	0.014	0.008	0.009	0.013	0.079
	PM_{0.056}	0.090	0.030	0.151	0.030	0.001	0.061	0.001	0.014	0.003	0.006	0.009	0.001
2-Methyltetrols	PM₁₀	520.888	38.673	774.242	54.863	1151.112	79.202	909.841	68.779	6323.073	425.974	49683.870	3275.919
	PM₁	319.647	13.080	587.959	12.055	621.980	18.740	379.248	8.907	4797.206	79.016	36271.182	54.332
	PM_{0.056}	44.801	4.223	84.122	4.806	57.731	4.082	45.415	4.374	394.023	12.064	1893.317	13.642
OS-215	PM₁₀	579.873	40.551	1089.142	74.701	3162.432	206.681	2330.185	152.673	3773.010	254.189	63895.724	4212.102
	PM₁	532.913	7.601	1015.215	2.283	2980.141	41.672	2205.177	32.393	3470.633	50.124	59599.232	51.813
	PM_{0.056}	4.756	0.101	19.847	0.402	43.032	1.046	95.032	2.393	68.343	1.820	1182.019	3.338

4.5 Conclusion

This study presents a comprehensive, size- and height-resolved molecular characterization of organic aerosols in the central Amazon rainforest, demonstrating that particle size is a critical parameter for resolving aerosol sources, formation pathways, and atmospheric aging processes. Through the combination of MOUDI sampling with targeted LC–HR-Orbitrap-MS quantification of 32 molecular marker compounds, we show that the molecular composition of organic aerosol varies systematically with particle size, altitude, season, and atmospheric conditions, reflecting the dynamic interplay between biogenic emissions, biomass burning, and secondary processing in this globally significant ecosystem.

Our results reveal distinct molecular patterns across particle sizes, illuminating key atmospheric processes. Secondary organic aerosol products derived from isoprene and monoterpenes exhibit pronounced contributions to sub-50 nm particles, indicating their involvement in new particle formation and early growth. In contrast, highly oxidized monoterpene SOA markers, such as MBTCA, peak in the accumulation mode and are suppressed under polluted, high-NO_x conditions, consistent with shifts in oxidation pathways under anthropogenic influence. Sesquiterpene oxidation products further emphasize the importance of low-volatility compounds in nucleating ultrafine particles under clean, biogenically dominated conditions. These size-dependent distributions underscore the distinct contributions of different volatile organic compound precursors to particle formation and growth in the Amazon atmosphere.

Biomass burning emissions emerge as a dominant and persistent influence on Amazonian organic aerosol composition, with unprecedented size-resolved complexity. Levoglucosan and hydroxymethylfurfural are strongly enriched in ultrafine particles under polluted conditions, with concentrations exceeding those observed in boreal forests and urban environments by orders of magnitude. This suggests unique Amazonian combustion regimes characterized by rapid vertical lofting and efficient nucleation onto biogenic seeds. The persistence of these biomass-burning markers even during the wet season challenges traditional assumptions about seasonal aerosol sources, suggesting that reduced wet deposition and enhanced vertical mixing sustain their influence throughout the year. The coexistence of fresh ultrafine and aged accumulation-mode biomass burning tracers further highlights the complex interplay between local emissions, regional transport, and atmospheric processing, particularly under the record drought conditions observed in 2023.

Primary biological markers and sulfur-containing aerosols reveal distinct vertical and seasonal patterns that complement our understanding of Amazonian aerosol sources. Sugar alcohols such as mannitol dominate the coarse mode, confirming their primary biological origin from fungal spores, while their contributions to ultrafine particles suggest additional submicron emissions from biological sources. Methanesulfonic acid shows accumulation-mode dominance at higher altitudes, indicating long-range transport of marine and biogenic sulfur, while ground-level enrichment under polluted conditions suggests additional terrestrial contributions. Organosulfates exhibit increasing relative contributions with particle size and altitude, reflecting multiphase processing and chemical aging during regional transport.

Collectively, these findings demonstrate that particle size resolves fundamental differences in aerosol sources and aging processes in the Amazon, with ultrafine particles dominated by fresh biogenic and pyrogenic emissions and accumulation-mode aerosols reflecting aged, regionally transported material. The persistent influence of biomass burning across seasons and altitudes - even during wet conditions - underscores its role as a continuous background source of organic aerosol in this ecosystem. Vertical gradients between 60 m and 320 m further reveal distinct chemical regimes, with ground-level measurements capturing local emission sources and higher-altitude data reflecting regional transport and free-tropospheric processing.

This study fills a critical knowledge gap in tropical aerosol chemistry by providing size-resolved molecular constraints on organic aerosol formation and aging. The unprecedented ultrafine enrichment of biomass-burning tracers in the Amazon, compared to other global ecosystems, underscores the need to revisit assumptions about combustion regimes and vertical transport in tropical atmospheric models. Future research should focus on high-time-resolution measurements to better capture episodic plume events, stereochemical analyses to improve the quantitative accuracy of secondary organic aerosol markers, and the development of coupled aerosol-cloud models that incorporate size-resolved molecular data to more accurately represent aerosol-cloud interactions in the tropics. By integrating molecular specificity with size resolution, this work establishes a new framework for understanding organic aerosol dynamics in the Amazon, where the convergence of biogenic emissions, biomass burning, and atmospheric processing fundamentally shapes aerosol properties and their climate impacts.

Data availability

The datasets are available upon request from the corresponding author, Thorsten Hoffmann (t.hoffmann@uni-mainz.de).

Author contributions

SH, CP, and TH planned and designed the study. SH conducted the aerosol sampling, the sample preparation and analysis, the evaluation, and wrote the manuscript. DG provided the OPS, rain, and fire data, evaluated the OPS data and total aerosol mass calculations, and revised the manuscript. LK provided and evaluated the SMPS data, helped with MOUDI sampling, and revised the manuscript. RVDS provided the BC data and revised the manuscript. BBM, PA and UP provided scientific input and revised the manuscript. All authors contributed to the discussion of the results and the finalization of the manuscript.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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5 The role of organic aerosols in new particle formation events in the Amazon rainforest

This chapter has been published in *Nature Geoscience* (Machado et al., 2024):

Summary

This chapter provides the environmental context for aerosol formation by examining nanoparticle bursts triggered by rainfall events within the forest canopy in the Amazon rainforest. This study shows how precipitation and canopy-mediated processes influence the nucleation of new particles and the potential generation of cloud condensation nuclei. These observations establish a mechanistic link between environmental dynamics and the chemical processes observed in chapters 2 and 3, emphasizing the importance of meteorology and vertical gradients in understanding aerosol formation in pristine tropical forests.

I am a co-author of this paper. I contributed to the chemical characterization of size-resolved aerosol particles using a Micro-Orifice Uniform Deposit Impactor (MOUDI), focusing on identifying and quantifying sesquiterpene oxidation products across particle sizes. My analysis revealed size-dependent distributions of these compounds, providing molecular-level insights into their role in new particle formation and growth. Additionally, I revised the manuscript to ensure clarity and scientific rigor in the presentation of results and discussion.

Frequent rainfall-induced new particle formation within the canopy in the Amazon rainforest

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5.1 Abstract

Atmospheric aerosol particles are essential for forming clouds and precipitation, thereby influencing Earth's energy budget, water cycle and climate on regional and global scales. However, the origin of aerosol particles over the Amazon rainforest during the wet season is poorly understood. Earlier studies showed new particle formation in the outflow of deep convective clouds and suggested a downward flux of aerosol particles during precipitation events. Here we use comprehensive aerosol, trace gas and meteorological data from the Amazon Tall Tower Observatory to show that rainfall regularly induces bursts of nanoparticles in the nucleation size range. This can be attributed to rain-related scavenging of larger particles and a corresponding reduction of the condensation sink, along with an ozone injection into the forest canopy, which could increase the oxidation of biogenic volatile organic compounds, especially terpenes, and enhance new particle formation. During and after rainfall, the nucleation particle concentrations directly above the canopy are greater than those higher up. This gradient persists throughout the wet season for the nucleation size range, indicating continuous particle formation within the canopy, a net upward flux of newly formed particles and a paradigm shift in understanding aerosol–cloud–precipitation interactions in the Amazon. Particle bursts provide a plausible explanation for the formation of cloud condensation nuclei, leading to the local formation of green-ocean clouds and precipitation. Our findings suggest that an interplay of a rain-related reduction in the condensation sink, primary emissions of gases, mainly terpenes, and particles from the forest canopy, and convective cloud processing determines the population of cloud condensation nuclei in pristine rainforest air.

5.2 Main

Cloud droplet formation and growth depend on the abundance and properties of atmospheric aerosol particles serving as cloud condensation nuclei (CCN) (Albrecht, 1989; Köhler, 1936; Pöhlker et al., 2016). Primary particles are directly emitted from natural or anthropogenic sources, and secondary particles can be generated in the atmosphere through new particle formation (NPF) (Kulmala et al., 2004). While the radiative forcing of trace gases is well known, the influence of aerosol particles on clouds and radiation is much more uncertain. The transformation of gases into particles (Kerminen et al., 2018) is critical for the radiative budget, hydrological cycle, climate, air quality and public health. Condensable vapours can form particles that scatter or absorb radiation and initiate cloud formation when they become large enough to serve as CCN (Andreae & Rosenfeld, 2008; Seinfeld, J. H. & Pandis, S. N., 2016).

Atmospheric NPF involves the oxidation of volatile compounds to generate condensable vapours that can form stable molecular clusters through nucleation and undergo further growth by condensation or coagulation (Kerminen et al., 2018; Kulmala et al., 2004). Chamber experiments have shown that the oxidation of biogenic volatile organic compounds (BVOC), such as terpenes, can generate organic vapours of extremely low volatility, initiate NPF and produce secondary organic aerosol in the absence of sulfuric acid, a common precursor of NPF (Ehn et al., 2014; Kirkby et al., 2016; Tröstl et al., 2016). A recent field study in the transition region between temperate and boreal forests in Canada confirmed that NPF can occur without sulfuric acid precursor sources and suggested nucleation of extremely low-volatility organics as a source (Andreae, Andreae, Ditas, & Pöhlker, 2022). Under pristine conditions in

the Amazonian wet season, sulfate concentrations are also very low, and the origin of the background aerosol population has remained enigmatic for decades (for example, refs. (Artaxo, Maenhaut, Storms, & van Grieken, 1990; Pöhlker et al., 2012; Pöschl et al., 2010).

NPF events in which the size distribution evolves in a characteristic 'banana' shape starting around 10 nm or even lower are rarely observed in the Amazon region (Rizzo, Artaxo, Karl, Guenther, & Greenberg, 2010), but rain-induced particle bursts occur frequently during the wet season (Wimmer et al., 2018). Ground-based measurements at the Amazon Tall Tower Observatory (ATTO) revealed that 28% of the days between January and June, which are the rainiest months, were characterized by a sudden occurrence of particles with diameters smaller than 50 nm (ref. (Franco et al., 2022)). In the course of rainfall events, particles in the nucleation mode size range (<50 nm) can increase in concentration, whereas levels of large Aitken particles and accumulation mode particles tend to decrease (Machado et al., 2021) due to CCN activation and precipitation scavenging (Khadir et al., 2023; Pöhlker et al., 2021). Rainfall further decreases the condensation sink and, accordingly, the rate at which vapours condense onto existing particles, thereby facilitating new particle formation.

Observational studies and large eddy simulations have demonstrated that deep convective clouds can efficiently transport BVOC and other reactive trace gases and promote NPF in the upper troposphere (Andreae et al., 2018; Bardakov et al., 2020; Ekman et al., 2008; Krejci et al., 2003). The appearance of new particles in the Amazonian boundary layer has been attributed to downdraft events that bring down particles from the upper troposphere, which is rich in freshly nucleated particles (Andreae et al., 2018; Krejci et al., 2003; Liu et al., 2023; Wang et al., 2016b). However, downdrafts occur mainly in the low to middle troposphere (Machado et al., 2021), and NPF in the upper troposphere occurs in the outflow of deep convective systems, that is, outside the boundaries and internal downdrafts of clouds (Williamson et al., 2019). Studies based on large eddy simulations (Bardakov, Krejci, Riipinen, & Ekman, 2022) have revealed that the primary source of particles in downdrafts is the middle troposphere at approximately 5 km altitude and that particles originating from the upper troposphere cannot reach the surface within a 2 hour time frame. Global model simulations incorporating a regional nested high spatial resolution model (Wang, Gordon, Grosvenor, Andreae, & Carslaw, 2023b) demonstrated that vertical transport of freshly nucleated particles in the upper troposphere is not expected to contribute to boundary-layer aerosol concentrations within the timescale of a few days.

Climate change and deforestation are rapidly changing the environmental balance of the Amazon (Andreae et al., 2015; Davidson et al., 2012). Unravelling fundamental processes in Amazonian atmosphere–biosphere exchange, such as the spatiotemporal patterns and importance of NPF as a potential source of the natural background aerosol, is thus of particular importance because the wet season in the central Amazon rainforest allows the study of the interaction and evolution of aerosols, clouds and precipitation under near-pristine and preindustrial-like conditions. In addition, atmospheric circulation patterns are altered on synoptic scales, for example, through a changing El Niño/La Niña frequency, affecting long-range transport, downdraft characteristics, rainfall patterns and, consequently, Earth's radiative budget. Our ability to forecast these changes in Amazonia and beyond will depend largely on a correct representation of fundamental processes, including aerosol–cloud interactions in regional and global climate and Earth system models.

In this Article, we combine multiple long-term measurement datasets from ATTO (Andreae et al., 2015) at different altitudes inside and above the rainforest canopy (0.05–325 m above ground). Moreover, we use data from the recently established ATTO Campina site, which is equipped with a broad spectrum of remote-sensing techniques. The combination of measurements and modelling of the vertical atmospheric profile and dynamics, as well as boundary-layer concentrations of aerosols and reactive and nonreactive trace gases, provide unique insights into the atmospheric processing of the Amazonian biogeochemical reactor. We explore largely unresolved processes in the complex cascades

of atmospheric chemistry–meteorology and aerosol–cloud interactions and feedback loops, which are characteristic of the Amazon ‘Green Ocean’ atmosphere. Our focal point is the interplay of rainfall, aerosols and new particle formation during rain events.

5.3 Interplay of rainfall, aerosols and NPF

During rain events, there is a marked increase in the concentration of particles in the sub-40 nm range, highlighting a direct link between aerosol particle bursts and precipitation. Figure 5.3-1 a illustrates the temporal evolution of aerosol particle number–size distributions observed above the rainforest canopy (60 m) during the wet season. The contour plot, which extends from 5 hours before to 5 hours after the maximum rainfall intensity, shows a marked decrease in the concentration of particles in the upper size range (accumulation and Aitken modes), concurrently with an increase in the concentration of particles in the size range below 40 nm (small particles from the Aitken mode and the nucleation mode). Figure 5.3-1 b shows the average size distributions before (–3 to –1 hour) and after (+1 to +3 hour) the maximum rain rate. Decreased particle concentrations in the accumulation and Aitken modes after rainfall and, by contrast, increased sub-40 nm mode concentrations after the rainfall event are evident.

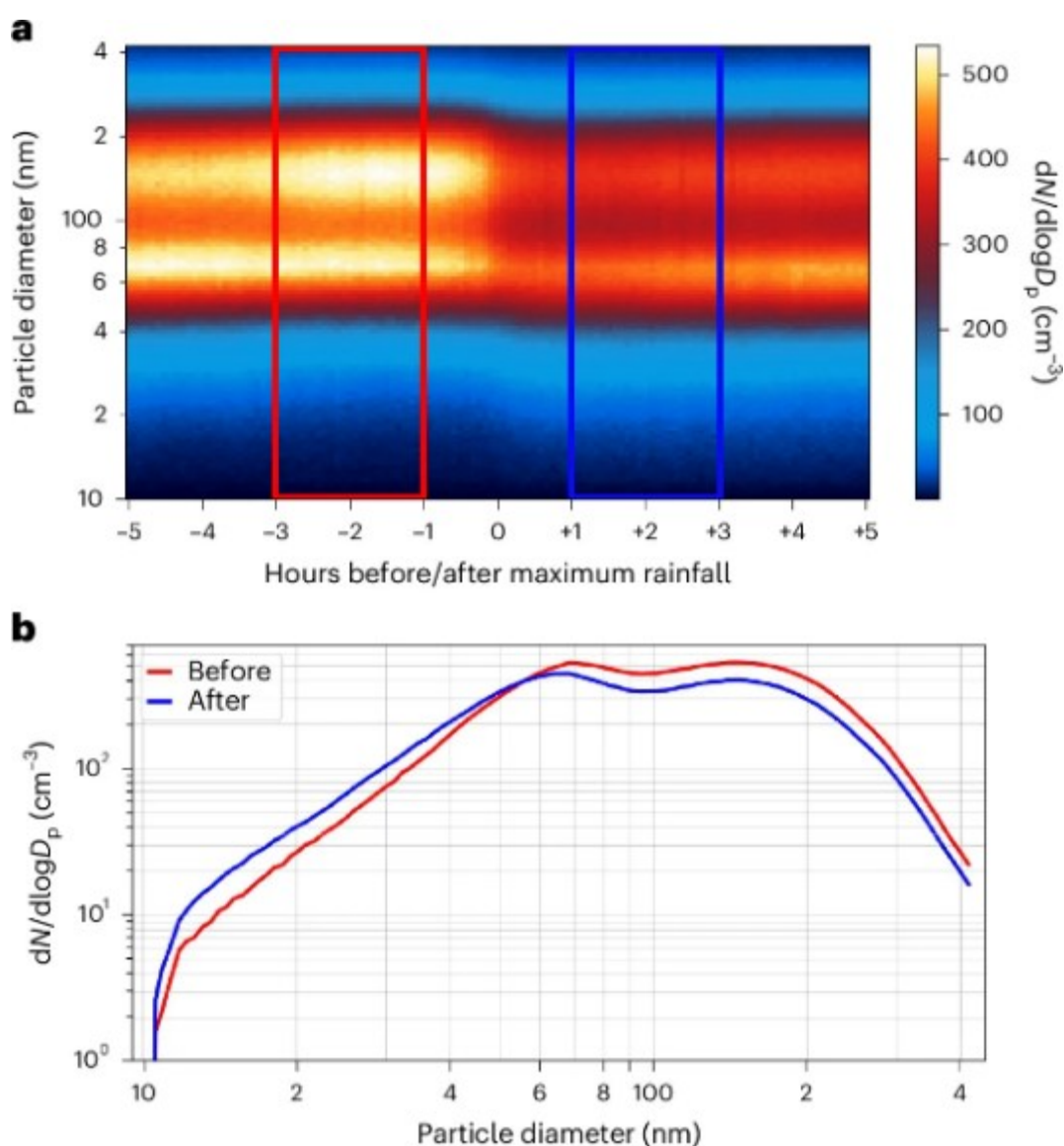


Figure 5.3-1: a, Evolution of aerosol particle number–size distributions at an altitude of 60 m from 5 hours before to 5 hours after the maximum rainfall intensity. Shown is a composite of 391 rain events between February and May from 2018 to 2020. $dN/d\log D_p$ denotes the particle distribution. b, Median size distribution for particles in the time ranges of –3 to –1 hour before and +1 to +3 hours after the maximum rain intensity. Details on the SMPS measurements and data processing can be found in Methods (‘SMPS and data processing’ and ‘Composites and data processing’ sections). The data were averaged over 391 rain events with rain rates $> 0.5 \text{ mm h}^{-1}$.

To investigate the processes related to NPF and rainfall, we analysed the temporal evolution of ultrafine particle number concentrations in five size classes with diameters from 10 to 100 nm, near the canopy at 60 m and at the top of the tall tower at 325 m. The lowest two size classes of 10–20 nm and 20–40 nm are characteristic for the nucleation mode of atmospheric aerosols, that is, newly formed particles that have undergone rapid initial growth by coagulation and condensation since they were freshly nucleated from molecular clusters with critical sizes around 3 nm (ref. (Kulmala et al., 2012)). The measurements performed immediately above the forest canopy (60 m above ground) reveal (**Figure 5.3-2 a**) an increase in particle number concentration in the nucleation size range, which is a clear indication for NPF (Kulmala et al., 2004), from about 1 hour before to 1 hour after maximum rainfall intensity. By contrast, the concentration of large Aitken and accumulation mode particles exhibits a strong decrease as expected due to CCN activation and precipitation scavenging. The measurements performed higher above the forest canopy (325 m above ground) exhibit similar patterns for Aitken and accumulation mode particles but at substantially lower concentration levels (**Figure 5.3-2 b**). The concentration decrease is even stronger for particles in the nucleation size range, and the increase after maximum rainfall intensity is much less pronounced. The data have been corrected for particle losses in the sample inlet to exclude systematic bias between the measurements at different altitudes. In addition, an elevator was installed at the ATTO tower, continuously profiling between 8 and 318 m, confirming the results (see **Methods** for scanning mobility particle sizer (SMPS) data ('**SMPS and data processing**' section) and for the composite methodology ('**Composites and data processing**' section) and Supplementary Figure S 11.3-1). The different concentration levels observed at 325 m and 60 m altitude suggest that the source of the new particles is in the forest near or within the canopy during rain events in the wet season over the Amazon.

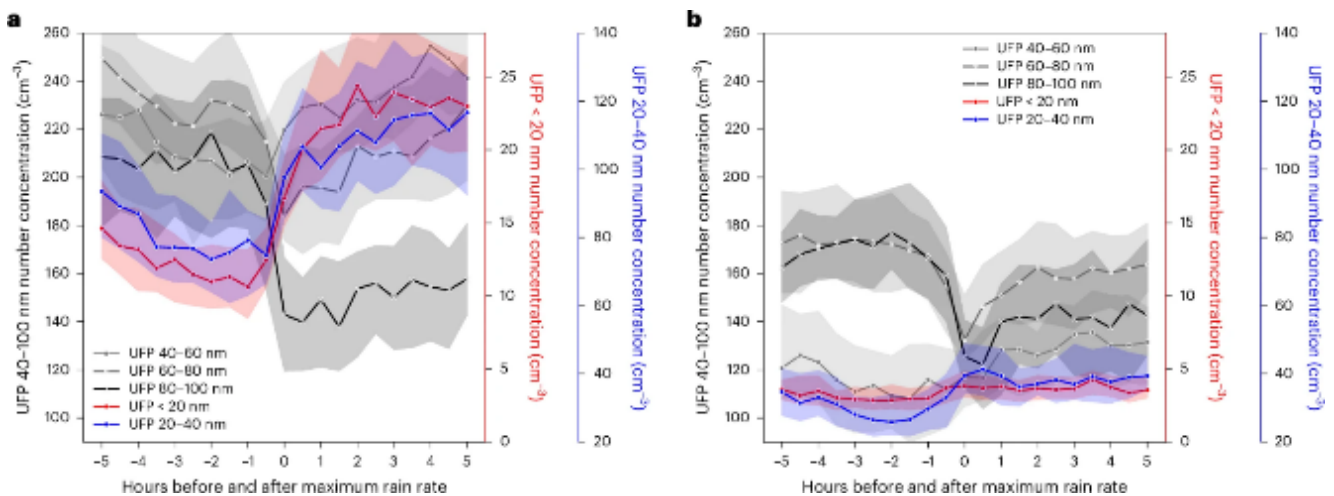


Figure 5.3-2: Median particle concentrations in different size ranges between February and May for 2018–2020, showing 5 hours before to 5 hours after the maximum rainfall event. a, 60 m elevation. b, 325 m elevation. Particle concentrations are divided into the following classes: 10–20 nm (blue), 20–40 nm (red) and the classes 40–60 nm, 60–80 nm and 80–100 nm (grey tones). For 60 m, the increase in the concentration of particles smaller than 40 nm was observed 0.5 hour before the maximum rainfall event up to 1.0 hour later. Larger particles decreased in concentration following rainfall. At 325 m, the increase in nucleation particles was not well defined. Colour-shaded bands represent 95% confidence intervals. The composite was made over 391 rain events with rain rates $> 0.5 \text{ mm h}^{-1}$. UFP, ultrafine particles.

The decrease in particles larger than 40 nm due to precipitation leads to a decrease in the condensation sink, thus promoting the formation of nucleation particles. Figure 5.3-3 presents a comprehensive analysis of the condensation sink (see **Methods** (Condensation sink) for details on the calculation), covering the 5 hours before and after the peak rainfall intensity. The condensation sink exhibits an increasing trend up to 1 hour before maximum rainfall, followed by a sharp decline from 1.3 to $0.9 \times 10^{-3} \text{ s}^{-1}$ within the $+0.5$ hour window and a gradual but continuous increase later. The temporal

reduction in maximum precipitation aligns with an increase in the concentration of nucleation particles, suggesting a fundamental role in the process of NPF. Notably, after 0.5 hour, the condensation sink gradually increases while the nucleation particles continue to rise modestly, indicating the involvement of distinct mechanisms in producing new particles. A box model was used to evaluate the formation of new particles from the surface up to 79 m, confirming the clustering process and subsequent atmospheric nucleation and the effect of reducing the condensation sink (see **Methods** (Box model) and Supplementary Figure S 11.3-2).

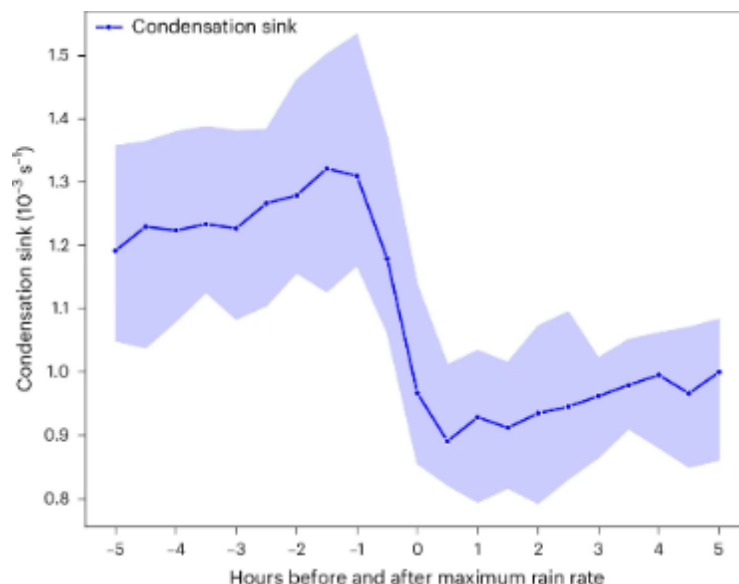


Figure 5.3-3: Median concentration of the condensation sink for ATTO between February and May for 2018–2020, computed from the SMPS data at 60 m from 5 hours before to 5 hours after the maximum rainfall event. The condensation sink increases before the rain until 1 hour before the maximum rainfall, followed by a drastic reduction from 1.3 to $0.9 \times 10^{-3} \text{ s}^{-1}$ until +0.5 hours and then a continuous slight increase. Colour-shaded bands represent 95% confidence intervals. The composite was made over 391 rain events with rain rates $> 0.5 \text{ mm h}^{-1}$.

5.4 New particles are observed forming close to the canopy

An important feature of rainfall events is the injection of O_3 from the relatively ozone-rich free troposphere into the boundary layer (Gerken et al., 2016; Sigler, Fuentes, Heitz, Garstang, & Fisch, 2002; Wang et al., 2016b). Figure 5.4-1 a shows the temporal evolution of the O_3 concentration at different heights (from 0.05 to 79 m) 5 hours before to 5 hours after maximum rainfall intensity. The O_3 concentration inside the forest canopy can increase by more than a factor of three. The O_3 enhancement is modulated by rainfall intensity, but with a phase lag (time interval) of approximately half an hour between the maximum rainfall and maximum O_3 concentration (Figure 5.4-1 b). A clear relationship exists between the ozone injected by the rainfall event and the NPF. The Amazon forest also releases large amounts of BVOC, including isoprene, monoterpenes and sesquiterpenes emitted by vegetation and soil (Guenther et al., 2012; Yáñez-Serrano et al., 2015). Mosses and lichen, which constitute a significant portion of the forest ground cover, release sesquiterpenes when they become moist.

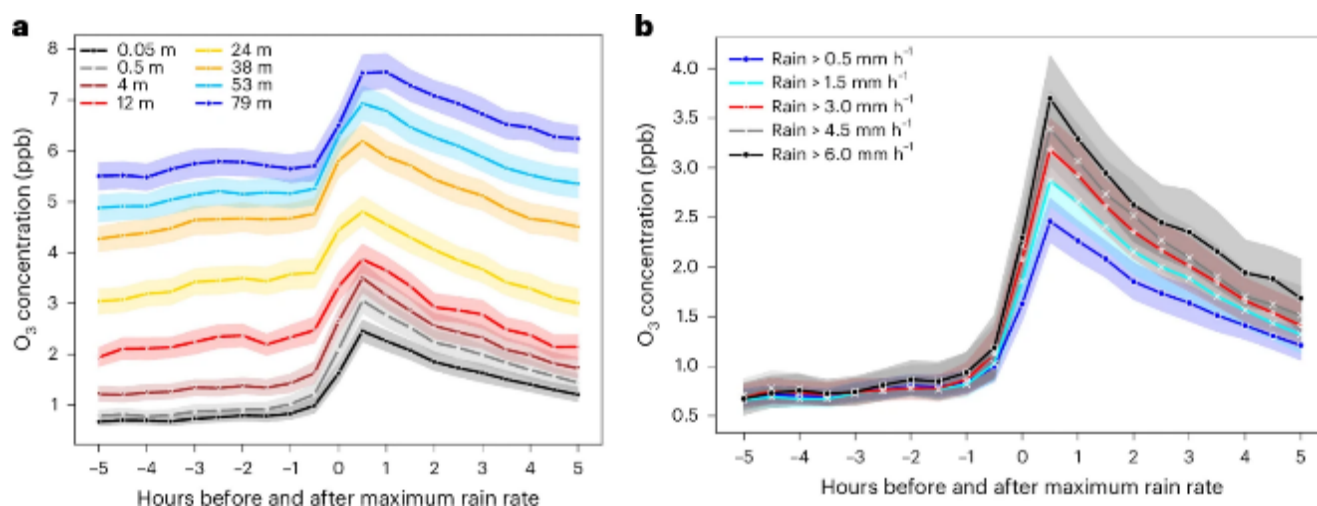


Figure 5.4-1: The O_3 concentration profiles between 0.05 and 79 m, averaged over the wet-season months (February to May) from 2018 to 2020. Representation here is synchronized to rainfall events, covering 5 hours before and 5 hours after maximum rainfall. a, The entire profile. b, The 0.5 m altitude, classified by different rainfall intensities. Colour-shaded bands represent 95% confidence intervals. The composite was made over 336 rain events with rain rates $> 0.5 \text{ mm h}^{-1}$. The O_3 concentration increases up to three times relative to the pre-rain conditions and peaks about 1 hour after the rainfall maximum. The offset between the peaks in rainfall and O_3 concentration does not depend on rainfall intensity, while the increase in O_3 concentration depends on rainfall intensity.

Figure 5.4-2 shows the temporal evolution of O_3 , NO, NO_2 , isoprene, monoterpenes (see **Methods** (O_3 , NO and NO_2 data processing periods and Isoprene and monoterpene data processing periods) for data description) and particles in the nucleation size range sub-40 nm during rainfall events. The O_3 increases while isoprene and monoterpenes decrease sharply. The concentrations of NO_2 and nucleation mode particles increase less steeply and reach a maximum approximately 1 hour after maximum rainfall intensity. During the following hours, the concentrations of O_3 and NO_2 decrease again, while the concentration of nucleation mode particles remains nearly constant. Monoterpene concentrations reach the minimum when sub-40 nm particles reach the highest concentration. The rapid decline in BVOC concentrations at 80 m can be explained by dilution caused by the downdraft, lower emissions due to reduced solar radiation and temperature, but also by increasing chemical loss through oxidation and the formation of highly oxygenated organic molecules (HOMs) and low-volatility organic compounds (LVOCs). Observations show that the concentration near the ground normally increases with rain (Rossabi, Choudoir, Helmig, Hueber, & Fierer, 2018; Schade, Goldstein, & Lamanna, 1999) or in chamber experiments (Faiola et al., 2013); the same behaviour was observed with sesquiterpenes (Bourtsoukidis et al., 2018). At maximum precipitation, the wind speed increased by more than 50%, and solar radiation intensity diminished (Supplementary Figure S 11.3-3). The decrease in air temperature by approximately 10% and the corresponding increase in relative humidity occur at a slower pace, reaching their maximum extent 0.5 to 1.0 hour after the maximum precipitation event (see **Methods** (Weather data processing and periods) for data description). The NO_2 , which is in the opposite phase to NO, shows a slower increase compared with the rapid increase of O_3 . The high concentration of O_3 favours the fast chemical conversion of NO into NO_2 . At the same time, rain continues to bring down ozone-rich air during the process. Size-resolved chemical analysis of aerosol particles conducted at the ATTO research site offers a compelling demonstration of the rapid formation of fresh particles resulting from swift chemical reactions occurring directly above the forest canopy (see **Methods** (Micro-orifice uniform deposition impactors data and experiment) and Supplementary Figure S 11.3-4).

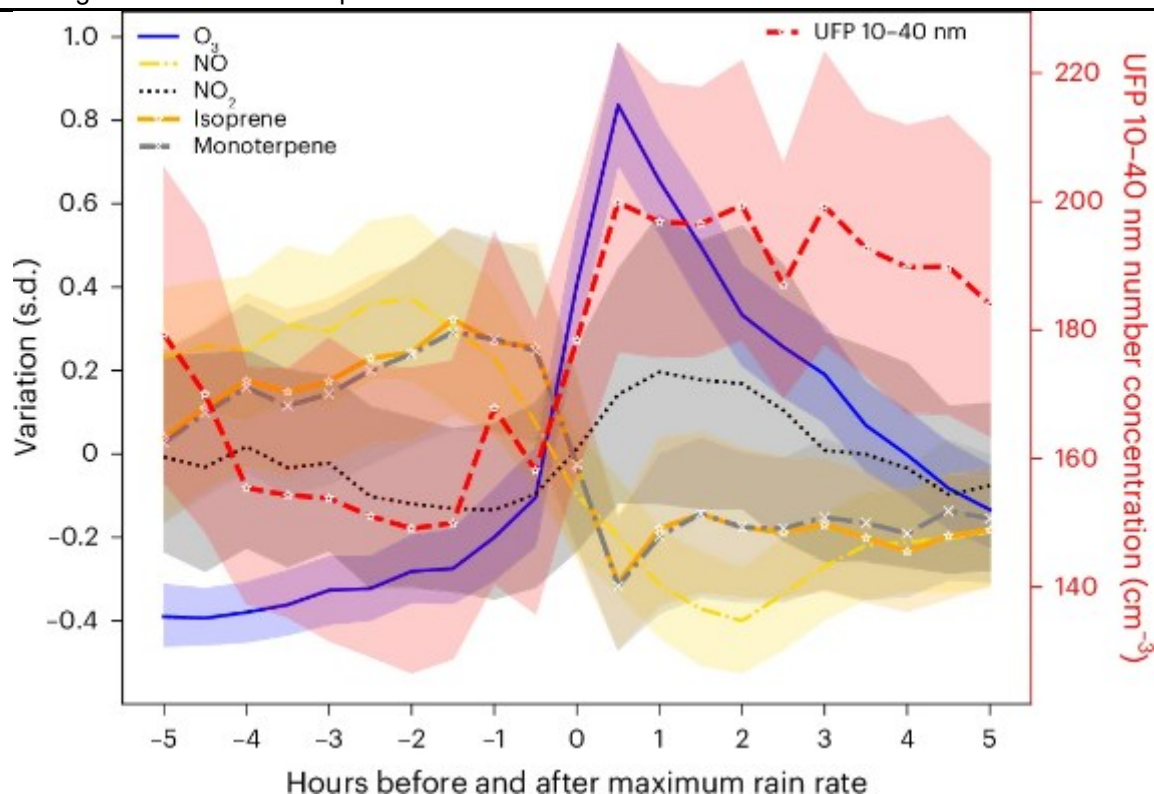


Figure 5.4-2: Composite plot of ATTO trace gas and aerosol data during rain events, using a normalized representation, which shows data from 5 hours before to 5 hours after the rainfall peak for the 2018–2020 wet seasons (February to May). The left axis shows the variation of NO_2 at 12 m height, NO at 0.5 m, O_3 at 4 m, isoprene at 80 m and monoterpenes at 80 m in units of standard deviations. The right axis shows the variation of nucleation particles (10–40 nm) at 60 m in absolute number concentration. The rain-related concentration changes show increases in O_3 and NO_2 , decreases in NO , isoprene and monoterpenes, and an increase in nucleation particles. All time series incorporate wet-season data (that is, February to May) from 2018 to 2020. Colour-shaded bands represent 95% confidence intervals. The composite was made over 391 rain events with rain rates $> 0.5 \text{ mm h}^{-1}$. For NO , NO_2 and O_3 , 114, 94 and 336 rain events, respectively, were used, and for isoprene and monoterpene, 90 rain events were used for the composite.

The nucleation mode particles show a slow increase, indicating that they are not brought down with the descending air current but rather are newly formed due to the reduction of the condensation sink and the chemical reactions that form secondary organic aerosol precursors. Concentrations of particles below 40 nm persist at elevated levels for up to 5 hours following a rain event. This phenomenon is probably linked to the release of sesquiterpenes after rain, as distinct sesquiterpene species continue to be emitted for up to 6 hours after heavy rainfall, in contrast to subsequent dry days (Bourtsoukidis et al., 2018). Another contributing factor is the rainfall timing, which typically occurs in the late afternoon and evening. Ultrafine particles become trapped within the nocturnal boundary layer, with their concentrations remaining relatively stable throughout the night. Subsequently, there is a significant decrease in the morning, accompanied by an increase in the Aitken and accumulation modes (Machado et al., 2021). All these processes highlight the importance of considering local processes in understanding particle dynamics during precipitation events.

A characteristic feature of NPF is the growth of newly formed particles from the nucleation to the Aitken size range. To investigate this process, we analysed the diurnal evolution of the aerosol particle size distribution for days with different O_3 concentration levels at night, as shown in Supplementary **Figure S 11.3-5**. Days with high nighttime O_3 levels are days with rainfall occurring during the late afternoon and nighttime. The physical mechanism responsible for higher nighttime O_3 concentrations was the late-afternoon and nighttime convection that injects O_3 into the canopy. High O_3 nighttime concentrations are associated with rainy nights; by contrast, low nighttime O_3 concentrations are associated with the absence of rain events during the night. The convective boundary layer begins to decay at sunset, giving

rise to the nocturnal boundary layer (Henkes, Fisch, Machado, & Chaboureau, 2021). During the wet season, the nocturnal boundary layer is lower than 400 m, and the air within the canopy becomes isolated from the free atmosphere. If a particle burst occurs in the evening or at night, the concentration of sub-40 nm particles remains nearly unchanged due to their relatively long lifetime of several hours (Williams, Reus, Krejci, Fischer, & Ström, 2002). The O₃ injected during nighttime rainfall events remains trapped inside the canopy and can lead to high nighttime O₃ concentrations despite the continuous production of NO from the soil that consumes O₃ throughout the night. When sunlight reaches the canopy, growth process events can be easily identified on days with higher previous nighttime O₃ concentrations. Measurements of the oxygenated and total organic aerosol concentrations at 60 and 325 m by two aerosol chemical speciation monitors (ACSMs) shed more light on the early morning growth process (see data description and methodology in **Methods (ACSM data periods)** and Supplementary Figure S 11.3-6).

5.5 Intrinsic link between nucleation, gases and precipitation

In this Article, we propose an intrinsic relationship between sub-40 nm particles, reactive trace gases and weather events in the Amazon. Rainfall events change the trace gas concentrations considerably just above the canopy and produce bursts of sub-40 nm particles, which grow into the Aitken mode size range during the early morning of the next day. Our findings highlight several aspects of the rainfall–aerosol interaction in central Amazonia. (1) Sub-40 nm particles frequently occur as bursts during rainfall events, probably associated with a series of reactions and the reduction of the condensation sink. (2) These bursts appear to be local features, occurring mostly below 325 m. They are not clearly observed at 325 m, and the model simulations indicate the main process occurs within and near the canopy. (3) The major sub-40 nm particle bursts occur together with injections of O₃ into or just above the canopy. (4) The maximum concentration of both particles and O₃ occurs around 0–30 minutes after the peak in rainfall. Furthermore, during this period, NO₂ also reaches its highest concentration, whereas NO, isoprene and monoterpene concentrations decrease to their minimum levels. (5) The condensation sink decreases with the rainfall, reaching its minimum value 30 minutes after the rain rate is at its maximum and facilitating the formation of the nucleation particles. (6) Model simulations indicate that the peak of HOMs and LVOCs and the biogenic nucleation rate occur mainly below 24 m, 30 minutes after the maximum rain rate. Finally, a clear growth process was observed in the early mornings after nights with ozone-rich air, typically following rain-rich days.

Figure 5.5-1 illustrates the atmospheric processes in the Amazon that occur during rain events in the afternoon/evening. The evolution of trace gas concentrations from the time before the onset of rain until up to 2 hours after the maximum precipitation suggests that the particle burst is produced by the reduction of the condensation sink and reactions involving O₃, terpenes and NO_x. Sesquiterpenes are likely to be a major player in particle formation. The growth process occurring after sunrise on days following high nighttime O₃ concentrations suggests that the growth of sub-40 nm organic particles to the Aitken mode is initiated by high nighttime O₃ concentrations, followed by photo-oxidation processes in the morning. The high concentrations of O₃ injected into the canopy during the evening and night stay trapped in the nocturnal boundary layer, favouring the oxidation of organic compounds (Crounse, Nielsen, Jørgensen, Kjaergaard, & Wennberg, 2013). As soon as the sun rises, the total and oxidized organic aerosol concentrations close to the canopy sharply increase, moving the particle size from the nucleation mode to the Aitken and accumulation mode.

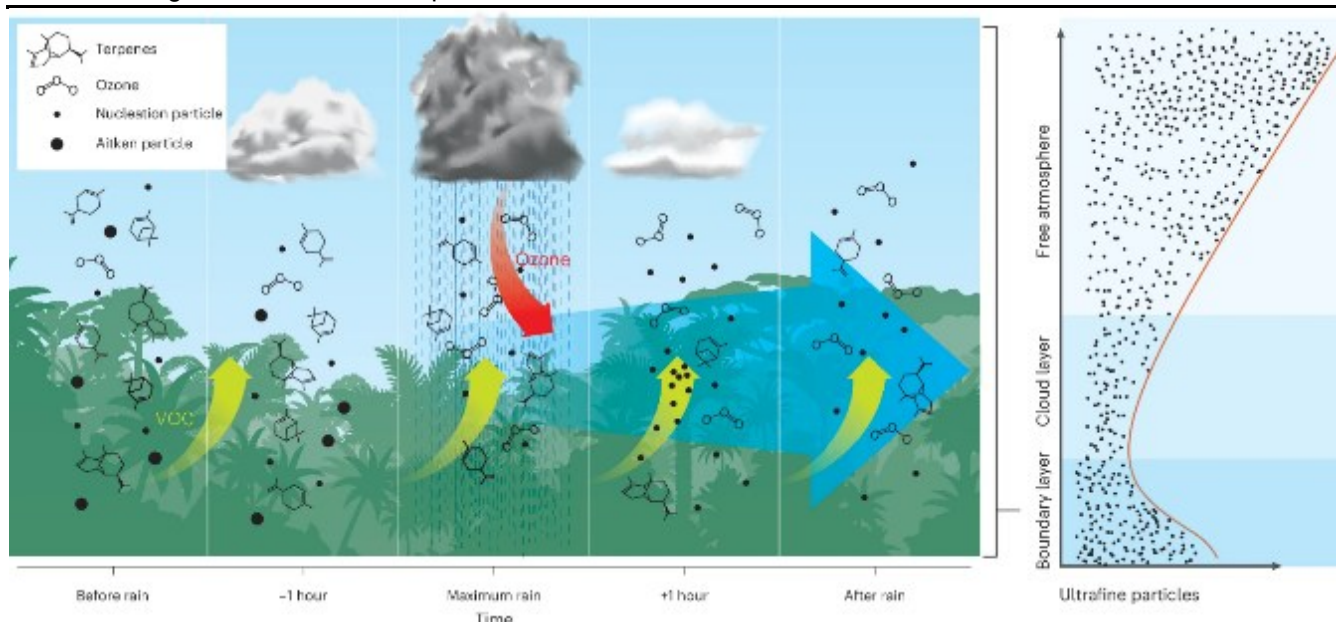


Figure 5.5-1: Concentrations of ozone, BVOC (monoterpenes–sesquiterpenes) and particles before and after the maximum rain rate, during the night and the early morning of the following day.

The locally formed nucleation particles grow mainly during the morning for the Aitken modes and are quickly transported to the free troposphere by the development of the convective boundary layer (Henkes et al., 2021). In the Amazon rainforest, three atmospheric layers can be defined with respect to the population of ultrafine particles: the mixed layer, between the surface and 1,200 m; a transitional layer between 1.2 and 4 km, called the convective cloud layer, where the lowest concentration of ultrafine particles is found; and the layer above, where the maximum concentration is near the tropopause (Andreae et al., 2018; Krejci et al., 2003). Above the mixed layer, at about 1,500 m, are the low-level jets of the Amazon (Anselmo, Schumacher, & Machado, 2020). When a new convective cloud forms, the air currents in these particle-rich layers converge on the convective cell, and the particle-rich air is transported in updrafts and contributes to the formation of raindrops. Deep convection does not occur everywhere simultaneously but only in a few areas. Therefore, the flux convergence receives air from all directions in the neighbouring areas and can easily feed the CCN into these small regions where deep convective clouds occur. A simple calculation can be made to highlight the importance of the NPF on the Amazonian Green Ocean clouds. From the results of ref. (Cecchini et al., 2017), we can derive the linear equation describing the cloud droplet concentration with height in Amazonas and integrate from the cloud base to the cloud top at 4,000 m (freezing level and average cloud top height of cumulus clouds). From this calculation, we can estimate the number of warm cloud droplets at 450,000 per cm^2 . Considering the NPF and the boundary-layer height of 1,000 m (ref. (Dias-Júnior et al., 2022)), there are about 250,000 particles per cm^2 in the boundary layer. If we now consider that the cloud cover near Manaus varies between 76% and 42% (ref. , and if we apply a factor to correct for the fact that we do not have clouds everywhere, we get a very close figure. This shows that the NPF processes in the boundary layer produce enough CCN for the Green Ocean clouds. Many other mechanisms produce CCN in the Amazon region, mainly from anthropogenic sources. However, only this mechanism can provide the basic background of CCN for the cumulus clouds in the remote forest region of the Amazon.

Finally, to test the hypothesis and prove whether ozonolysis is the main process in the formation of new particles in the boundary layer, we propose for future work the use of a chamber experiment at the canopy level, controlling the ozone concentration. The chamber should have a particle size magnifier to measure particles from 1 to 2 nm and a mass spectrometer to measure HOM composition, such as nitrate chemical ionization–atmospheric pressure interface time of flight. With this configuration, it will be possible to characterize the influence of ozone on particle formation.

Understanding the feedback mechanism between rainfall, trace gas and aerosol concentrations is of utmost importance on a planet experiencing a rapidly changing climate. The nucleation of particles, which subsequently become CCN and enable cloud formation, is closely tied to previous rainfall events. While anthropogenic emissions from biomass burning and fossil fuels can produce CCN, only this specific mechanism can generate the CCN concentrations required to create the Green Ocean Amazon pattern characteristic of the wet season. This pattern is distinguished by cloud droplet concentrations as low as a few hundred droplets at cloud base (Cecchini et al., 2016), of the same order as the newly formed particles described in this study.

5.6 Methods

5.6.1 SMPS and data processing

ATTO is situated 120 m above sea level and 150 km northeast of Manaus. The ATTO and the co-located Campina site are nested in the heart of the central Amazon rainforest within the Uatumã Sustainable Development Reserve. This pristine site has remained largely untouched by deforestation and is characterized by an ecosystem known as a lowland evergreen rainforest. The canopy rises between 30 and 40 m, and the trace gas and aerosol instrumentation used here spans from ground level up to 325 m. The particle number–size distribution measurements were collected from two SMPSs (TSI), each comprising a differential mobility analyser and condensation particle counter. Both SMPS systems were operated in parallel at two different sampling heights at the ATTO site. One SMPS was sampling from the 60 m inlet of the triangular mast and the second from the 325 m inlet of the Tall Tower. The two SMPS instruments cover a particle size range from 10 to 400 nm, and the sizing accuracy was frequently checked using monodisperse polystyrene latex particles. Data were acquired and exported with Aerosol Instrument Manager software (versions 9 and 10; TSI). The original temporal resolution was 5 minutes and this was converted to 30 minutes to maintain the same time resolution as the other data. The data were adjusted to standard temperature (273 K) and pressure (1,013.25 hPa). The theoretical losses due to the long inlets at 60 and 325 m were corrected on the basis of a methodology using size-dependent correction factors (Weiden, Drewnick, & Borrmann, 2009). For the SMPS measurements at 60 m and 325 m, the composites were computed with 236 rain events, using the particle size distribution from 2018 to 2020. The robotic lift is an automatic elevator platform installed at ATTO's southern corner on the Tall Tower that allows continuous measurements of vertical profiles between 8 and 318 m. Its regular configuration carries an SMPS (NanoScan SMPS, Model 3910, TSI) along with various other counting and sizing instruments. SMPS data were collected during May 2023 following a strategy of consistently acquiring profiles at a rate of two per hour, where each profile takes 15 minutes to cover the 310 m elevation range. The data were compiled by selecting the 0–80 m and 240–320 m layers and computing the sub-20, sub-40, and sub-60 nm concentrations. The data were resampled to 30 minute time steps, which include one upward and one downward measurement. The 30 minute concentrations at 0–80 m and 240–320 m were analysed as a function of the rainfall events following the same methodology used in the other composites. During this month, the rain gauges at 81 m and 32 m had some gaps. A new dataset was built by combining the measured data at 81 m and 325 m with those of NASA's (National Aeronautics and Space Administration's) IMERG (Integrated Multi-satellite Retrievals for Global Precipitation Measurement) to produce one continuous data point every 30 minutes.

5.6.2 Composites and data processing

Composites were based on the time of maximum rainfall events (intensity greater than 0.5 mm h^{-1}) to analyse the evolution of different gases and particles during rainfall events. Tests were performed using the rainfall events at the maximum, the beginning and the end of the event, and the results were conceptually similar, except for the lag time. Composite analyses are useful tools with which to formulate physical hypotheses on the associations between environmental variables that occur over time (Boschat, Simmonds, Purich, Cowan, & Pezza, 2016) and to determine the basic characteristics of a

particular phenomenon. Each rainfall event was selected in a 10 hour window with rain rate $> 0.5 \text{ mm h}^{-1}$, and the time was selected as the maximum rain rate in this window. This analysis involves collecting large numbers of standardized cases (the maximum rainfall cases in each event) and compositing them with all other variables as a collection. The computing composite median and statistical significance (95%) of the selected pattern, in this case, the gas and particle concentrations during rainfall events, are computed.

5.6.3 Condensation sink

The condensation sink was based on the particle number–size distribution, similarly to ref. (Franco et al., 2022). The condensation sink (CS) is described by (Dal Maso et al., 2002; Kulmala et al., 2012)

$$CS = 2\pi D \int_{D_{p,min}}^{D_{p,max}} D'_p \beta_m(D'_p) dD'_p = 2\pi D \sum_{D'_p} \beta_m(D'_{p,i}) D'_{p,i} N_i [s^{-1}] \quad \text{Equation 5.6-1}$$

where N_i represents the particle concentration at the diameter of the i -th size bin, D is the diffusion coefficient of the precursor condensable vapour, and β_m is the transition-regime correction (Fuchs & Sutugin, 1971). The condensation sink quantifies the ability of particles to remove condensable vapours from the atmosphere, incorporating them into the particle population and directly influencing the particle growth. This study considers $D = 0.117 \text{ cm}^2 \text{ s}^{-1}$, the value for sulfuric acid (H_2SO_4) to obtain CS (Gong et al., 2008), commonly used in the literature for comparisons with other studies. In this study, each PNSD returned a single condensation sink based on Equation 5.6-1, with a starting diameter of 10 nm and a final diameter of 400 nm, as described in the ‘SMPS and data processing’ section.

5.6.4 Box model

A box model was used to calculate the HOM and LVOC concentrations and the pure organic nucleation rate. We assume a steady state between production and loss for both HOMs and LVOCs, and then the concentration of HOMs ([HOM]) and LVOCs ([LVOC]) can be estimated, respectively, from

$$[\text{HOM}] = \frac{Y_{\text{AP} \cdot \text{O}_3^-} \text{HOM } k_{\text{AP} \cdot \text{O}_3} [\text{AP}][\text{O}_3]}{CS_{\text{HOM}}} \quad \text{Equation 5.6-2}$$

$$[\text{LVOC}] = \frac{Y_{\text{AP} \cdot \text{O}_3^-} \text{LVOC } k_{\text{AP} \cdot \text{O}_3} [\text{AP}][\text{O}_3] + Y_{\text{ISO} \cdot \text{O}_3^-} \text{LVOC } k_{\text{ISO} \cdot \text{O}_3} [\text{ISO}][\text{O}_3]}{CS_{\text{LVOC}}} \quad \text{Equation 5.6-3}$$

where $_{\text{HOM}} = 2.9\%$ is the HOM yield from the α -pinene oxidation by ozone (Kirkby et al., 2016), and the LVOC yields from the ozonolysis of α -pinene ($Y_{\text{AP} \cdot \text{O}_3^-} \text{LVOC}$) and isoprene ($Y_{\text{ISO} \cdot \text{O}_3^-} \text{LVOC}$) are assumed to be 13% and 3% (Gordon et al., 2016), respectively. $k_{\text{AP} \cdot \text{O}_3}$ and $k_{\text{ISO} \cdot \text{O}_3}$ are the reaction rate constants for the oxidation of α -pinene and isoprene by ozone, respectively, the values of which follow the International Union of Pure and Applied Chemistry (Atkinson et al., 2006). The concentration of α -pinene, [AP], is approximated by that of monoterpenes. CS_{HOM} and CS_{LVOC} are the CSs of HOMs and LVOCs, respectively, and are substituted by the condensation sink of H_2SO_4 as an approximation here. The pure biogenic nucleation rate (J_{org}), contributed by neutral and ion-induced processes (Kirkby et al., 2016), is parameterized as a function of HOM and ion concentration (Liu et al., 2023). Here the model assumes the ion concentration as 500 cm^{-3} , typical for the near-ground condition in boreal forests (Hörrak et al., 2008). In addition, a temperature dependence of J_{org} is applied (Dunne et al., 2016).

5.6.5 O₃, NO and NO₂ data processing periods

The vertical profiles of NO_x (NO and NO_2) and O_3 were obtained from 2014 to 2020 with an Ecophysics CLD TR 780 and a 49i ozone analyser (Thermo Scientific 49i), respectively (Andreae et al., 2015;

Nascimento et al., 2022). The CLD measurements are based on a gas-phase chemiluminescence technique that directly retrieves the mixing ratio of NO. The NO₂ is measured through the conversion of NO₂ to NO by a photolytic converter, based on blue light (Solid-state Photolytic NO₂ Converter (BLC); DMT). The detection limits for NO and NO₂ are 0.05 and 0.1 ppb, respectively. The zero-point noise limits the signal noise to less than 0.5% of the signal. The O₃ measurements are based on the ultraviolet-absorption technique, which provides detection limits of 0.5 ppb. To reduce the effects of varying water vapour concentrations, the O₃ set-up uses Nafion dryers. To ensure high-quality measurements, the instruments were calibrated from time to time with a dynamic gas calibrator (Thermo Environmental Model 146C). This device has four different modes that are useful for obtaining (1) the detection limits (zero air calibration), (2) NO calibration (gas dilution mode), (3) NO₂ calibration (gas-phase titration mode) and (4) O₃ calibration (transfer standard mode). The data were collected at the Instant tower at eight different heights (0.05, 0.5, 4, 12, 24, 38, 53 and 79 m), where 0.05 m is just above the surface and 79 m is about 40 m above the canopy. These different levels provide a good vertical resolution of the gas concentration. The gases were sampled every 5 minutes, and the time step was rescaled to 30 minutes for each height, the same period as the other aerosol and gas parameters used in this study. The O₃, NO and NO₂ measurements were collected from 2018 to 2020. Owing to the complexity of the NO and NO₂ measurements, there were several periods for which data were missing, which affected the compositing with the rainfall data. For O₃, 336 rain events were computed, but for NO and NO₂, only 114 and 94 rain events, respectively, were used for the composite.

5.6.6 Isoprene and monoterpene data processing periods

Observations of isoprene (C₅H₈) and monoterpenes (C₁₀H₁₆) at ATTO were conducted using a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS; Ionicon Analytik). It was operated with H₃₀⁺ as primary ions, a drift tube pressure of 3.5 hPa and E/N (ratio of the electric field to the number density) of 120 Td. Isoprene (*m/z* 69.069) and monoterpenes (*m/z* 137.132) are detected with an uncertainty of about 20%. Their detection limits are 40 and 21 ppt, respectively. Mixing ratios were calibrated using a VOC (volatile organic compound) gas standard (Apel-Riemer Environmental), which contains isoprene and α -pinene to represent the sum of monoterpenes. To obtain a vertical profile of VOC mixing ratios, sample inlets (9.5 mm OD insulated Teflon) from 80 m, 150 m and 320 m were connected to the PTR-TOF-MS, installed at the foot of the ATTO tower. The sampling height varies with a frequency of 5 minutes. Thus, air from each height is analysed for 5 minutes every 15 minutes. Each inlet line was flushed before the sampling occurred. The data cover the period from 2018 to 2019. The data were resampled to 30 minutes. The composite with rainfall events was computed using 90 rainfall events during the wet season.

5.6.7 Weather data processing and periods

This study used local air temperature (*T*), relative humidity (RH), precipitation (*P*), and wind and solar radiation measured at the ATTO site from May 2013 to December 2016. The variables *T* and RH were measured using a Thermohygrometer (CS215, Rotronic Measurement Solutions), rainfall was obtained by a rain gauge (TB4, Hydrological Services), the wind parameters were obtained through a two-dimensional sonic anemometer (WindSonic, Gill Instruments) and the solar radiation with a net radiometer (NR-LITE2, Kipp & Zonen). All the instruments operate at a height of about 80 m on the Instant tower (Andreae et al., 2015; Franco et al., 2022). Rainfall data for 2018 and 2020 were collected at the ATTO tower. The composites were computed using 236 rain events.

5.6.8 Micro-orifice uniform deposition impactors data and experiment

Aerosol sampling was done with a micro-orifice uniform deposit impactor sampler (MSP, Model 125-R) connected to an aerosol inlet at 60 m height to collect aerosol particles according to their aerodynamic diameter. Thirteen stages, equipped with baked quartz filters (Whatman, QM-A), enabled sampling of particles covering diameters between 10 nm and 10 μ m at a constant flow of 10 l minute⁻¹. Blank filters

were collected by the same procedures, but with a HEPA filter (PALL 12144, HEPA capsule filter) connected between the aerosol inlet and the inlet of the micro-orifice uniform deposit impactor. Sampling was performed in May 2022 for 5 days at both heights. The aerosol sample analysis was performed using filter samples extracted three times by adding 1.5 ml of a 9/1 mixture of methanol and water (Fisher Scientific, Optima grade). The samples were subsequently agitated for 30 minutes on a laboratory shaker. The combined liquid phases were evaporated by a stream of N_2 (0.5 l min^{-1}) using a Turbovap LV (Biotage) to approximate 200 μl . The residue was then filled to 1 ml with a 1/1 (v/v) mixture of water and acetonitrile (Fisher Scientific, Optima grade). The extracts were sonicated for 10 minutes and filtered through a $0.2\text{ }\mu\text{m}$ PTFE syringe filter (Carl Roth, Rotilabo KC 94.1). We added 5 μl of a 3,500 ppb solution of Camphor-10-sulfonic acid (Sigma Aldrich, 98%) in a 1/1 (v/v) mixture of water and acetonitrile (Fisher Scientific, Optima grade) as internal standard to correct the volume uncertainty. Ten microlitres of each sample were analysed three times by ultra-high-performance liquid chromatography (ThermoFisher Scientific, UltiMate 3000) coupled to a high-resolution Orbitrap mass spectrometer (ThermoFisher Scientific, Q Exactive). A heated electrospray ionization (ESI) source was installed and operated in the negative ionization mode. The instrument was externally calibrated with a calibration solution (Fisher Scientific, Pierce) and a 2 mM sodium acetate aqueous solution, providing mass accuracy below 1 ppm. The analysis was performed in the m/z 50–750 range at a mass resolving power of 140,000 at m/z 200. The following ESI-MS parameters were used for the measurements: ESI capillary temperature $300\text{ }^\circ\text{C}$; spray voltage 3.2 kV; sheath gas flow 30; auxiliary gas glow 10; S-lens RF level 50%. The ultra-high-performance liquid chromatography system was operated with an Acquity UPLC CSH fluoro-phenyl column ($100 \times 2.1\text{ mm}$, $1.7\text{ }\mu\text{m}$) from Waters and the mobile phase A (water with 2% acetonitrile and 0.04% formic acid) and mobile phase B (acetonitrile with 2% water). The conditions for gradient elution were as follows: 0–11 minutes, 10% B; 11–12 minutes, linear increase to 99% B; 12–12.5 minutes, linear decrease to 10% B; 12.5–13 minutes, 10% B at a constant flow rate of $500\text{ }\mu\text{l min}^{-1}$. The column temperature was maintained at $30\text{ }^\circ\text{C}$. To ensure the identification of β -nocaryophyllonic acid and β -caryophyllinic acid, standard compounds were synthesized as described by ref. (van Eijck et al., 2013). Fourteen-point calibration curves were generated with concentrations of β -nocaryophyllonic acid and β -caryophyllinic acid ranging from 0.5 ng ml^{-1} to 500 ng ml^{-1} . All reported values were normalized by the internal standard and field blank corrections.

5.6.9 ACSM data periods

The non-refractory aerosol species' fine-mode aerosol chemical composition measurements were performed using two quadrupole ACSMs (described previously (Ng et al., 2011)). The instrument vaporizes the non-refractory fraction of aerosols at around $600\text{ }^\circ\text{C}$ to the gas phase and ionizes the resulting vapours by an electron beam. This process disintegrates the molecules, whose fragments are observed at their specific mass-to-charge ratios (m/z). Thereafter, the signal of each fragment is used to reconstruct the mass concentration of each chemical aerosol species (organic, nitrate, sulfate, ammonium and chloride) using a fragmentation table (Allan et al., 2004), which contains the known fragmentation pattern of each aerosol species. In addition, some specific compounds are used to gain insight into the aerosol composition. In particular, a high signal from the fragment with m/z of 44 (Org44), related mainly to CO_2^+ , which was decomposed from organic aerosols, is a proxy for highly oxygenated organic aerosol (Canagaratna et al., 2015). The samples were collected from December 2021 to March 2022 simultaneously at 60 and 325 m heights at the ATTO site. The time resolution was 30 minutes. The data for each instrument were corrected for their air beam, flow rate, and collection and ionization efficiency through ammonium nitrate and ammonium sulfate calibrations. Then the dataset was averaged to a common time basis and corrected for standard temperature and pressure (273 K and 1,013.25 hPa). The aerosol range of measurement is from 75 nm to 650 nm.

Data availability

The datasets presented here are available on GitHub (<https://gitlab.gwdg.de/luiz.machado/newparticleformation.git>).

Code availability

The scripts are available on GitHub (<https://gitlab.gwdg.de/luiz.machado/newparticleformation.git>).

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Contributions

CDL.A.T.M., C.P., J.W. and H.H. conceived and designed the study. L.A.T.M., M.A.C., G.R.U., M.A.F., A.R., L.A.K., B.B.M., S.B., S.H., M.L.P., A.R., B.H., J.C., M.A.C., A.E., T.K., R.K., I.R. and S.W. worked on data curation and interpretation. U.P., P.A., J.L., T.H., C.A.Q., C.P. and S.T. were responsible for funding acquisition and management. L.A.T.M. developed the methodology and carried out the data analysis. Y.C. and Y.L. ran and analysed the box model; L.A.T.M., C.P., U.P. and M.O.A. wrote the original draft, with all authors contributing to and revising the text.

Competing interests

The authors declare no competing interests.

6 The role of dissolved organic matter for Amazonia nutrient cycles

This chapter has been published in *Biogeochemistry* (Lange et al., 2024):

Summary

Chapter 5 situates these atmospheric observations within the ecosystem context by analyzing the molecular composition and nutrient limitations of dissolved organic matter (DOM) in Amazonian soils using non-targeted HR-Orbitrap-MS. This approach enables the comprehensive characterization of phosphorus-, nitrogen-, and sulfur-containing organic compounds, providing detailed insights into the potential precursors of biogenic volatile organic compounds that subsequently contribute to secondary organic aerosol formation. Although this work focuses on soil and nutrient dynamics rather than aerosol chemistry, it highlights the ecological controls on precursor availability and illustrates the interconnectedness between ecosystem chemistry and atmospheric processes.

I am a co-author of this paper. I did the sampling, analysis and interpretation of soil volatile organic compound (VOC) data by developing a method for non-targeted gas chromatography high-resolution Orbitrap mass spectrometry. My work included soil gas sampling, mass spectrometric analysis, and the evaluation of VOC profiles in relation to soil DOM composition, particularly focusing on how nutrient limitations and the molecular characteristics of DOM may influence BVOC emissions. I helped contextualize these findings within the broader framework of ecosystem–atmosphere interactions, emphasizing the role of soil-derived precursors in atmospheric aerosol formation.

Cycling of dissolved organic nutrients and indications for nutrient limitations in contrasting Amazon rainforest ecosystems

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6.1 Abstract

In the nutrient-poor soils of the Amazon rainforest, phosphorus (P) emerges as a critical limiting factor for ecosystem productivity. Despite these limitations, the Amazon exhibits remarkable productivity that is maintained by its efficient nutrient recycling mechanisms. Central to this process is the role of organic matter, particularly its dissolved (DOM) fraction, which serves as a crucial nutrient reservoir for both plants and microorganisms. This study delves into the dynamics of nutrient-containing DOM within the soils of two contrasting rainforest ecosystems: clayey *terra firme* forests, known for their robust nutrient recycling and presumed P-limitation, and sandy white-sand forests, characterized by reduced nutrient recycling capacity and presumed nitrogen (N)-limitation. Utilizing ultra-high resolution mass spectrometry (HR-MS), we analyzed the molecular composition of dissolved organic nutrient species. We evidenced nutrient limitation applying innovative concepts: (1) assessing nutrient depletion in DOM via nutrient-to-carbon ratios, (2) comparing the composition of nutrient-enriched DOM pools across soil depth profiles to infer microbial nutrient processing, and (3) examining the temporal variability of nutrient-containing DOM as an indicator of nutrient uptake and production. Our results corroborate the hypothesis of P-limitation in *terra firme* forests, with significant processing of N-containing DOM also observed, indicating a synergistic demand for both P and N. Surprisingly, white-sand soils exhibited no signs of N-limitation but instead sulfur (S)-limitation, a novel finding for these ecosystems. This study highlights the diversity of potential nutrient limitations in the central Amazon and the importance of the bioavailable “black box” DOM for tropical nutrient cycles.

6.2 Introduction

The Amazon rainforest plays a critical role in the global carbon cycle and may mitigate negative climatic effects of increasing atmospheric CO₂ levels by increasing productivity (. It is highly productive and stores large amounts of carbon in biomass and soils ((Malhi et al., 2009; Saatchi et al., 2011; Trumbore & Barbosa de Camargo, 2009). However, soils in the Amazon are highly weathered and largely infertile (Camenzind, Hättenschwiler, Treseder, Lehmann, & Rillig, 2018; Quesada et al., 2010), with phosphorous (P) being considered the main limiting element for ecosystem productivity (Lugli et al., 2020; Turner, Brenes-Arguedas, & Condit, 2018; Vitousek, 1984). P-limitation likely constrains the productivity response to increasing atmospheric CO₂ concentrations (Martins et al., 2021; Terrer et al., 2019). The Amazon rainforest however is very heterogeneous, and not all rainforest types are hypothesized to be P-limited. Lowland *terra firme* forests constitute the majority of the central Amazon rainforest region. They occur on widespread clayey soils and are hypothesized to be P-limited (Andreae et al., 2015; Cunha et al., 2022; Quesada et al., 2011). *Terra firme*-like forests occur across diverse edaphic conditions, with P-limitations more prevalent in ecosystems with older pedogenesis. Recent evidence strongly supported P-limitation in *terra firme* forests with old and extremely P-depleted soils, while it has been questioned for *terra firme*-like forests on younger soils with higher P availability (Cunha et al., 2022). Although older soils prevail in the central Amazon, *terra firme*-like forests also occur on younger soils, for which P-limitation remains uncertain.

Less productive white-sand forests occur on strongly leached sandy soils and are potentially more nitrogen (N) limited (Anderson, 1981; Herrera, Jordan, & C.F., 1981; Quesada et al., 2011; Zanchi et al., 2015). White-sand soils are highly deficient in most nutrients, but N-limitations have been inferred

because white-sand forests are typically more deprived of N than P (Adeney, Christensen, Vicentini, & Cohn-Haft, 2016; Matson & Vitousek, 1987). In addition to their relative depletion in N, the infertility of these soils may render multiple other elements co-limiting, such as P or sulfur (S). Nutrient dynamics in white-sand forests are understudied compared to other rainforest types, with more direct evidence of nutrient limitations, e.g. from fertilization experiments, being notably absent. Although *terra firme* forests cover more area overall, white-sand forests cover ~5% of the Amazon basin (Adeney et al., 2016; Quesada et al., 2011). To accurately predict the response of the Amazon rainforest to rising CO₂ levels, it is crucial to investigate the nutrient dynamics that govern primary productivity and carbon sequestration in diverse Amazon ecosystems. This includes assessing the extent of P-limitation in *terra firme* forests and the potential N-limitation in white-sand forests. Understanding these nutrient interactions will allow for more precise modeling of carbon cycling processes and ecosystem responses to climate change across the diverse rainforest types of the central Amazon (Fleischer et al., 2019).

Amazonian soils are predominantly characterized by their low levels of accessible inorganic nutrients. This deficiency arises from two main factors: the weaker ability of these soils to retain some mineral nutrients efficiently due to greater leaching losses caused by high precipitation (Gurmesa et al., 2022) (e.g., N, S), and the overall strong retention of nutrients by the high abundance of iron (Fe) and aluminum (Al) oxides that limit P availability (Quesada & Lloyd, 2016; Schaap et al., 2021). The low availability of inorganic nutrients favors the recycling of nutrients from organic matter in the Amazon rainforest (Cunha et al., 2022; Lugli et al., 2020). Nutrient recycling occurs to a large degree in the organic and litter layer above the mineral soil, facilitated by extensive root growth and microbial activity (Martins et al., 2021). While this process is not unique to the Amazon rainforest, these ecosystems rely more strongly on aboveground nutrient recycling due to soil infertility, low-reactivity mineral assemblages in white-sand soils, and lower soil organic carbon contents. White-sand forests have evolved specialized strategies for maximizing aboveground nutrient retention through the development of thick root mats on the soil surface (Adeney et al., 2016; Matson & Vitousek, 1987). The dependence on aboveground cycles may reduce soil carbon sequestration and increase ecosystems vulnerability to disturbances like drought or fire. Efficient belowground nutrient retention therefore could be a key aspect in enhancing resilience of these ecosystems (Singh, Raghubanshi, Singh, & Srivastava, 1989) and may play an important role in the Amazon's response to global change, but efficiencies of belowground cycles are not well characterized for *terra firme* and white-sand forests.

The breakdown of larger polymers releases inorganic nutrients and dissolved organic matter (DOM). DOM is a highly reactive and complex mixture including thousands of N-, S- and P-containing molecules (Gmach, Cherubin, Kaiser, & Cerri, 2020), which serve as a critical nutrient reserve. Plant-derived DOM leaching from the litter layer is transported through the soil profile and progressively degraded, mineralized or taken up by microorganisms (Kaiser & Kalbitz, 2012; Steinbeiss, Temperton, & Gleixner, 2008). These processes will be jointly referred to as *DOM processing* herein (Freeman et al., 2024), which represents a major pathway for resupplying nutrients to plants and soil microorganisms (Schaap et al., 2021). DOM processing is accompanied by a shift in DOM composition from higher abundance of plant-derived products to more microbial compounds (Roth et al., 2019). DOM derived from early plant matter decomposition is characterized by abundant aromatic compounds (Gleixner, 2013; Klotzbücher, Kaiser, Filley, & Kalbitz, 2013), greater oxygen content and oxidation state (Hertkorn, Harir, Cawley, Schmitt-Kopplin, & Jaffé, 2016; Simon et al., 2021) and lower saturation (D'Andrilli, Cooper, Foreman, & Marshall, 2015). In contrast, microorganism-derived DOM is depleted in aromatic compounds (Drake et al., 2019) and is characterized as more aliphatic, saturated, reduced and oxygen-depleted (Benk et al., 2019; Butturini et al., 2020; Riedel et al., 2016). DOM processing and cycling can be investigated with ultra-high resolution mass spectrometry (HR-MS) (Roth et al., 2019).

HR-MS enables the detection and characterization of thousands of mass spectrometric peaks per sample, providing chemical information through molecular formula assignments (Hawkes & Kew, 2020; Hertkorn, Harir, Koch, Michalke, & Schmitt-Kopplin, 2013; Hutchins et al., 2017). Untargeted analysis of

DOM using HR-MS offers a promising avenue for understanding DOM sources and changes in their contributions (Drake et al., 2019; Orme et al., 2022; Schroeter et al., 2022). Research on DOM composition in pristine Amazon rainforest soils is scarce, particularly with focus on organic nutrients. The compositional differences between major nutrient pools (N, P, and S) and their variance across contrasting rainforest types remains poorly understood. Knowledge gaps persist in regards to belowground processes, specifically in the transport of organic nutrients through the soil profile and microbial processing of them. Elucidating DOM compositional dynamics can provide insights into ecosystem nutrient demands.

Low nutrient abundance can result in nutrient limitation, which can be reflected in low nutrient-to-carbon ratios of DOM (Cui et al., 2022; Klaus et al., 2016). Furthermore, we hypothesize that limiting nutrients undergo more pronounced DOM processing (Feyissa et al., 2022) because elevated demand drives nutrient mining and preferential processing. This enhanced processing should result in greater compositional shifts of nutrient-DOM during downward transport through the soil. Enhanced DOM processing and nutrient mining can also result in higher temporal variability of nutrient species. Marine ecosystem studies have observed lower temporal variability of dissolved or particulate organic carbon compared to organic N and P (Knudsen-Leerbeck et al., 2017), amino acids (Gaye et al., 2022), or inorganic N and P (Martínez-García et al., 2022). Moreover, higher relative nutrient variability in the biologically active photic zone compared to deeper waters suggests higher variability with higher biological demand (Ramírez et al., 2005). Analogously, in terrestrial settings higher temporal variability of N and S than C has been reported for groundwater (Kwon, Koh, Cho, & Jung, 2022) and soils (Mobley et al., 2019; Monokrousos, Papatheodorou, Diamantopoulos, & Stamou, 2004). Because organic nutrient concentrations are governed by the release and processing of individual molecules, temporal nutrient variability can be assessed similarly using the molecular composition of DOM. We propose that the dissimilarity in the nutrient-DOM composition between sampling events may serve as an indicator of nutrient variability and limitation also in soils.

This study analyzed the molecular DOM composition of soil porewater from two *terra firme* and two white-sand forests to investigate DOM processing and organic nutrient cycling in contrasting rainforest types. We employed the aforementioned proxies as indicators to diagnose nutrient limitations. Our investigation tested for signs of P-limitation in two *terra firme* forests at different stages of pedogenesis (old and younger) and for N-limitation in two white-sand forests. Additionally, we assessed the relative importance of above- versus belowground processing by comparing nutrient-DOM processing in the soil profile with variability in the 0–5 cm soil layer. We hypothesized that belowground processing would be more pronounced in the clay-rich soils of *terra firme* forests.

6.3 Methods

6.3.1 Field sites

Sampling for this study was conducted around the Amazon Tall Tower Observatory (ATTO) in the Utumã Sustainable Development Reserve, which is located around 150 km northeast of Manaus, Brazil, in the central Amazon rainforest. The region is characterized by a mosaic of valleys and elevated plateaus with distinct types of rainforests and an altitude range of around 35 to 130 m above sea level. The tropical humid climate is marked by a rainy season from November to May with a pronounced peak from February to May, and a drier season from June to October (Andreae et al., 2015).

We investigated four sites belonging to two major rainforest types: *terra firme* forest (plateau and terrace sites) and white-sand forest (*Campina* and *Campinarana* sites). Most of the reserve is covered by upland *terra firme* forests that are highly diverse and productive forests on fine-textured, strongly acidic and clay-rich soils (plateau site; PL). Soils on the plateaus around ATTO are classified as Ferralsols, which are highly weathered and well-drained soils on ancient geological surfaces (Andreae et al., 2015; Chauvel, Lucas, & Boulet, 1987). Another type of *terra firme* forest covers fluvial terraces along rivers

(terrace site; TE). The clayey soils of these terraces are classified as Alisols, which represent a more recent pedogenic status with lower clay content than the Ferralsols (Andreae et al., 2015). White-sand forests are low-diversity, lower-statured forests on coarse-textured sandy soils. Soils in the white-sand forests are classified as Arenosols. They are characterized by very high sand content with high water permeability, low water holding capacity, severe acidity and often very low nutrient contents (Quesada et al., 2011). Both white-sand sites showed thick organic layers and root mats above the mineral soil that are important for nutrient retention and recycling (Stark & Jordan, 1978). The *Campina* (CD) and *Campinarana* (CW) sites feature the same specialized vegetation characteristic for white-sand forests, but the CW forest is denser with larger trees.

6.3.2 Sampling

Soil porewater was sampled using sintered glass suction plates (pore size 1–1.6 μm , 1 cm thickness, 12 cm diameter; SPG120 by Meter, Germany) that were installed in all four sites at soil depths of 5, 10, 20 and 30 cm in October 2017 in a fan-like fashion around a central box containing the collection flasks. Thick root mats and organic layers in the two white-sand sites allowed the installation of additional suction plates at 0 cm soil depths directly at the interface between organic layer and mineral soil. The suction plates were connected to glass flasks using PTFE tubes. The sampling bottles were evacuated to an average suction pressure of -150 mbar to collect only freely percolating porewater (Ekberg, Buchmann, & Gleixner, 2007; Malik & Gleixner, 2013; Roth et al., 2019). Sampling was conducted biweekly during the wet seasons in 2019, 2020 and 2021 (October to May). Each site had three independent replicates of the suction plate setup described above.

6.3.3 Soil chemistry: TOC, TN, iron and aluminum contents, soil texture fractions, soil pH and exchangeable cations

Soil samples were taken in November 2017 during the installment of the suction plates. All analyses of soil samples were conducted in the Instituto Nacional de Pesquisas da Amazônia in Manaus, Brazil (INPA). Soil samples were air-dried and sieved ($< 2 \mu\text{m}$) to remove coarse material and roots. Organic carbon and total nitrogen concentrations of soil samples were measured using an automatic C and N analyzer (Vario Max CN, Elementar Instruments, Germany). Particle size fractions (clay, silt, coarse sand and fine sand; the latter two were summarized as sand) were measured using the pipette method (Gee & Bauder, 1986) and are reported in percent. Soil Fe and Al fractions were separated by sequential extraction (van Reeuwijk, 2002). Fe and Al concentrations of all extracts were measured using atomic absorption spectrometry (AAS) at INPA (Quesada et al., 2010). Soil pH was determined at a 1:2.5 ratio of soil:liquid using H_2O and 1 M KCl. (Quesada et al., 2010). Exchangeable cations of Ca^{2+} , Mg^{2+} , K^+ and Na^+ were determined using the silver thiourea method (Pleysier & Juo, 1980; Quesada et al., 2010).

6.3.4 Soil porewater chemistry: DOC, pH, electrical conductivity

Aliquots of soil porewater samples were measured for dissolved organic carbon (DOC) at INPA (Laboratório de Águas do INPA/ CPRHC). DOC concentrations of water samples were measured using a total organic carbon analyzer (TOC- V_{CPH} model, Shimadzu, Kyoto, Japan) ((Monteiro et al., 2014). Before DOM extraction, pH and electrical conductivity (EC) were measured using a Multi 340i probe system (WTW, Weilheim, Germany).

6.3.5 Solid-phase extraction of DOM and Orbitrap MS measurements

The soil porewater from the three independent replicates was collected bi-weekly and mixed equally to obtain a representative sample per site and soil depth. Directly after sampling, water samples were stored frozen at -20°C at ATTO for up to 1.5 years before performing solid-phase extraction on-site following (Dittmar, Koch, Hertkorn, & Kattner, 2008). Samples were acidified to pH 2 with ultrapure hydrochloric acid (Rotipuran Supra 30%; HCl) before loading on the solid phase extraction column (Bond Elute PPL, Agilent, Germany). Procedural blanks of acidified ultrapure water (pH 2) were extracted along samples for each campaign. The PPL columns were transported to Germany after drying them on-site. The samples were subsequently eluted with ultrapure methanol, stored frozen at -20°C and analyzed

within three months. DOC concentrations of the solid-phase extracted DOM were measured on a TOC analyzer (vario TOC cube, Elementar, Germany) (Orme et al., 2022). The extraction efficiency was $72 \pm 22\%$ on a carbon basis. Before measurement, samples were adjusted to a mixture of 1:1 methanol and purified water at a concentration of 20 mg C l^{-1} . We conducted HR-MS measurements at an Orbitrap Elite (Thermo Scientific) as described previously (Schroeter et al., 2022; Simon, Roth, Dittmar, & Gleixner, 2018). Conventional approaches of investigating DOM provide either very specific data (e.g., targeted measurement of amino acids) or broad information (e.g., size-exclusion chromatography separating DOM into a few fractions). HR-MS offers unparalleled resolution of the highly complex composition of DOM and ecosystem-scale dynamics that are reflected therein (Hawkes et al., 2020). In short, the instrument was operated with a continuous flow of $\text{H}_2\text{O}/\text{MeOH}$ 50:50 solvent ($20 \text{ }\mu\text{l}/\text{min}$) and an ESI (electrospray ionization) needle voltage of 2.65 kV. $100 \text{ }\mu\text{l}$ of DOM extract were infused into the HR-MS and spectra were acquired in negative ESI mode. Measurements were conducted for the mass over charge (m/z) range of 100–1000 at a nominal resolution of 480,000 (at m/z 200) and a maximum ion accumulation time of 100 ms. At least 100 scans per measurement were averaged and combined using the software Thermo Xcalibur (Version 3.0.63). Only peaks above a signal-to-noise ratio of 8 were kept for further analysis.

6.3.6 Data processing

Samples were recalibrated post-measurement using the MFassignR script with 3 ppm error range (Schum, Brown, & Mazzoleni, 2020) and molecular formulas were assigned using the ICBM-Ocean routine (Merder et al., 2020). Subsequently, all mass spectra were normalized relative to the sum of their peak intensities. We used the following elemental constraints for molecular formula assignment: ^{12}C 1–70, ^1H 2–160, ^{16}O 0–70, ^{14}N 0–7, ^{32}S 0–3, ^{31}P 0–3 and ± 0.5 ppm tolerance. Formulas containing isotopes, formulas that were assigned more than once, and ambiguous assignments with multiple formula suggestions were removed. Finally, 7188 masses with successful formula assignment were considered for further analysis. Based on the molecular formula data, the following DOM parameters were calculated for each molecular formula: H/C, O/C, N/C, P/C, S/C, N/P, modified aromaticity index (AI_{mod}) (Koch & Dittmar, 2006; Koch & Dittmar, 2016), and the nominal oxidation state of carbon (NOSC) (Boye et al., 2017). Molecular subgroups were assigned as follows (Riedel et al., 2016): “Aromatic”, “highly unsaturated”, “aliphatic” (Khatami, Deng, Tien, & Hatcher, 2019), and “lipid-like” (Rivas-Ubach et al., 2018) (see **Supporting Text S1** for more detailed information on data processing).

To compare different pools within DOM, the total set of molecular formulas was separated based on occurrence of N, S and P assignments (Table S 11.4-2). We classified DOM based on molecular formulas as follows: without N, S and P assignment as “CHO-DOM” (only C, H and O assigned), with N assignment as “N-DOM”, with P assignment as “P-DOM” and with S assignment as “S-DOM”. This approach allowed to compare the dynamics of nutrient and non-nutrient pools separately.

6.3.7 Data analysis

All data analysis and creation of figures were conducted in RStudio 4.2.0. The molecular formula data were analyzed by principal coordinate analysis (PCoA; “cmdscale” function, “stats” 4.2.0) based on Bray–Curtis dissimilarities (“vegdist” function, “vegan” 2.6.2). The intensity-weighted means of DOM parameters were then calculated using the “weighted.mean” function (“stats” package 4.20). The averaged DOM parameters were fitted as vectors onto the ordination plots by post-ordination gradient fitting analysis (“envfit” function, “vegan” 2.6.2). The significance level for statistical tests was $\alpha = 0.05$, and p-values were adjusted for multiple testing using the Benjamini & Hochberg method (Jafari & Ansari-Pour, 2019) (“p.adjust” function, “stats” 4.2.0). We determined molecular formulas with significant association to one rainforest type using two-sided Mann–Whitney U tests based on their relative intensities (“wilcox.test” function, “stats” 4.2.0): First, the association to one rainforest type was tested (*terra firme* or white-sand). Subsequently, the association to one site was tested to determine site-

specific markers within the sets of ecosystem markers (PL vs. TE; CD vs. CW). Based on this, ecosystem markers were defined as the formulas that showed significant associations with one ecosystem but were not correlated with site-specific differences. Site-specific markers were defined as formulas that showed further statistical association with one site. Subsequently, intensity-weighted means of the markers were calculated for each sample. These markers were used to differentiate the characteristic DOM of rainforest types and individual sites.

We further compared the DOM composition from our sites with groundwater data from similar ecosystems in the same broader region north of Manaus (*terra firme* plateau and upland white-sand forests; sampled using piezometers in < 2 m soil depths) (Simon et al., 2021). Samples from the study were measured on the same instrument as our samples and raw data were re-processed along with data from our samples by the same routine as described above.

The change in chemical characteristics of DOM with soil depth was quantified using the Bray–Curtis dissimilarity comparing samples from 5 to 30 cm depth, separated per site and sampling event. This was done to estimate the magnitude of DOM processing during soil passage. The Bray–Curtis dissimilarity was chosen to quantify DOM processing because it is a robust and well-established metric to quantify differences in composition between samples. The advantage of the approach lies in analyzing the change of all DOM parameters simultaneously and calculating a single metric that quantifies the overall change. The Bray–Curtis dissimilarity was calculated from intensity-weighted DOM parameters instead of the relative intensities of the molecular formulas. The following intensity-weighted DOM parameters were used: H/C and O/C ratios, NOSC, molecular mass (m/z), and fractions of aromatic [% of ion intensity], lipid-like [% of ion intensity], highly unsaturated [% of ion intensity] and aliphatic formulas [% of ion intensity]. We did not consider N/C, P/C and S/C ratios to ensure comparability with the CHO-DOM group that does not have these elements assigned. All DOM parameters were scaled with min–max scaling to values between 0 and 1 prior to calculating the Bray–Curtis dissimilarity.

The temporal variability of the molecular DOM composition was calculated for the individual DOM pools and used as a proxy for DOM and nutrient-DOM cycling. For this purpose, sampling events were regarded as replicates of the same sample. The Bray–Curtis dissimilarity based on presence-absence data was then calculated for each site and 5 cm soil depth and all temporal replicates were compared in pairwise comparisons. The dissimilarity of all comparisons was used as an estimate for the temporal variability of the composition of respective DOM pools. We chose to assess nutrient variability through Bray–Curtis dissimilarity of the DOM composition because this allows to investigate the dynamics of nutrients contained in a variety of organic species.

6.4 Results

6.4.1 Bulk soil properties and soil porewater chemistry

The *terra firme* and white-sand soils differed strongly in their soil characteristics (Table 6.4-1). Clay content in the *terra firme* soils was much higher (PL, 69.4 ± 3.0 and TE, 41.3 ± 2.6) than in white-sand soils (CD, 0.7 ± 0.1 and CW, 1.5 ± 0.1), same as organic carbon and total nitrogen concentration. *Terra firme* soils also showed much higher total extractable Fe and Al (11.7–16.6 and 4.7–7.8 g/kg Fe or Al, respectively) than white-sand soils (< 1.5 g/kg of both elements, Table 6.4-1). Exchangeable cations were up to 6.5-fold higher in clayey soils than in sandy soils. While they were more depleted in white-sand sites, cation exchange capacities were overall extremely low compared to those of temperate forests (Gruba & Mulder, 2015). Soil pH was very low in all sites (range 3.6–4.8 in H₂O) with high amounts of exchangeable hydrogen (range 2.9–4.0 in KCl).

Table 6.4-1: Soil and porewater chemistry for *terra firme* (PL, TE) and white-sand sites (CD, CW)

Site	Soil depth [cm]	Fe _{total} [g/kg]	Al _{total} [g/kg]	Sand [%]	Silt [%]	Clay [%]	Cations [cmolc/kg]	N [wt%]	C _{org} [wt%]	pH (H ₂ O)	pH (KCL)	pH*	EC [μS cm ⁻¹]*	DOC [mg l ⁻¹]*
CD	0–5	1.1	0.4	95.7	3.6	0.7	0.18	0.04	0.66	4.8	3.02	3.7	67.0	102
CD	20–30	1.3	0.6	97.2	2.3	0.5	0.02	0.00	0.12	4.5	3.31	3.8	58.4	40.9
CW	0–5	0.8	0.1	93.5	5.1	1.4	0.07	0.05	0.90	4.1	2.86	3.7	60.0	56.8
CW	20–30	0.8	0.1	95.0	3.4	1.6	0.03	0.03	0.54	4.1	3.21	3.7	76.4	31.6
PL	0–5	16.6	7.8	7.2	18.1	74.8	0.46	0.30	3.98	4.1	3.55	4.4	21.8	6.3
PL	20–30	11.7	6.4	5.6	24.5	69.9	0.07	0.12	1.32	4.4	3.96	4.9	11.9	1.2
TE	0–5	13.3	4.7	43.7	17.7	38.6	0.33	0.23	2.71	3.6	3.32	4.3	33.9	16.5
TE	20–30	15.2	6.3	38.8	16.8	44.5	0.12	0.10	1.31	4.2	3.78	5.0	12.0	2.5

Fe_{total} and *Al_{total}* the sum of pyrophosphate-extractable, oxalic acid-extractable and dithionite-extractable fractions of Fe and Al; *Cations* the sum of exchangeable cations of Ca²⁺, Mg²⁺, K⁺ and Na⁺; *N* soil nitrogen content, *C_{org}* soil organic carbon content; *soil pH (H₂O)* soil pH measured in water, *soil pH (KCL)* soil pH measured in potassium chloride; *EC* electrical conductivity [μS cm⁻¹]; *DOC* dissolved organic carbon [mg C l⁻¹]

*Parameters were measured in soil porewater that was also used for DOM extraction. Soil porewater samples were derived from 5 to 30 cm depth

The *terra firme* and white-sand soils were also strongly differentiated by their porewater chemistry (Mann–Whitney U test, $p < 0.05$; Table 6.4-1, Figure S 11.4-1). DOC concentrations were on average ~sevenfold higher in the white-sand soils compared to *terra firme* soils, which contrasted the results from soil carbon. Soil porewater pH was approximately one pH unit higher in *terra firme* samples whereas electrical conductivity (EC) was three- to four-fold lower. DOC concentrations decreased significantly (Spearman rank correlation, $p < 0.05$) with soil depth in *terra firme* soils (decrease from 13.1 ± 5.6 in 5 cm to 2.0 ± 0.8 in 30 cm) and in the CW site (decrease of 56.8 ± 17.5 to 31.6 ± 5.7). This trend was not found in CD soils where DOC levels remained similar up to 30 cm soil depth. Porewater pH and EC showed significant depth trends in *terra firme* sites with increasing pH and declining EC values, whereas values did not change significantly in white-sand sites.

6.4.2 Proxies for nutrient limitation

In all sites, molecular formulas containing only C, H, and O constituted the largest fraction of ion intensity (> 80%) and were assigned in similar numbers in all samples. In contrast, the number of nutrient-containing molecular formulas and nutrient-to-carbon ratios revealed differences between the two rainforest types (Table 6.4-2). Differences in N/C ratios between *terra firme* and white-sand sites were not pronounced (Figure 6.4-1 A), with slightly higher values in white-sand DOM. P-DOM was strongly depleted in *terra firme* sites compared to that of white-sand sites (Figure 6.4-1 B; Table 6.4-2), as displayed by much lower P/C ratios. P was also strongly depleted relative to N in *terra firme* DOM, with over factor 5 higher N/P ratios than in white-sand DOM (Figure 6.4-1 D). In contrast, S-DOM was considerably depleted in white-sand compared to *terra firme* forests, as displayed by much lower S/C ratios (Figure 6.4-1 C).

Table 6.4-2: Numbers of formula assignments per DOM pool and nutrient-to-carbon ratios for the terra firme forests (PL and TE sites) and the white-sand forests (CD and CW sites).

Rainforest type	CHO formulas (n)	N formulas (n)	S formulas (n)	P formulas (n)	N/C (× 1000)	S/C (× 1000)	P/C (× 1000)
<i>Terra firme</i>	1927 ± 222	1849 ± 152	316 ± 53	72 ± 23	14.2 ± 3	1.08 ± 0.5	0.14 ± 0.1
White-sand	1856 ± 95	848 ± 126	50 ± 14	76 ± 12	14.9 ± 2	0.27 ± 0.2	0.92 ± 0.2

CHO formulas (n) number of molecular formulas per sample that contain only C, H and O assignment; *N formulas* molecular formulas with N assignment; *S formulas* molecular formulas with S assignment; *N/C* intensity-weighted nitrogen-to-carbon ratio; *S/C* intensity-weighted sulfur-to-carbon ratio; *P/C* intensity-weighted phosphorus-to-carbon ratio. Number of samples: white-sand sites 122, *terra firme* sites 79

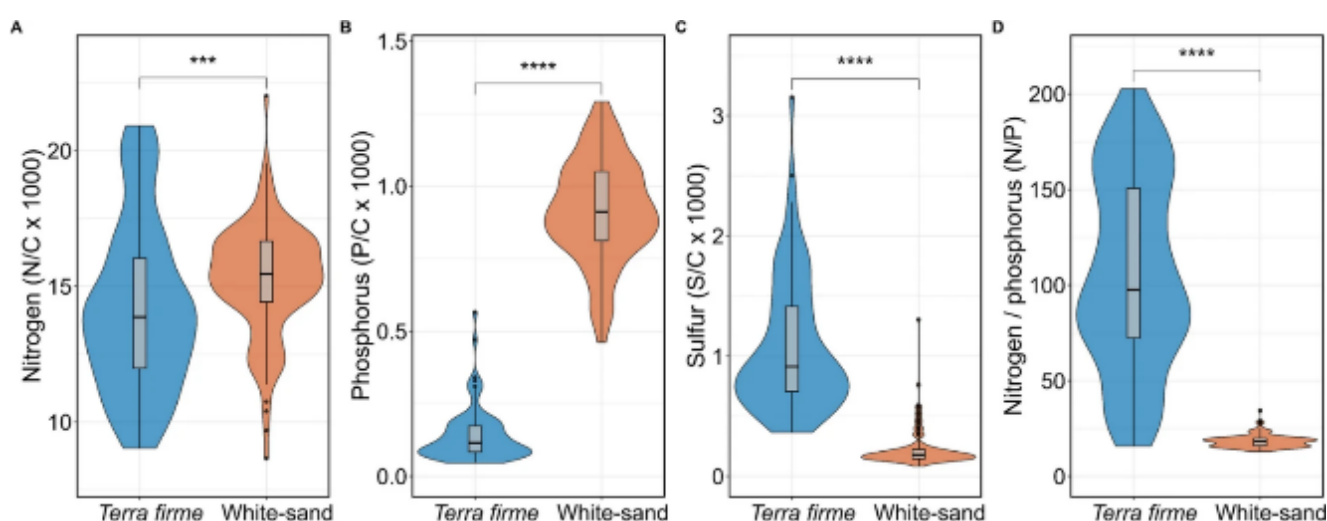


Figure 6.4-1: Intensity-weighted nutrient-to-carbon (C) ratios of DOM for N (nitrogen; A), P (phosphorus; B), and S (sulfur; C), and nitrogen-to-phosphorus ratio (N/P; D) displayed for white-sand and *terra firme* sites. Stars indicate significant differences between white-sand and *terra firme* DOM (Mann–Whitney U test, $p < 0.05$).

The analysis of the processing of individual DOM pools during soil passage revealed a differential processing (Figure 6.4-2). In the *terra firme* sites, processing was highest for N- and P-DOM (Figure 6.4-2 A), with respective means ~40–50% higher than those of CHO-DOM. DOM processing was much lower in S-DOM, with approximately four-fold lower values than for CHO-DOM. In contrast, processing of CHO-, N- and S-DOM was of similar magnitude in white-sand sites (Figure 6.4-2 B), and only P-DOM exhibited lower processing magnitudes. In comparison, DOM processing was overall much higher in *terra firme* sites except for S-DOM. Processing of N- and P-DOM was ~3.5 to 4.5 times higher than in white-sand sites, whereas it was only factor 2 for CHO-DOM. For S-DOM a reversed trend was observed, where processing was > 50% higher (Mann–Whitney U, $p < 0.05$) in white-sand sites. Overall, the processing of the DOM pools showed a preferential processing of N- and P-DOM in *terra firme* soils. For white-sand DOM, no preferential processing of individual DOM pools was apparent.

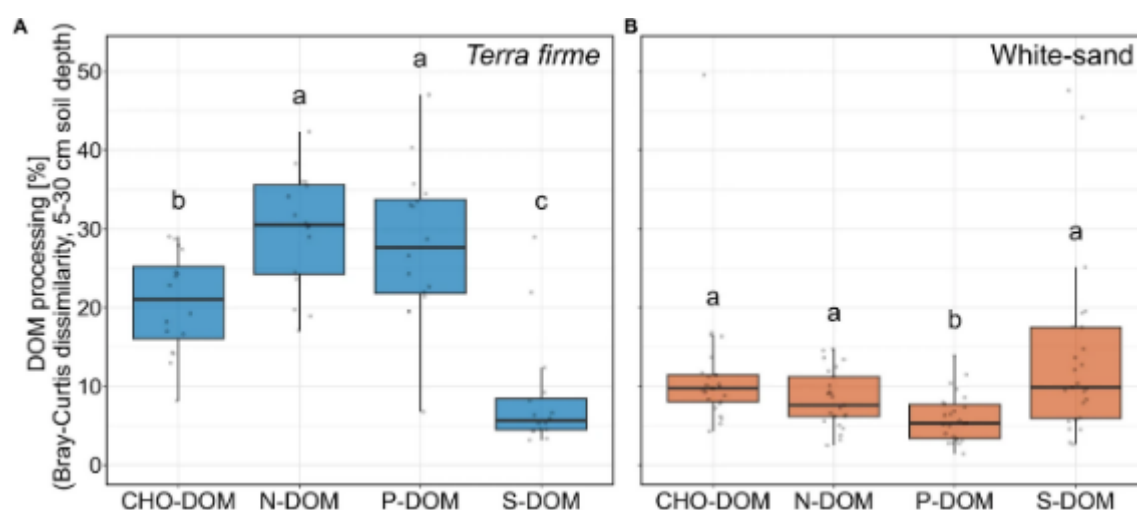


Figure 6.4-2: DOM processing in % between 5 and 30 cm soil depth in *terra firme* (A) and white-sand sites (B) calculated as Bray–Curtis dissimilarity. The Bray–Curtis dissimilarity was used to quantify the difference in chemical characteristics of samples from 5 and 30 cm depth, based on nine DOM parameters specified in the methods section. Data are displayed for DOM pools: CHO-DOM (molecular formulas with only C, H and O assigned), N-DOM (molecular formulas that contain N), P-DOM (molecular formulas that contain P) and S-DOM (molecular formulas that contain S). Letters indicate significant differences between the DOM pools (Kruskal Wallis test, adjustment of p-values by Benjamini & Hochberg method, $p < 0.05$).

In both rainforest types, the temporal variability of nutrient-containing DOM pools was substantially higher than that of CHO-DOM (Figure 6.4-3). The magnitude of the variability was generally similar in both rainforest types and did not show higher values in the *terra firme* sites as observed for the DOM processing. In *terra firme* forests, the variability was highest for P-DOM, with two-fold higher values than for the second-most variable pool S-DOM (Figure 6.4-3 A). The variability of N-DOM was lower but still two-fold higher than that of CHO-DOM. In the white-sand forests, the highest variability was observed for S-DOM, with values approximately 1.7-fold higher than those of N- and P-DOM, which were not statistically different from each other (Figure 6.4-3 B). Similar to the *terra firme* sites, variability was the lowest for CHO-DOM with a large three-fold difference compared to N- and P-DOM. The dataset used in this study covered samples collected in the wet seasons of three consecutive years. Therefore, the variability observed in this study was related to both intra-seasonal variability and variability between years.

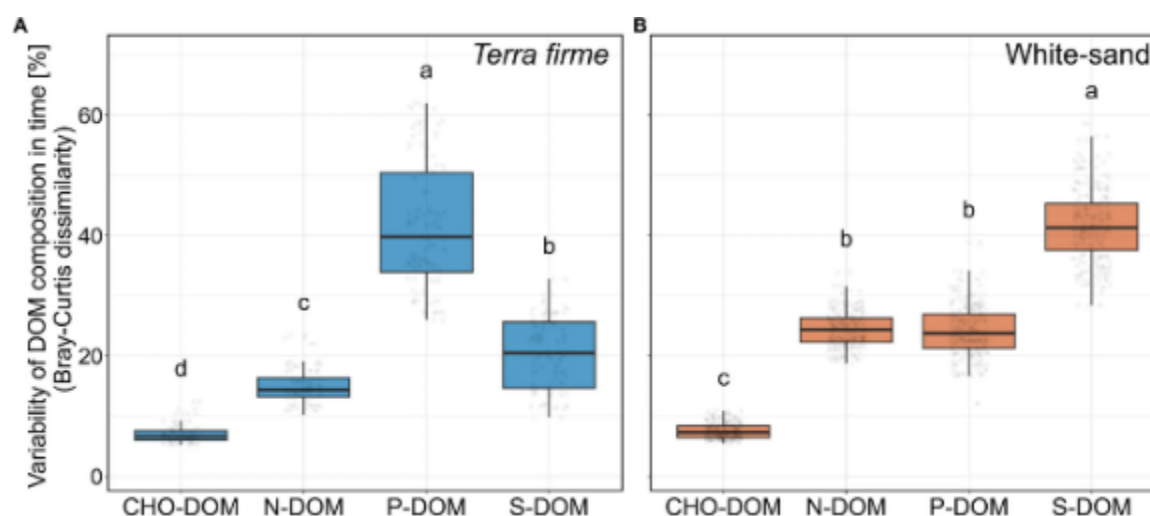


Figure 6.4-3: Temporal variability of the DOM composition in % for 5 cm soil depth in *terra firme* (A) and white-sand sites (B) calculated as Bray–Curtis dissimilarity between all replicate samplings of the same site in 5 cm soil depth compared against each other. The Bray–Curtis dissimilarity was used to quantify the difference in the molecular composition in pair-wise comparisons of repeated sampling events. Data

are displayed for DOM pools: CHO-DOM (molecular formulas with only C, H and O assigned), N-DOM (molecular formulas that contain N), P-DOM (molecular formulas that contain P) and S-DOM (molecular formulas that contain S). Letters indicate significant differences between the DOM pools (Kruskal Wallis test, adjustment of p-values by Benjamini & Hochberg method, $p < 0.05$).

6.4.3 DOM processing as reflected in the molecular composition of DOM

The analysis of the DOM composition revealed two main clusters related to white-sand and *terra firme* samples in a principal coordinate analysis (PCoA; Figure 6.4-4 A). Samples were separated mainly on the first principal coordinate (PCo1) that explained 85% of variance, showing the dominant effect of differences between clayey and sandy soils. Although clustering together, PL and TE samples were clearly separated (Figure 6.4-4 A, blue/ green dots). Site-specific separation was not apparent for the white-sand samples. The separation between *terra firme* and white-sand clusters was linked to significant (Pearson correlation, $p < 0.05$) trends in porewater chemistry and soil parameters such as clay content that followed the separation by rainforest type. In addition to this primary separation, soil depth also showed a significant correlation with the molecular composition, shifting samples both on the first and second (5% of variance) coordinates (Figure 6.4-4 A). The depth trend was linked to PCo2 and was more apparent in *terra firme* samples (shown by brighter and darker colors in Figure 6.4-4). The separation of the clusters by rainforest type was also reflected in correlations with DOM parameters.

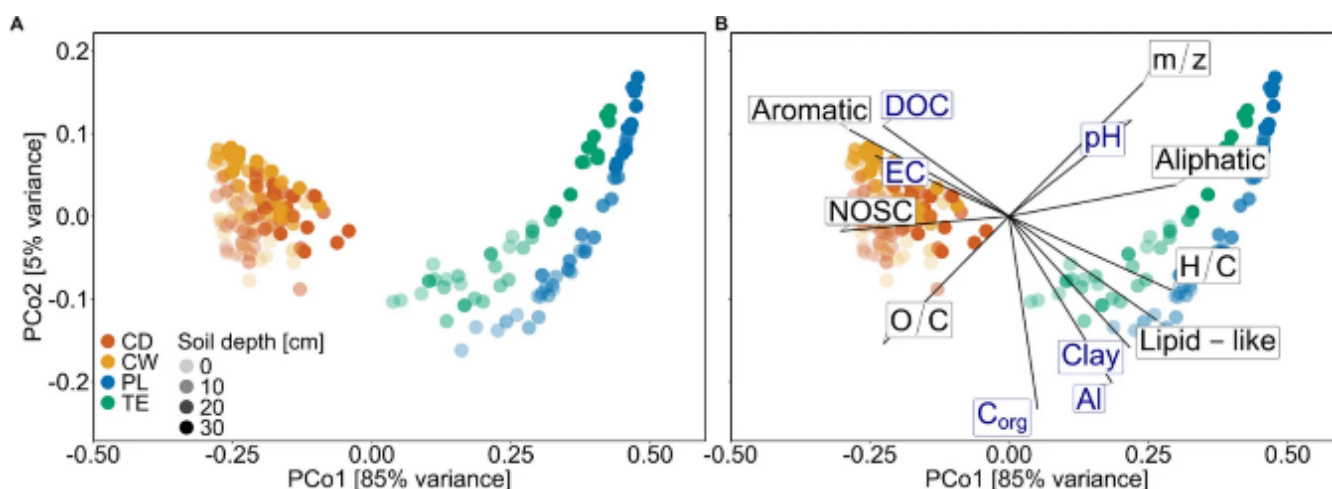


Figure 6.4-4: Ordination plot from a principal coordinate analysis (PCoA) based on Bray–Curtis dissimilarity of the molecular DOM composition (A). All masses with molecular formula assignment and their relative intensities were used. Site abbreviations: CD = Campina (white-sand), CW = Campinarana (white-sand); PL = plateau (old *terra firme*), TE = terrace (young *terra firme*). Soil depth is displayed by continuous alpha shading with lighter shade marking 5 cm, and darker shade marking 30 cm. Intensity-weighted DOM parameters (displayed in black font) and parameters of soil porewater chemistry and soil (displayed in blue font) were fitted as vectors (B): aromatic (fraction of aromatic formulas in %), NOSC (nominal oxidation state of carbon), O/C ratio, m/z (mass to charge ratio), aliphatic (fraction of aliphatic formulas in %), H/C ratio, lipid-like (fraction of lipid-like formulas in %), (DOC (dissolved organic carbon concentration of soil porewater, mg l⁻¹), EC (electrical conductivity of soil porewater, $\mu\text{S cm}^{-1}$), pH (soil porewater), Clay (clay content of soil in %), Al (Altotal, the sum Al fractions in soil, g/kg), Corg (organic carbon content of soil, wt%).

Molecular formulas were separated into unique markers for the individual sites, and shared markers for the rainforest type (*terra firme* / white-sand; Table 6.4-3, see Online Resource 2 for list of markers). 1850 formulas were indicative of *terra firme* forests as a whole, differentiating them from white-sand systems. In line with the stronger distinction between the *terra firme* sites apparent in the PCoA, the *terra firme* sites (PL and TE) had more unique markers ($n = 1310$ and 1132 , respectively) than the white-sand sites (CD and CW). 2052 markers were indicative of white-sand forests but only few markers differentiated the sites from each other ($n = 140$ and 175 for CD and CW). Intensity-weighted means of *terra firme* markers were characterized by high molecular mass (m/z) and H/C ratios and low NOSC (Table 6.4-3). The fraction of aromatic compounds was extremely low ($< 2\%$), whereas aliphatic and lipid-like compounds were much more abundant. White-sand forest markers were highly aromatic

($74 \pm 4.9\%$) while the non-aromatic compounds were mostly highly unsaturated. White-sand markers further displayed lower molecular mass and H/C ratios and were more oxidized. Lipid-like structures made up less than 0.1% of white-sand markers. Overall, DOM was more aliphatic and lipid-like, and less aromatic in soils with higher clay content. The distinction between the rainforest types observed for the DOM parameters considering all molecular formulas (Figure 6.4-4) was also reflected in each DOM pool separately (Table S 11.4-2; Figure S 11.4-2; Figure S 11.4-3).

Table 6.4-3: Intensity-weighted means of classes of molecular formulas that correlated significantly with rainforest type (shared markers for white-sand/ *terra firme* sites that were not enriched in one site) and site (site-specific markers that were enriched in one site).

Site	Aromatic [%]	Aliphatic [%]	Lipid-like [%]	m/z [Da]	H/C ratio	O/C ratio	NOSC
CD	47 ± 4.0	1.7 ± 0.8	0.0 ± 0.0	389 ± 9.2	0.90 ± 0.01	0.50 ± 0.02	0.20 ± 0.03
CW	81 ± 1.7	1.2 ± 0.5	0.0 ± 0.0	269 ± 7.6	0.69 ± 0.01	0.66 ± 0.01	0.74 ± 0.02
White-sand	74 ± 4.9	0.8 ± 0.4	0.1 ± 0.0	350 ± 21	0.73 ± 0.02	0.49 ± 0.03	0.39 ± 0.03
PL	0.2 ± 0.1	71 ± 5.2	37 ± 6.1	414 ± 12	1.28 ± 0.02	0.42 ± 0.03	-0.38 ± 0.09
TE	15 ± 8.4	10 ± 2.1	1.5 ± 2.0	450 ± 31	1.04 ± 0.02	0.46 ± 0.05	0.04 ± 0.03
<i>Terra firme</i>	1.9 ± 1.2	33 ± 2.6	5.7 ± 1.1	436 ± 18	1.16 ± 0.01	0.45 ± 0.03	-0.16 ± 0.06

The DOM composition was significantly different between 5 and 30 cm soil depth in all four sites (Permanova, $p < 0.05$). Almost all investigated DOM parameters were significantly correlated with soil depth (Pearson correlation, $p < 0.05$; **Figure 6.4-5**), except for the fraction of lipid-like formulas, for which trends were only significant in *terra firme* sites. The DOM composition in both rainforest types shifted in the same direction. m/z and H/C values and the fraction of aliphatic, lipid-like and highly unsaturated compounds increased, whereas the fraction of aromatic compounds and the NOSC and O/C values decreased. Groundwater DOM data from similar *terra firme* plateau and white-sand sites in the same geographic region ((Simon et al., 2021) showed a continuation of the depth trends described for topsoil DOM from the sites of this study (Table S 11.4-2; Table S 11.4-3). Relative to DOM from 30 cm soil depth of the respective sites, the content of aromatic compounds, the O/C ratio and NOSC values decreased further while the content of aliphatic, lipid-like and highly unsaturated formulas as well as the H/C ratio increased further.

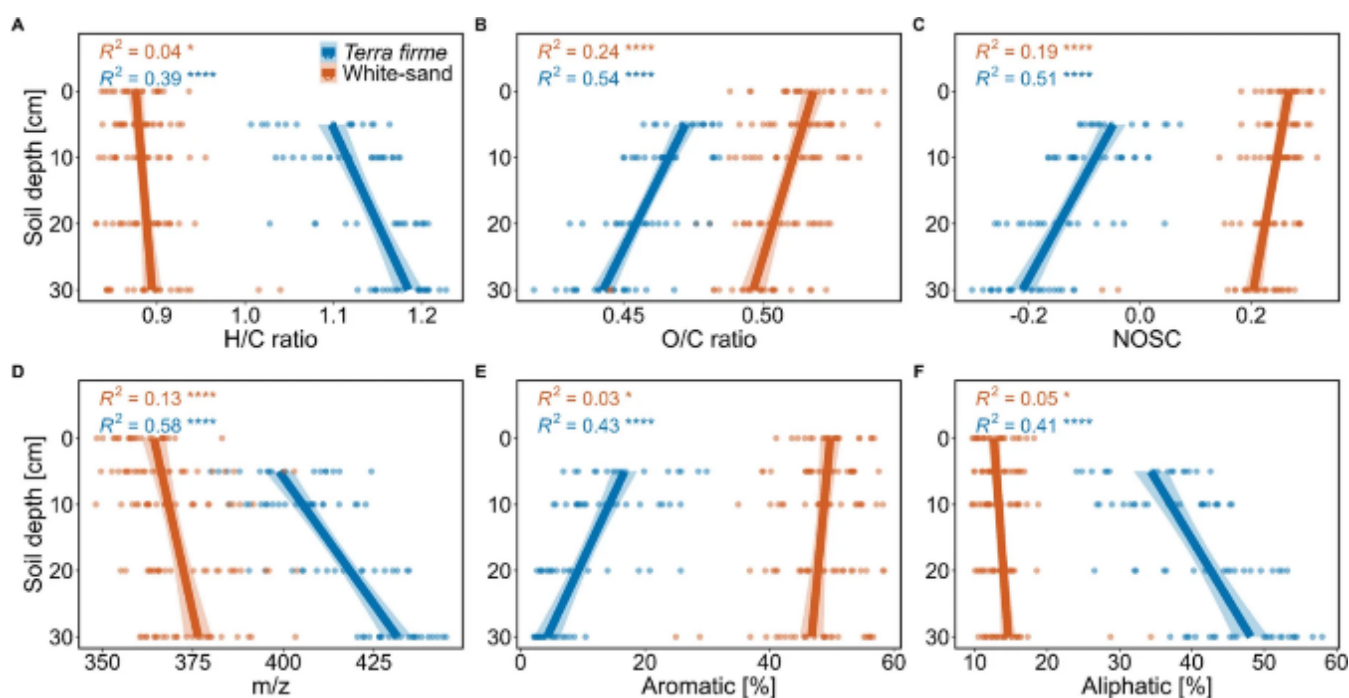


Figure 6.4-5: Pearson correlation of intensity-weighted DOM parameters with soil depth (0/5–30 cm). The following parameters are shown: H/C ratio (A), O/C ratio (B), NOSC (nominal oxidation state of carbon) (C),

m/z (mass to charge ratio) (D), aromatic (fraction of aromatic formulas in %) (E), aliphatic (fraction of aliphatic formulas in %) (F). Stars indicate significant correlations (Pearson correlation, $p < 0.05$). Only significant correlations are displayed as linear regression line. DOM from microbial sources has typically higher H/C values and higher aliphatic content, and lower O/C and NOSC values and aromatic content compared DOM from plant sources. An increase m/z with soil depth was also associated with increasing microbial processing of DOM (Roth et al., 2019).

6.5 Discussion

6.5.1 Evidence for nutrient limitations in *terra firme* and white-sand forests

We hypothesized P-limitation in *terra firme* forests. In line with our hypothesis, DOM was, on average, more than six-fold depleted in P compared to the white-sand forests based on P/C ratios (Figure 6.4-1 A). In addition to low P/C ratios, also high N/P ratios of leaves in tropical trees have been regarded as evidence for tropical forest P-limitation (Vitousek, 1984). Similarly, the N/P ratio of DOM was considerably higher in *terra firme* ($N/P = 106 \pm 50.2$) than in white-sand soils ($N/P = 18 \pm 3.8$). This is consistent with the frequently reported N abundance and P scarcity in tropical forests similar to our *terra firme* sites (Hedin, Brookshire, Menge, & Barron, 2009; Reich & Oleksyn, 2004). The pronounced P depletion and high N/P ratios of DOM support the proposed P scarcity in the *terra firme* forests investigated.

DOM processing in the soil profile of *terra firme* sites was highest for P- and N-DOM (Figure 6.4-2 A). This was accompanied by an increase in the number of P- and N-containing formulas with soil depth, whereas the number of CHO-containing formulas decreased (Mann–Whitney U test, $p < 0.05$). Increasing molecular diversity can result from microbial DOM processing (Chen et al., 2022; Zhao et al., 2019), and implies the synthesis of new compounds that were not present in upper soil layers, likely by microorganisms. The extensive processing of P-DOM is consistent with our hypothesis of P-limitation. However, the high processing of N-DOM was unexpected, although tropical forests have been proposed to cycle large amounts of nitrogen (Brookshire, Gerber, Menge, & Hedin, 2012; Hedin et al., 2009). The elevated processing of P- and N-containing pools over CHO- and particularly S-DOM suggests a high demand for these nutrients by microorganisms or plants in the 5–30 cm mineral soil.

While DOM processing, as investigated in this study, reflected processes in the topsoil from 5 to 30 cm, the temporal variability of the molecular DOM composition in 5 cm soil depth was potentially a result of processes in the organic layer or in the first 5 cm of mineral soil, or both. In the white-sand sites, the temporal variability was extremely similar in soil depths of 5 and 0 cm (Figure 6.4-3 A; Figure S 11.4-4). Because the 0 cm samples derived DOM directly from the organic layer, this suggests that in white-sand soils the temporal variability of DOM was a signal of processes occurring in the organic layer. For the *terra firme* sites, no samples from 0 cm soil depth were available because they lacked thick root mats. We could therefore not infer whether the variability was created above or within the first 5 cm of mineral soil. In *terra firme* sites, the temporal variability of the DOM composition was also highest for P-DOM, which further supports our hypothesis of P-limitation in these systems.

Overall, all three proxies supported the hypothesized P-limitation in *terra firme* forests. P-limitation is likely for the *terra firme* forest type present at our PL (plateau) site, characterized by ancient highly weathered Ferralsol soils (Cunha et al., 2022; Quesada et al., 2011). It is less expected in forests on river terraces, such as our TE (terrace) site, where Alisol soils reflect a more recent pedogenetic status with often higher P availability (Quesada et al., 2010; Quesada et al., 2011). Soil total P contents of forest plots near our PE and TE sites were however highly similar (Andreae et al., 2015) and extremely low in global comparison (He et al., 2021; Turner & Engelbrecht, 2011). In tropical soils P availability is not only regulated by overall low P contents but also strong sorption. The TE site features ~50% lower Al oxide content and 25% less Fe and Al bound in crystalline phases, both of which potentially increase P availability due to fewer binding sites. Additionally, its ~40% lower aboveground biomass (Andreae et al., 2015) could decrease ecosystem P demand. Nonetheless, our findings suggest that P-limitations may occur in *terra firme-like* forests on ancient river terraces such as our TE site, despite their younger

pedogenesis, potentially higher P availability, and lower aboveground biomass. Previous studies on nutrient limitations have focused on more common rainforest types occurring on different soils (Cunha et al., 2022). While Alisols are not ubiquitous in the Amazon, they may be underrepresented in soil classifications of the Amazon (Quesada et al., 2011). Our findings imply that P-limitation may extend to rainforest types where it is less commonly assumed, which has implications for basin-wide nutrient limitations of the central Amazon.

Terra firme forests are largely not considered N-limited (Brookshire et al., 2012). The observed extensive processing of N-DOM may be caused by a generally high N demand of microbial communities or plants, or due to low N use efficiencies. Alternatively, it could also be linked to elevated production of microbial cell wall components and extracellular enzymes for P acquisition, for example using phosphatases or phytases (Yao et al., 2018) both requiring N. If the *terra firme* sites are in fact P-limited, it is likely that microorganisms and plants will allocate resources preferentially towards P acquisition (Zhang et al., 2018). This implies that any limitation of P is likely to cause elevated enzyme production, which in turn is a significant N investment and automatically imposes a higher demand for N. Our data showed substantial cycling of organic N in the soil profile, which indicates a potential interlinked demand for N and P to counteract P-limitation. Despite the common assumption of N abundance in tropical forests, the N content in the top 10 cm of *terra firme* soil (~0.22 wt%) was comparable to temperate forests, which typically range between 0.1 and 0.5 wt% (Perakis & Sinkhorn, 2011; Prieto-Fernández & Carballas, 2000; Spohn & Stendahl, 2022). If P is already limiting today, this constraint is likely to intensify with rising atmospheric CO₂ concentrations. Plant nutrient demands are projected to increase in tandem with plant productivity as a response to CO₂ fertilization (Terrer et al., 2019). Alongside increasing severity of potential P-limitations, our results indicate that the increasing P demand may render N co-limiting due to more resource-intensive P acquisition. If demand for both P and N rises, ecosystems are expected to increase both P- and N-mining. P-mining can occur independently of organic matter decomposition through cleavage by extracellular enzymes (Martins et al., 2021), while N-mining requires decomposition. Elevated N-mining might consequently lead to increased decomposition of soil organic matter, which could decrease soil organic carbon stocks. Another effect might be the upregulation of biological N fixation to meet nutrient demands (Moreira et al., 2021).

We hypothesized that N- instead of P-limitation would occur in white-sand forests. The soil N content was more than ten-fold lower than that of *terra firme* soils (Table 6.4-1), which suggests a relative scarcity of total N in soils of the investigated white-sand forests. However, the N/C ratios of DOM did not differ strongly between the two rainforest types, and were even higher in white-sand DOM than in the PL site (Figure 6.4-1 B). Our hypothesis of N-depletion in white-sand DOM therefore was not confirmed. Unexpectedly, white-sand DOM showed instead a strong depletion in S. Tropical forests are not considered S-limited, but research on S cycling in tropical soils is very scarce. Contrary to our hypothesis, we did not observe preferential processing of N-DOM over other nutrients in the soil profile, at least in terms of signatures reflected in DOM (Figure 6.4-2 B). The processing of all DOM pools was considerably lower than that in *terra firme* soils. This suggests a lesser importance of the first 30 cm of mineral soil for DOM and nutrient cycling in white-sand forests in general. In addition, the temporal variability of DOM was not highest for N-DOM, which contradicted our hypothesis as well. Variability was instead highest for S-DOM, in both 5 and 0 cm soil depths. Our analysis of DOM variability revealed higher variability in low-abundance DOM pools in all sites. This pattern could be expected because higher relative variability occurs more readily for nutrients in low concentration. Nonetheless, ecological meaning can be inferred because high variability of low abundant nutrient pools suggests a rapid and tight nutrient cycle. We caution however that our results could have been affected by analytical insensitivity, where the occurrence of very low abundant compounds might not have been detected by our instrument, thereby increasing the observed variability of these nutrient pools.

The high variability of S in DOM derived directly from the organic layer (0 cm soil depth; Fig. S4) implies extensive cycling of organic S species in the organic layer. Overall, none of the three proxies supported the hypothesized N-limitation in the white-sand forests. The depletion and high temporal variability of S-DOM on the other hand suggest a high demand for S by plants or microorganisms living in the root mats or humus layer. High S demand or any S-limitation have not yet been proposed for these rainforest types. White-sand forests are generally understudied compared to other rainforest types (Adeney et al., 2016), and S has rarely been investigated. To the best of our knowledge, soil S contents have not been reported for white-sand soils to date. There are possible causes for an elevated S demand in white-sand forests. Sandy soils are generally more prone to S deficiency (Narayan, Kumar, Yadav, Dua, & Johri, 2023). Importantly, atmospheric S deposition has decreased in recent decades due to reduced S emissions from air pollution and coal combustion, and it is generally lower in remote regions (Feinberg et al., 2021). Lower S deposition may thus increase S scarcity also in these systems. The high variability and low abundance of S-DOM could reflect rapid turnover of organic S compounds, suggesting a tightly coupled S cycle where demand closely matches supply. Microbial communities therefore might show specialization for organic S mineralization (Manzoni, Chakrawal, Spohn, & Lindahl, 2021) or might be structured by their ability to compete for scarce S resources (Cui et al., 2018b). A high S demand could furthermore drive plant adaptations towards increased resource allocation to S-acquiring mycorrhizae (Allen & Shachar-Hill, 2009; Vasco-Palacios, Hernandez, Peñuela-Mora, Franco-Molano, & Boekhout, 2018). Lastly, organic S compounds are also of particular interest because of their connection to S-containing gas species that are emitted from tropical soils and that play an important role in the formation of aerosol particles and act as nuclei for cloud condensation (Jardine et al., 2015b; Lehnert et al., 2024). Decomposition of organic S compounds can be an important source of volatile S species, such as dimethyl sulfide, methanethiol and H_2S . We sampled volatile organic compounds in the soil of one white-sand (CW, *Campinarana*) and one *terra firme* site (TE, Terrace) (Supporting Text S3). Volatiles with S and simultaneous S–N assignment were detected in both sites. S-containing species exhibited ~2.5-fold higher intensities in the white-sand site, constituting 2% of all detected volatiles, with CHOS species showing sevenfold higher intensities (Table S4). Soil DOM also contained six oxygen-free CHS compounds ($\text{C}_{11}\text{H}_{10}\text{S}_2$, $\text{C}_{11}\text{H}_{12}\text{S}_2$, $\text{C}_{12}\text{H}_{12}\text{S}_2$, $\text{C}_{12}\text{H}_{14}\text{S}_2$, $\text{C}_{12}\text{H}_{14}\text{S}_2$, $\text{C}_{13}\text{H}_{16}\text{S}_2$, $\text{C}_{14}\text{H}_{20}\text{S}_2$). Such compounds are more volatile than oxygen-containing species due to their low polarity. Despite a much lower number of S-containing compounds in white-sand than in *terra firme* DOM (50 vs 316 per sample, respectively; Table 6.4-2), CHS compounds occurred much more frequently in white-sand samples (108 vs 14 total occurrences, respectively). The higher abundance of S-containing volatiles in white-sand soils support our findings of elevated variability of S-DOM in these forests. Jointly, these findings suggest the possibility of enhanced production of S-containing volatiles in white-sand forests. These compounds are poorly soluble in water and easily degas from soils (Jardine et al., 2015b; van Leerdam, van den Bosch, Lens, & Janssen, 2011). Small quantities of volatile S compounds can have important effects on aerosol and cloud formation (Jardine et al., 2015b). Despite the smaller area covered by white-sand forests, S-production in the white-sand soils might therefore affect regional atmospheric chemistry. Overall, our findings warrant further investigation of S dynamics in white-sand forests of the Amazon.

6.5.2 Above- and belowground nutrient cycling

We hypothesized a greater magnitude of belowground DOM and nutrient cycling in the *terra firme* forests. In support of our hypothesis, DOM in the clayey *terra firme* soils exhibited a stronger imprint of microbial processing already in 5 cm soil depth Figure 6.4-4 as evidenced by more aliphatic, lipid-like and saturated DOM (Butturini et al., 2020; Li et al., 2021; Riedel et al., 2016; Roth et al., 2019). In contrast, DOM in white-sand soils was dominated by products of early plant matter decomposition, with dominance of aromatic, oxidized and more oxygen-rich compounds (Gleixner, 2013; Hertkorn et al., 2016; Klotzbücher et al., 2013; Spencer et al., 2019). This distinction was supported by annotation of molecular formulas in the ChEBI database (Hastings et al., 2016) (**Supporting Text S2**). The differences were also reflected in the nutrient pools of DOM (Figure S 11.4-2; Figure S 11.4-3). N-, P- and S-containing DOM consistently showed higher aromaticity and oxygenation in white-sand sites and

higher saturation, and aliphatic and lipid-like content in *terra firme* sites. The molecular composition changed remarkably similarly with soil depth in the white-sand and *terra firme* sites. The DOM composition shifted consistently towards higher DOM processing in greater depth, i.e. decreasing aromatic and increasing aliphatic content. The magnitude of DOM processing in the soil profile was two- to three-fold higher than in white-sand soils (Figure 6.4-2), supporting our hypothesis of higher belowground cycling in *terra firme* sites. The DOM composition generally can be influenced by adsorption processes on mineral surfaces (Subdiaga et al., 2020; Zhang, Liu, Huang, Min, & Sun, 2020a). Specific DOM fractions may preferentially bind to sorption sites, leading to compositional shifts that are determined by the mineralogy of the soil. However, the white-sand soils in our study are virtually sorption-free environments containing mostly quartz. If sorption was driving compositional shifts, we would expect qualitatively different trends in the clayey *terra firme* soils with high sorption capacity. The similarity observed in the depth trends of all soil types strongly suggests that the increasing DOM processing imprint in greater soil depth is primarily driven by the biological processes of decomposition, mineralization and assimilation by microorganisms and plants. Additionally, the importance of sorption was recently demonstrated to strongly decrease when mineral surfaces were already preconditioned (Zhu et al., 2023). In our field setting, we assume that a large portion of available mineral surfaces in *terra firme* sites is already preconditioned due to continuous leaching of litter DOM. Characteristics of fine-textured soils, such as longer residence times, likely increase the effect of biological DOM processing (Simon et al., 2021). In addition to the chemical characteristics of DOM, also the much lower DOC concentrations in *terra firme* sites indicated more intense processing and mineralization of DOM, leading to lower accumulation of DOC in soil solution.

Our findings highlight the importance of mineral soils for nutrient cycling in *terra firme* forests. DOC concentrations decreased strongly from 5 to 30 cm soil depth (Table 6.4-1), and plant-derived, N- and P-containing organic nutrients were processed rapidly and broken down or converted into microorganism-derived compounds during soil passage. The first 30 cm of mineral soil appear important for nutrient retention, at least when considering the bioavailable nutrient pool of DOM. A previous study investigated the molecular DOM composition in groundwater from highly similar *terra firme* plateau and white-sand forests in the same region (Simon et al., 2021). Re-processed data from this study were used to compare DOM processing between 30 cm soil depth and groundwaters. Groundwater DOM from a *terra firme* plateau site revealed a continuation of the depth trends observed in our *terra firme* sites, such as an increasing content of aliphatic and lipid-like formulas compared to 30 cm soil depths (Table S3). For example, in P-DOM, the content of aliphatic compounds increased from 35% in 30 cm soil depth to 62% in groundwater DOM. This implies that significant DOM processing persists even in deeper soil horizons below 30 cm depth. *Terra firme* forests however often have very deep soils (> 10 m). Although roots and microbial activity are typically concentrated near the soil surface (Broedel, Tomasella, Cândido, & Randow, 2017), our findings suggest that deeper soil compartments may contribute substantially to DOM processing and nutrient cycling. While the significance of aboveground nutrient cycling in tropical forests frequently has been emphasized (Cuevas & Medina, 1988; Sayer et al., 2024; Vitousek, 1984), our results highlight the crucial role of mineral soils and belowground processes in nutrient (re-)cycling within *terra firme* forests.

In contrast, the lower DOM processing in coarse-textured soils suggests that the mineral soil may be of lower importance for nutrient recycling in white-sand forests, confirming our hypothesis of reduced belowground cycling in these systems. Indeed, also nutrient pools in DOM were only weakly processed in the first 30 cm of white-sand soil. This is supported by the DOM composition of white-sand groundwater (Simon et al., 2021), which was highly similar to DOM leached from the white-sand forest organic layer (0 cm soil depth). For example, the abundance of aromatic compounds was not significantly different between organic layer- and groundwater-derived DOM for N-, S-, and P-containing pools (Kruskal Wallis test, $p > 0.05$). This strongly suggests that the mineral soil is less important for

nutrient recycling in white-sand forests than in *terra firme* forests. While the processing of nutrient-DOM in the soil profile was much lower than that in *terra firme* sites, the temporal variability in 0 cm soil depth was of a similar magnitude in both rainforest types (Figure 6.4-3). This suggests that nutrient cycling in white-sand forests was more pronounced in the organic layer than in the mineral soil, and supports the reports that the organic layer and specifically root mats are more important for nutrient retention in these forests, in line with the classic notion of aboveground nutrient recycling (Stark & Jordan, 1978; Vitousek, 1984). Those organic nutrients that entered the mineral soil were not processed strongly during soil passage compared to the *terra firme* forests. Upland white-sand forests have been shown to export characteristic plant-derived DOM to the aquatic continuum (Simon et al., 2021), and our research suggests that these markers originate from the surface organic layers of white-sand areas, and may thus be directly linked to litter production and recycling. At our white-sand sites, DOC concentrations did not decrease significantly with soil depth (CD, *Campina*) or remained high in 30 cm soil depth ($> 30 \text{ mg C l}^{-1}$; CW, *Campinarana*). In the groundwater of the white-sand site (Simon et al., 2021), DOC concentrations were $> 25 \text{ mg C l}^{-1}$, suggesting that white-sand forests export considerable amounts of DOC to the groundwater and downstream rivers. The low processing of organic nutrient pools during soil passage indicates that organic nutrients were likely not processed efficiently by microbial communities in the mineral soil. Despite indications for higher nutrient cycling in the organic layer, plant-derived organically-bound nutrients could be lost to the groundwater instead of being recycled. Our results support the hypothesis that nutrient retention in white-sand forests occurs primarily above the mineral soil. We provide novel evidence that minimal DOM processing occurs during transport from the organic layer into groundwater. The limited belowground nutrient processing potentially makes these ecosystems much more vulnerable to disturbances that disrupt the intact aboveground nutrient recycling.

6.6 Conclusion

Our study derived three proxies for estimating the nutrient cycling intensity through the DOM pool and indicate potential nutrient limitations: relative nutrient depletion, DOM processing in the soil profile, and temporal variability of the DOM composition. The three proxies supported the hypothesized P-limitation in both *terra firme* forest sites, including one with younger pedogenesis and higher P availability. This implies that P-limitation may extend Amazon rainforests on less infertile soils. As P-limitation on ecosystem productivity is more commonly assumed for ancient soils, this has implications for the distribution of nutrient limitations in the central Amazon and its response to global change. The observed high processing of N-DOM raises the possibility of N co-limitation, further influencing the Amazon's response to global change. Contrary to our hypothesis, N-limitation in white-sand forests was not confirmed. Instead, two proxies unexpectedly indicated elevated demand and cycling of S. These findings highlight the need for a better understanding of the diverse nutrient limitations within the Amazon basin to forecast productivity responses accurately.

Our results further emphasize the important role of the mineral soil for nutrient recycling in *terra firme* but not white-sand soils. Effective belowground processes may alleviate increasing P-limitation to a degree by retaining nutrients efficiently and possibly accessing P reserves present in the soil. Considering the diversity of ecosystems in the Amazon, their individual nutrient dynamics will be key to forecast basin-wide dynamics. The proxies used in this study open avenues to investigate nutrient cycling, which can help understand ecosystem nutrient demands and limitations. HR-MS techniques provide an important analytical means to disentangle the complex composition and dynamics of DOM and the contained organic nutrient species.

Data availability

The data generated and analyzed for this study are publicly available on the 'Environmental Data Initiative' repository (edirepository.org; <https://doi.org/10.6073/pasta/0f91c0935840c0eaae74d8091a1d5bf1>).

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Contributions

Carsten Simon, Gerd Gleixner and Carlos A. Quesada conceived and designed the frame of the study; D. Frederik Lange, Carsten Simon and Gerd Gleixner coordinated the sampling campaigns; Fernanda M. da Luz and Yago R. Santos helped during field work and performed soil and water chemistry measurements; Elaine Pires and Jonismar S. da Silva performed water chemistry measurements; Stefanie Hildmann performed sampling of soil gas, and Stefanie Hildmann and Thorsten Hoffmann helped with measurements and data analysis of soil gas; D. Frederik Lange and Simon A. Schröter analyzed the data. D. Frederik Lange, Carsten Simon, Thorsten Schäfer and Gerd Gleixner interpreted the data; D. Frederik Lange led the writing of the manuscript, and Carsten Simon and Gerd Gleixner contributed to the writing of the first draft; all authors contributed to the drafts and gave final approval for submission.

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

7 Resolving the challenge of determining organosulfates in ambient organic aerosol samples

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Summary

In this chapter, the analytical challenge of quantifying organosulfates in ambient organic aerosol samples is addressed by presenting a novel solid-phase extraction (SPE) method coupled with high-resolution Orbitrap mass spectrometry (HR-Orbitrap-MS) and charged aerosol detection (CAD). The study quantifies ~130 and ~65 chromatographically resolved organosulfates in urban (China) and rural (Germany) aerosols, respectively, while revealing an additional 12–21% contribution from unresolved organosulfate fractions. These findings underscore the significant role of sulfur emissions in organic aerosol pollution and demonstrate the potential of targeted emission reductions to improve air quality. By combining SPE, HR-Orbitrap-MS, and CAD, this work not only provides a detailed molecular-level characterization of anthropogenic organosulfates but also demonstrates the broader applicability of advanced mass spectrometric approaches to environmental aerosol studies.

I am a co-author of this paper. I developed and implemented a hydrophilic interaction liquid chromatography (HILIC)-HR-Orbitrap-MS method specifically optimized for the separation and detection of small organosulfates. My contributions included method validation, optimization of chromatographic conditions, and application of the HILIC technique. Additionally, I assisted in conducting potential aerosol mass (PAM) chamber experiments to investigate organosulfate formation under controlled atmospheric conditions, supported the interpretation of mass spectrometric data, and assisted with manuscript preparation.

Unveiling a large fraction of hidden organosulfates in ambient organic aerosol

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7.1 Abstract

Organosulfates are key compounds driving the anthropogenic enhancement of ambient organic aerosol, however, total organosulfate quantification remains elusive due to their molecular diversity and the scarcity of authentic standards. Here, we present a solid-phase extraction method that isolates organosulfates from ambient aerosol samples and enables their identification and quantification using mass spectrometry and a charged aerosol detector, respectively. We investigate ambient aerosol samples from urban China and rural Germany and quantify ~130 and ~65 chromatographically resolved organosulfates, respectively, contributing less than ~2% to the total organic matter. We find a significantly larger organosulfate fraction appearing as a broad peak in the chromatograms from the charged aerosol detector. Confirming its origin from chromatographically non-resolved organosulfates, an all-ion fragmentation experiment reveals specific sulfate-related ions. Integrating this peak, we find the contribution of organosulfates to organic aerosol is 12-17% and ~21% in samples from urban China and rural Germany, respectively. These findings emphasise the potential of sulfur emission reduction for mitigating both sulfate-related and organic aerosol pollution.

7.2 Introduction

Atmospheric fine particulate matter (PM) has major implications for human health, Earth's radiative balance and air quality (Stocker., et al., 2013) (Daellenbach et al., 2020; Lelieveld et al., 2020; Stocker., et al., 2013; Stocker., et al., 2013). Organic aerosol (OA) is a major component in ambient PM, typically contributing 30-50% of the fine aerosol mass in the lower troposphere, though this can reach up to 90% in pristine environments (Huang et al., 2014; Jimenez et al., 2009; Kanakidou et al., 2005; Zhang, Cai, Wang, He, & Zheng, 2017). Therefore, understanding the chemical composition and atmospheric transformation of OA is vital for identifying their sources and developing effective mitigation strategies. Due to a large variety of natural and anthropogenic emissions, transformed by intricate multiphase chemical processes, the chemical characterization of secondary OA (SOA) is extremely challenging. Organosulfates (OSs) are an important subclass of OA (Hettiyadura, Al-Naiema, Hughes, Fang, & Stone, 2019; Iinuma et al., 2007b; Iinuma, Müller, Böge, Gnauk, & Herrmann, 2007c; Romero & Oehme, 2005; Surratt et al., 2006a; Surratt et al., 2008), comprising up to 30% of the OA (Surratt et al., 2008). They can form through different pathways such as heterogeneous reactions between OA and SO₂ (Brüggemann et al., 2020b; Gao & Zhu, 2021; Liu, Chan, & Abbatt, 2021; Passananti et al., 2016; Wang et al., 2019a), sulfuric acid-driven condensation reactions within aerosol particles (Brüggemann et al., 2020b; Froyd et al., 2010), or even through heterogeneous reactions on building surfaces (Deng et al., 2022). The reactive uptake of semi-volatile organic compounds, particularly isoprene epoxydiols (IEPOX), onto acidic particles can result in the formation of low-volatile OSs and, consequently, add to the OA mass (Brüggemann et al., 2020b; Riva et al., 2016a; Surratt et al., 2006c; Surratt et al., 2006a; Wang et al., 2016a). If the involved organics are of biogenic origin, SO₂ emissions can effectively lead to an anthropogenic enhancement of biogenic SOA (Hoyle et al., 2011; Surratt et al., 2008; Surratt et al., 2010). Further studies on OSs have demonstrated that they can change the hygroscopic growth of OA and even have the potential to promote heterogeneous ice nucleation (Estillore et al., 2016; Wolf et al., 2020).

Several studies have analyzed OSs in different environments, e.g., in the urban OA of Chinese megacities, in which rapid formation of OSs during pollution events has been observed (Han et al., 2023; Ma et al., 2022; Wang et al., 2018; Xie et al., 2020). However, Brüggemann et al. reported significant sampling artifacts in the detection and quantification of monoterpene-derived OSs under atmospheric conditions (Brüggemann et al., 2020a). LeBreton et al. used a Filter Inlet for Gases and Aerosols coupled to a Chemical Ionization Mass Spectrometer to measure OSs in near-real time, and therefore minimizing sampling artifacts, at a semi-rural site in Beijing. They quantified 17 single OSs, estimating their overall contribution to OA at 2%, suggesting that OSs are not merely artifacts of the sampling process (Le Breton et al., 2018). Similarly, a study conducted in Beijing using high-performance liquid chromatography (HPLC) combined with high-resolution mass spectrometry (HRMS) reported a ~4% contribution of OSs to OA (Ma et al., 2022).

In urban and rural OA, studies have shown significant seasonality in both biogenic and anthropogenic OSs at various sites, with biogenic OSs peaking in summer and anthropogenic OSs in winter (Chen et al., 2021; Meade et al., 2016). In marine OA, in the Yellow and Bohai Seas, the contribution of biogenic OSs ranges from 0.04 to 6.9% (Wang et al., 2023c). In the central Amazon, Glasius et al. found ~0.1 and ~0.6 $\mu\text{g}/\text{m}^3$ of isoprene-derived OSs downwind of Manaus during the wet and dry seasons, respectively (Glasius et al., 2018c). OSs can be transported in the atmosphere over long distances, since relatively elevated OS concentrations (~20–40 ng/m^3) during Arctic haze events at Svalbard have been reported, probably originating from northern Eurasia (Hansen et al., 2014). Even in Alpine ice core samples from the Fiescherhorn glacier, OSs from both biogenic and anthropogenic organics were detected in a sample that dates back to the year 1984 (Vogel et al., 2019). Although the direct analysis of molecularly resolved OSs enables the determination of their contribution to total OA, a degree of uncertainty remains in using this approach since it relies on the individual detection of single molecules and the application of surrogate standards for quantification. If no authentic standard is available, Brüggemann et al. suggested camphor-10-sulfonic acid ($\text{C}_{10}\text{H}_{16}\text{O}_4\text{S}$) as an appropriate surrogate standard (Brüggemann et al., 2019). Nevertheless, direct quantification can easily introduce a large uncertainty due to different ionization efficiencies or by missing low-abundant or chromatographically unresolved OSs that can result in the underestimation of the total content of OSs in ambient aerosol.

Besides the direct quantification of individual OSs, indirect methods are available that quantify the total content of OSs by determining the difference between total sulfur (e.g., determined by X-ray fluorescence) and inorganic sulfate (e.g., determined by ion chromatography). These indirect approaches have suggested that OSs contribute 6–14% and up to 20% of the total sulfate at a rural Hungarian site (Lukács et al., 2009) and in urban Shenzhen, China (Cao, Zhao, Di Hu, Zhu, & Ouyang, 2017), respectively, and 5–10% to the organic matter (OM) in the United States (Tolocka & Turpin, 2012). Aerosol mass spectrometry (AMS) has been used to quantify OSs in real time (Chen et al., 2019; Farmer et al., 2010; Huang, Li, Lee, & Chan, 2015; Liggio & Li, 2006; Vogel et al., 2016). Farmer et al. reported ~12% of total sulfate being present as OSs in Riverside, California, by comparing the AMS measurements of total sulfate and the ion chromatography measurements of inorganic sulfate, while the same approach at a rural station in Germany indicated that OSs can account for up to 46% of OA during single pollution episodes (Farmer et al., 2010; Vogel et al., 2016). Organosulfur abundance typically follows a seasonal cycle with the formation of isoprene-derived OSs during summer, providing direct evidence for the anthropogenic enhancement of biogenic SOA, although the majority of organosulfur species remain unattributed (Chen et al., 2021; Glasius et al., 2022). Thus, the larger OS concentrations consistently observed through indirect methods indicate that the direct quantification of individual OSs likely underestimates the total OS concentration in ambient OA.

To improve the detection of individual, low-abundant OSs in ambient aerosol samples, we developed a solid-phase extraction (SPE) method for their enrichment and fractionation. To overcome the need for authentic OS standards, we made use of HPLC coupled to a charged aerosol detector (CAD) alongside a HRMS for separation, quantification and identification, respectively. The CAD is favorable for the

quantification of non-volatile species due to its universal response, regardless of the chemical structure (Vehovec & Obreza, 2010). Owing to the terminal sulfate groups ($\text{R-OSO}_3\text{H}$), in particular, OSs exhibit a low saturation vapor pressure, thus making them well-suited for quantification using a CAD. In addition to the CAD measurements for quantification, we employed two different mass spectrometric experiments for unambiguous molecular identification: (1) full-scan measurements (fullMS) as a basis for non-target analysis and unambiguous molecular formula attribution of chromatographically well-resolved compounds, and (2) all-ion fragmentation (AIF) experiments for the detection of OS-specific ion fragments across the whole chromatogram. Applied on ambient aerosol filters from different environments, we directly quantified a large fraction of unresolved OSs, indicating their significant presence in both urban and rural environments and, furthermore, highlighting that their contribution to the formation of the aerosol mass cannot be overlooked.

7.3 Results and discussion

7.3.1 Organosulfate isolation

In the field of atmospheric sciences, water or organic solvents are commonly used for liquid extraction of aerosol filter samples. The application of SPE for enrichment and fractionation of compounds is rarely practiced, but this sample preparation enables novel analytical approaches. Here, we used a mixed-mode anion-exchange (MAX) cartridge and reversed-phase sorbent that has a strong affinity to bind OSs, thus allowing the isolation of acidic compounds from the complex sample matrix of ambient aerosol filters (Vogel et al., 2019). A fundamental property of OSs, the terminal $\text{R-OSO}_3\text{H}$ group, leads to a higher acidity ($\text{pK}_a \sim -2.4$ to -4.6) for most of the (nitrooxy-)OSs compared to other acidic organic compounds in ambient air (e.g., nitro-phenols or organic acids), ensuring their almost complete dissociation under typical aerosol pH conditions (1–4) (Hytinen, Elm, Malila, Calderón, & Prisle, 2020).

We extracted $\text{PM}_{2.5}$ filter samples from Handan, China, and the Taunus Observatory (TO), Germany, representing the North China Plain with severe air pollution, and a relatively clean, rural background station in central Europe, respectively. In the following, we first describe a representative sample from Handan with regard to our new enrichment and quantification approach, before discussing all analyzed samples from both field sites. We have compared the chemical fingerprint with retention time (RT) vs. the mass-to-charge ratio (m/z) of an aliquot of the native aerosol filter extract against the two isolated fractions and the flowthrough after SPE (Figure 7.3-1). The two SPE fractions are diluted to the same concentration level as the native extract. This enabled a quantitative comparison and the evaluation of the absolute SPE-recovery of the single organic compounds detected by non-target analysis. Most of the identified organic compounds in the native extract were found to be smaller than 350 Da and eluted over the entire retention time range (Figure 7.3-1 a). CHNO compounds (containing carbon, hydrogen, nitrogen, and oxygen) were the predominant compound class, followed by CHO compounds. The sulfur-containing compounds (CHOS, CHNOS) contributed 37% (by intensity) to the overall detected compounds (Figure 7.3-1 a, Figure 7.3-2). By using a weak acid dissolved in methanol for the first SPE elution, we removed the less acidic compounds, including (nitro-)aromatics and organic acids (Figure 7.3-1 b). Subsequently, we used diluted hydrochloric acid dissolved in methanol to elute the OSs from the cartridge. We did not observe any evidence for degradation of the OSs, confirming their chemical stability at low pH (Olson et al., 2011a). With this increased solvent acidity for the second SPE elution, we were able to elute the CHOS and CHNOS compounds and, hence, isolate the OSs in a specific fraction. The diluted aliquot of this fraction will now be referred to as the diluted OS fraction (Figure 7.3-1 c). The compounds in the flowthrough were found to be mainly neutral compounds that were not retained by the MAX cartridge (Figure 7.3-1 d).

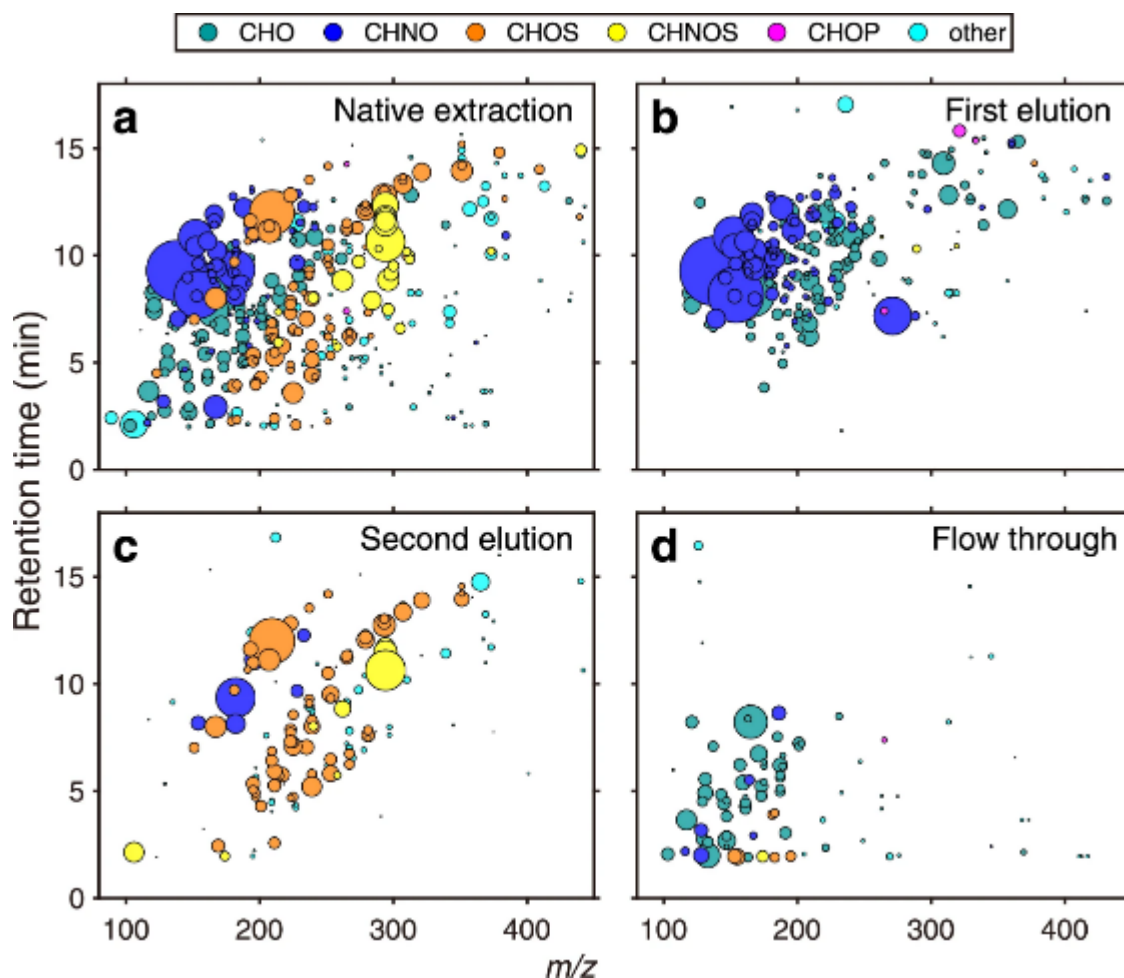


Figure 7.3-1: Particulate matter (PM) sample fractionation by solid-phase extraction. Mass-to-charge ratio (m/z) vs. retention time space showing single organic compounds extracted from a representative Handan ambient PM_{2.5} filter (Handan 1: 18.10.2018, daytime) with negative electrospray ionization. Each circle represents a detected compound with the circle size illustrating the signal intensity. The six compound classes are classified by color (CHO, dark cyan; CHNO, dark blue; CHOS, orange; CHNOS, yellow; CHOP, pink; other, light blue). The compound class names refer to the elemental composition of the classes (i.e., CHNOS must contain the elements carbon, hydrogen, nitrogen, oxygen and sulfur); “other” refers to the compounds excluded from the major compound classes mentioned above. Graph a shows the native extraction: ambient PM_{2.5} filter extracted with a water/methanol mixture (98/2 (v/v)), b the first solid phase extraction (SPE) elution: fraction containing (nitro-)aromatics and organic acids, c the second SPE elution: isolated fraction containing organosulfates (OSs) and nitrooxy-OSs, and d the flowthrough: native extraction after passing through the SPE cartridge, containing mostly neutral and polar compounds.

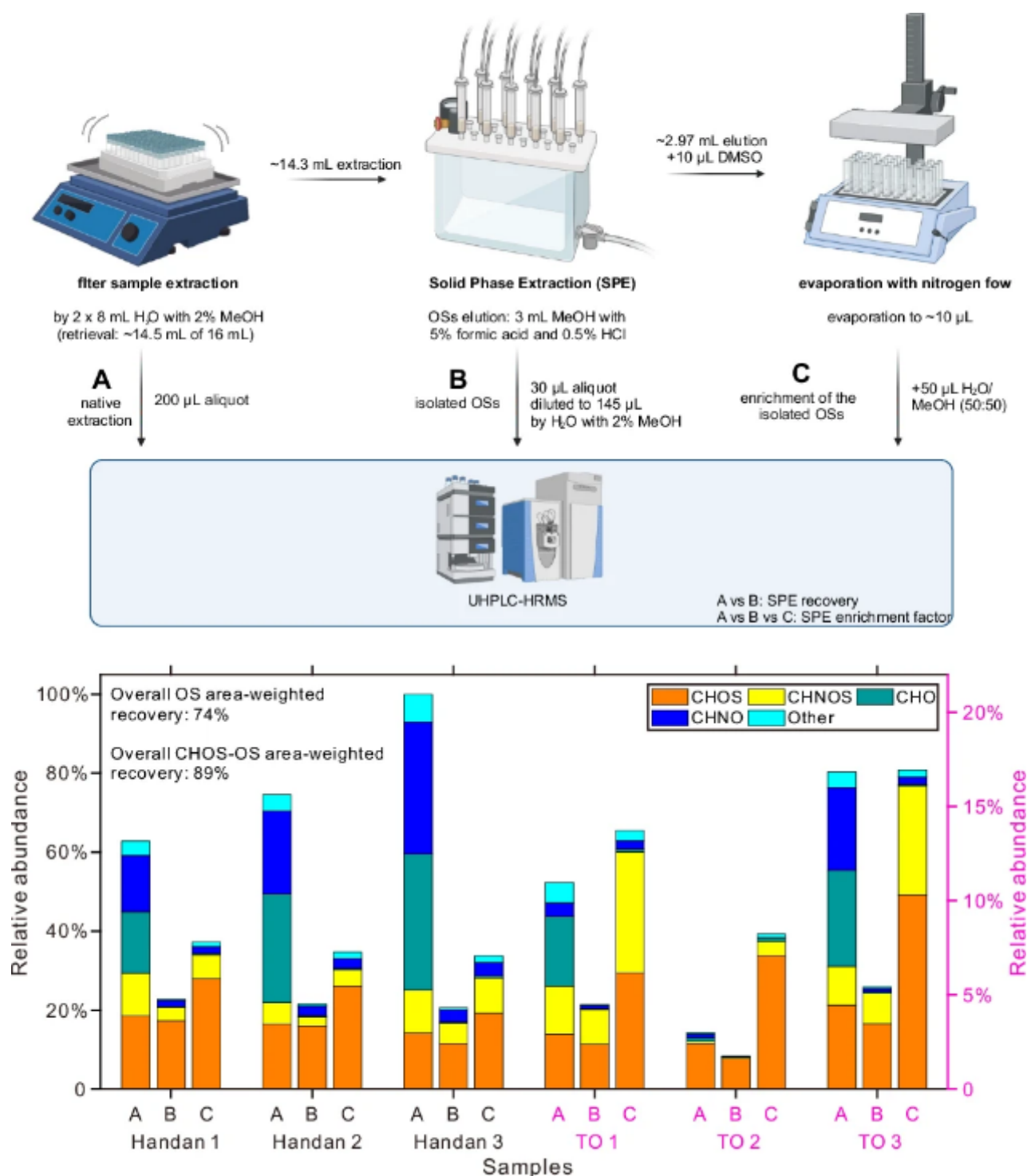


Figure 7.3-2: Schematic of the extraction and enrichment procedure. Relative abundance (%) of summed peak areas (negative electrospray ionization) of the different compound classes in the native extraction (A), diluted organosulfate (OS) fraction (B) and enriched OS fraction (C). The y-axis shows the relative abundance of the compound classes, normalized to the most intense sample (native extraction of the Handan 3 sample). For better clarity, the left y-axis refers to the Handan samples (black; 0–100%), and the right y-axis to the Taunus Observatory (TO) samples (pink; 0–20%). The samples used were Handan 1: 18.10.2018, daytime; Handan 2: 21.10.2018, daytime; Handan 3: 21.10.2018, night-time; TO 1: 11.12.2021, daytime; TO 2: 14.01.2022, night-time, and TO 3: 28.02.2022, night-time. In order to make the native extraction (A), the diluted OS fraction (B) and the enriched OS fraction (C) comparable, we accounted for the enrichment factor by the SPE (~240) and the different experimental setup in (C): (A) and (B) were acquired using HPLC-HRMS (100% of mobile phase flow into the MS) and (C) by using HPLC-HRMS/CAD (16.5% of mobile phase flow into the MS). The consistently larger relative abundance of OSs in fraction (C), therefore, solely originates from additionally detected OSs following SPE. Created in BioRender. Reininger, N. (2025) <https://BioRender.com/n70h222>.

Within the diluted OS fraction, the MS² spectra revealed that over 99% of the CHOS and CHNOS compounds (by signal intensity) formed a fragment at m/z 96.9601 (HSO₄⁻), indicating the existence of R-OSO₃H groups (Thoma et al., 2022). Furthermore, 72% of the compounds in the OS fraction had an absolute recovery above 50% compared to the native extraction. Some OSs had a poorer recovery of between 10 and 50%, showing relatively small signal intensities (Figure S 11.5-1a). The low recovery of some compounds can be explained by their strong retention on the ion exchange cartridge. By extracting one sample via SPE in triplicate, we found that the intensity-weighted average of the relative standard deviation (RSD) of the SPE recovery was ~15% for OSs, with larger uncertainties for the low-intensity compounds (Figure S 11.5-1 b). The recovered OSs spanned a large range regarding the polarity and mass-to-charge ratio, ranging from relatively small (~150 Da) and polar (short RT) to large (~350 Da) and non-polar compounds (long RT). However, we did note that the used SPE cartridge provides a low recovery of small and highly polar OSs, which may include certain isoprene-derived OSs, an important class of atmospheric OSs. To a lesser extent, reversed-phase LC (used in this study) is also less effective for separating these compounds, highlighting the complementary role of hydrophilic interaction LC methods in analyzing smaller OSs .

With our SPE method, we obtained an overall mean OS (CHOS and CHNOS) recovery of 75% (with a standard deviation of 7%) for the six ambient aerosol samples (area-weighted mean, Figure 7.3-2). We calculated the overall mean recovery by calculating the sum of all isolated OSs, instead of averaging the recovery of individual OSs. In particular, the mean overall recovery for CHOS-only OSs was found to be 89%. Distinguished by the sampling site, the recovery of all OSs (CHOS and CHNOS) for the Handan samples was 73%, with the CHOS-OS recovery being 91%. The OS recovery for the TO samples was 76%, with the recovery of CHOS-OSs also being 76%. The difference in CHOS-OS recovery for the two sites was likely caused by different OSs with different properties and total aerosol mass loadings. However, we note that larger, less polar OS compounds may exhibit a reduced extraction efficiency, which should be considered in future studies. Overall, the SPE isolation method was found to be capable of effectively isolating the OSs from complex aerosol filter extracts, thereby allowing the subsequent chemical analysis of the enriched fraction and the quantification of the OSs by the CAD.

7.3.2 Organosulfate enrichment and quantification

In the enriched OS fraction (second SPE elution after evaporation and reconstitution, see Figure 7.3-2—workflow (C)), the OSs were enriched by a factor of ~240 compared to the native extraction, which thus enables their detection by the less sensitive CAD. This large enrichment factor also increased the number of detected OSs after the non-target analysis of HRMS data (diluted fraction vs. enriched fraction of sample “Handan 1”: 79 and 490 detected OSs, respectively; see Figure 7.3-1 vs. Figure 7.3-3 a) due to the improved signal-to-noise ratio of low-abundant OSs. The molecular fingerprints of the enriched OS fraction of all samples are shown in Figure S 11.5-2. After SPE, the larger number of OSs revealed the specific molecular characteristics for both field sites, especially for the aliphatic OSs—likely to be of anthropogenic origin—that were clearly visible at the rural TO station during winter time (Riva et al., 2016b; Riva et al., 2016a). For example, sample TO 2 (Figure 7.3-2), a PM_{2.5} sample obtained during relatively clean conditions, showed the largest increase in area-weighted CHOS compounds after enrichment. Note that the increase in relative abundance from TO 2-A to TO 2-C (Figure 7.3-2) originates from the larger number of detected OSs following SPE-enrichment. The signal intensity of the enriched OS fraction was 2.8–3.4 times higher than the diluted OS fraction in the TO samples. For the Handan samples this factor ranged from 1.2 to 1.6 (Figure 7.3-2). With our regular liquid extraction method (i.e., Figure 7.3-1 a, native extraction) many OSs remained below the HRMS detection limit, leading to a potential underestimation of the OS contribution to total OA, especially for rural stations.

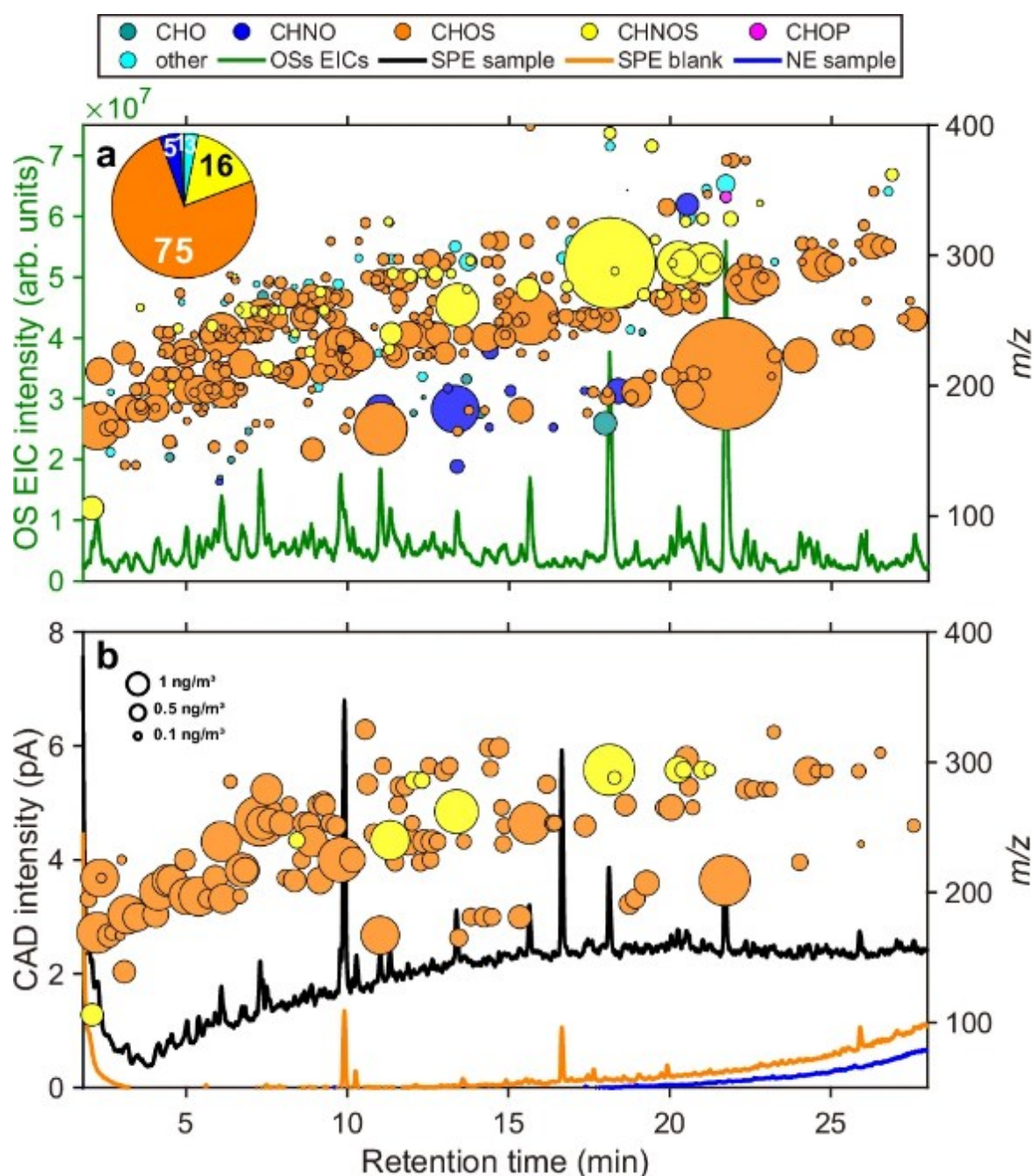


Figure 7.3-3: Comparison of the chromatograms and fingerprints of the enriched organosulfate fraction of a representative Handan filter (Handan 1: 18.10.2018, daytime). The x-axis, displaying the retention time (RT (min)), is zoomed into 2.5–28 min of a total method duration of 40 min. There are no peaks outside this time window. The complete CAD chromatogram is shown in Figure S 11.5-9. Graph a shows the UHPLC-HRMS data of the enriched OS fraction: RT- m/z plot (circles, right y-axis) and the sum of the extracted ion chromatograms (EIC, dark green line, left y-axis) of all the OSs appearing in the RT- m/z plot. The pie chart illustrates the peak area contribution (%) of the different compound classes to the total detected compound area. Graph b shows the comparison of the UHPLC-CAD chromatograms and the quantified concentrations of individually identified OSs (circles). The three chromatograms show the enriched OS fraction of the Handan 1 filter sample (SPE sample, black line), the corresponding procedural blank of a field filter blank (SPE blank, orange line), and the native extraction (regular liquid extraction technique) of the same ambient filter sample (NE sample, blue line). The circle size represents the organosulfate concentration, determined from the calibration surface (Figure S 11.5-4).

Figure 7.3-3 b shows the differences of the CAD chromatograms obtained for the native extract and the enriched OS fraction of the same sample (Handan 18.10.2018, daytime), and the corresponding aerosol filter blank that experienced the full SPE procedure. These chromatograms clearly demonstrate the necessity of the enrichment by SPE for quantification with CAD (Figure 7.3-3 b). Our regular liquid

extraction of the ambient aerosol filters yielded no detectable peaks in the CAD, whereas strong signals appeared in the OS fractions following SPE. The two highest peaks in the CAD chromatograms (RT ~ 9.91 and ~16.66 min) appear in both the ambient aerosol samples and the blanks following SPE. The parallel detection by HRMS showed no signal of OSs, thus indicating background signals originated from either the SPE cartridge, HPLC column, or aerosol filter extraction procedures. Apart from these two peaks, the majority of the CAD peaks lay within a three seconds retention time tolerance within the summed extracted ion chromatograms (EICs) of the OSs, after correcting for the retention time offset between both detectors. Furthermore, the two largest CHNO-signals (m/z 182.01, RT ~ 11.01 and ~13.34 min; Figure 7.3-3 a) did not result in prominent CAD peaks (Figure 7.3-3 b), indicating that their ionization efficiency in HRMS was either very large, or that they were not detected by CAD due to volatilization. The two signals were tentatively identified as 3-nitrosalicylic acid (RT ~ 11.01 min) and 5-nitrosalicylic acid (RT ~ 13.34 min), which have been reported as markers for biomass burning (Kitanovski et al., 2012a; Wang et al., 2017a). From a chemical perspective, it is reasonable that these organic acids appear in the OS fraction, as the electron-withdrawing mesomeric effect (–M-effect) of the nitro group stabilizes the negative charge of the conjugated base of the carboxylic acid group (electron delocalization), thereby increasing the acidity of the nitrosalicylic acids.

For quantification of the OSs by CAD, we measured eight OS standards at five different concentrations evenly distributed across the mobile phase gradient. In contrast to (–)ESI-HRMS, the CAD has a universal response to the mass of non-volatile compounds, independent of their chemical structure and functionality (Figure S 11.5-3). However, by running an HPLC gradient, the CAD's sensitivity increases with the increasing organic solvent fraction, which is why we calibrated the CAD with eight OS standards. The resulting calibration surface (Figure S 11.5-4) enables quantification of unknown signals across the whole chromatogram. It is worth mentioning that the sample matrix showed no signal suppression in the CAD measurements for all the standards used (Figure S 11.5-5), thus justifying the quantification obtained through external calibration. To quantify each individual OS, we subtracted a fitted baseline of the chromatographically unresolved peak from the CAD chromatogram (Figure S 11.5-6) and, subsequently, fitted the remaining peaks (Figure S 11.5-7 b) by referencing the OS EICs (Figure S 11.5-7 a). Following this approach, we quantified all the chromatographically resolved OSs based on the CAD chromatogram.

By comparing signals from the OSs in the HRMS against the CAD, we observed a strong discrepancy of the ionization efficiency for the different OSs. For instance, the signal of monoterpene-derived nitrooxy-OS $C_{10}H_{17}NO_7S$ (RT 18.1 min and m/z 294.0653; Figure 7.3-3 a and b) was ~20 times higher than the smaller nitrooxy-OS $C_6H_{11}NO_7S$ (RT 11.3 min and m/z 240.0183; Figure 7.3-3 a and b) (Brüggemann et al., 2020b; He et al., 2014; Iinuma et al., 2007b; Ma et al., 2022). However, their quantified concentrations obtained by CAD were 5.5 ng/m³ and 3.3 ng/m³ (Figure 7.3-3 b), respectively. Nevertheless, we found the monoterpene-derived nitrooxy-OS ($C_{10}H_{17}NO_7S$) to be the most abundant OS in the representative Handan aerosol filter sample, thereby indicating the importance of the anthropogenic enhancement of biogenic emissions through OS formation. We identified the highest signal in HRMS (RT 21.7 min and m/z 209.1; Figure 7.3-3 a) as anthropogenic octyl sulfate ($C_8H_{18}SO_4$) by comparing the retention time and fragmentation pattern with the authentic standard (Figure S 11.5-8), and quantified its concentration to 5.4 ng/m³. A recent study reported octyl sulfate as likely being formed through heterogeneous reactions of octyl hydroperoxide with sulfur dioxide or sulfuric acid (Huang et al., 2023).

Overall, we were able to quantify ~130 individual OSs in each Handan sample and ~65 OSs in each Taunus Observatory sample (Table S 11.5-1-Table S 11.5-6). The total quantifiable OS concentrations by integration of chromatographically resolved OS peaks for the three Handan samples (18.10.2018, daytime; 21.10.2018, daytime; 21.10.2018, night-time) were 149 ng/m³, 157 ng/m³, and 156 ng/m³, respectively. The similar OS concentration of the three samples indicates relatively constant conditions during the two investigated winter days. Certainly, a full seasonal analysis would provide a more variable

picture. In the rural samples at the TO, the OS concentrations ranged from 44–57 ng/m³. It is worth mentioning that the three TO aerosol filter samples used in this study were chosen from a large dataset of ~350 samples, collected from August 2021 to August 2022, due to their previously identified high occurrence of OSs. The difference in concentrations between the two sites indicated, as expected, a much stronger anthropogenic influence on OS formation in the North China Plain, although there was still a significant abundance of OSs at the European rural station.

7.3.3 Unresolved organosulfates

In five of the six investigated samples, we observed a chromatographically unresolved broad peak over the full range of the CAD chromatogram. We did not identify single OSs from the non-target analysis that can explain this broad chromatographic peak (Figure 7.3-3). This is expected, as the non-target analysis requires sharp chromatographic peaks for their detection. A similar feature of the broad chromatographic peak appears in the CAD chromatograms of all three Handan samples (Figure 7.3-3 and Figure S 11.5-10; Figure S 11.5-11). The CAD chromatograms for the TO samples were less elevated (Figure S 11.5-12-Figure S 11.5-14), but an unresolved broad peak was still significantly different from the field aerosol filter blank that experienced the whole sample preparation procedure. Our explanation for the broad peak in the CAD is that it was caused by chromatographically unresolved OSs that remained hidden after mass spectrometry-based non-target analysis. Possibly, a large number of low-abundant OSs contributed in sum to the CAD signal. To confirm the relationship between the broad peak in the CAD and the potentially hidden OSs, we performed an all-ion fragmentation (AIF) experiment. In this setup of the mass spectrometer, all formed ions are guided through the quadrupole into the collision cell where all ions are fragmented simultaneously. Specific ion fragments from OSs (HSO_4^- , HSO_3^- , SO_4^- and SO_3^-) are clearly visible in the Handan samples. We found that the sum of these four ions produced a similar broad peak over the whole AIF chromatogram compared to the CAD chromatogram (Figure 7.3-4 a,b). Therefore, we interpreted the elevated baseline in the AIF sample chromatogram to be caused by unresolved and low-abundant OSs in the sample. The blank measurement (with internal OS standards, numbers 1–8, Figure 7.3-4 b) did not result in an elevated baseline using the AIF mode. To investigate the correlation between the CAD and AIF measurements, we averaged the two chromatograms in three second intervals to plot the blank-subtracted scatter diagram (Figure S 11.5-15). In Figure S 11.5-15, the data points appear relatively widely scattered ($R = 0.45$) with a low RT-dependence. After applying the calibration function on the integrated CAD area (see the polynomial function, Figure S 11.5-4), we found a clear RT-dependent gradient between the CAD concentration and the signal of OS fragment ions of the AIF mode ($R = 0.18$). Division of the AIF chromatogram by the methanol content of the mobile phase at each consecutive time step resulted in an improved correlation between the OS concentration and AIF signal (Figure 7.3-4 d, $R = 0.90$). This observation indicates that the ionization efficiency of the OSs is strongly dependent on the mobile phase composition, with a better ionization efficiency of OSs observed at a higher organic content. Therefore, we suggest that further studies can use this correlation between the quantitative OS measurements by CAD and the quotient of the OS AIF signal over the methanol mobile phase fraction, with the goal to quantify OSs via HRMS only. Besides this observation of a novel way to quantify the total content of resolved and unresolved OSs in ambient aerosol, the detection of OS-specific ions by AIF that correlate strongly with the CAD signal supports our hypothesis that the chromatographically unresolved broad peak in the CAD chromatograms was mainly induced by hidden OSs.

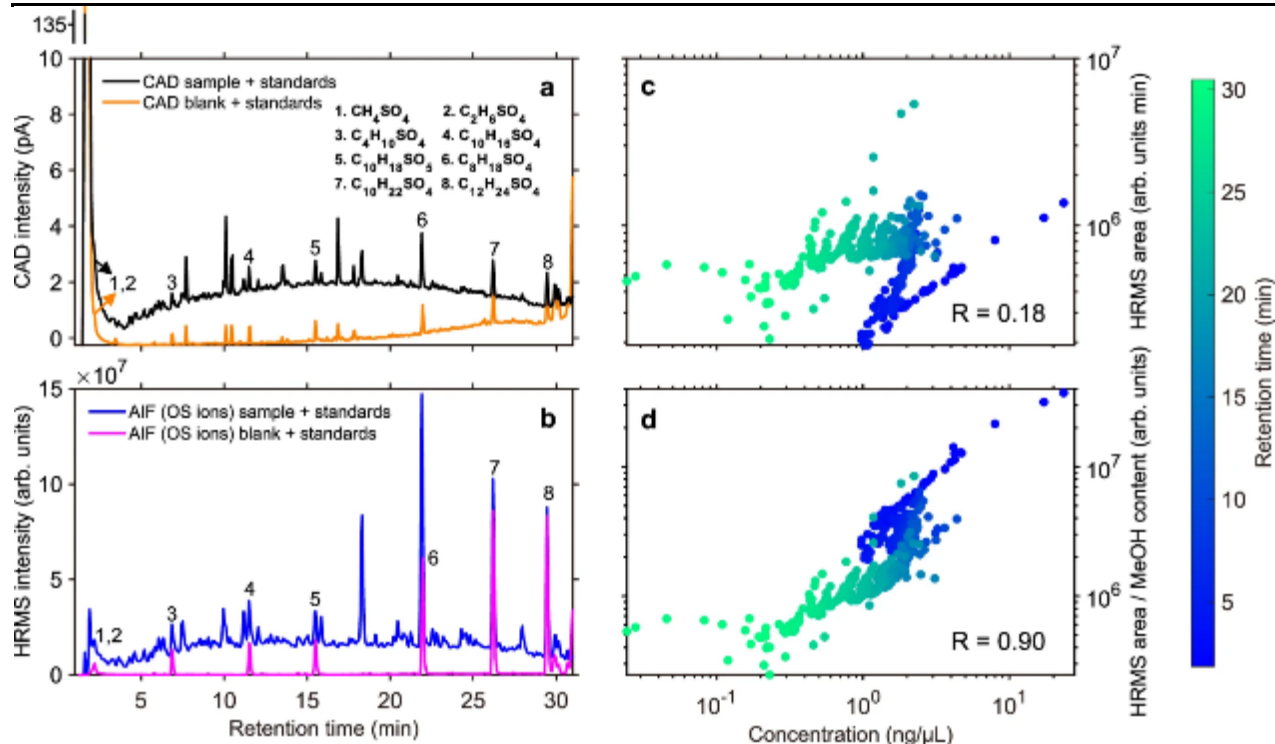


Figure 7.3-4: UHPLC-CAD and UHPLC-HRMS chromatograms of the second organosulfate-containing fraction. The HRMS chromatogram is the sum of the extracted ion chromatograms (EICs) of the organosulfate-specific ions HSO_4^- , HSO_3^- , SO_4^{2-} and SO_3^{2-} recorded in the all ion fragmentation (AIF) mode. This correlation is demonstrated by using results from the Handan 1 aerosol filter. Graph a shows the UHPLC-CAD chromatograms of the Handan ambient aerosol sample (black) and the ambient aerosol filter blank (orange), b the UHPLC-HRMS chromatograms of the Handan ambient aerosol sample (blue) and the ambient aerosol filter blank (pink), c correlation of the blank-subtracted OS concentration (determined by the external calibration of the UHPLC-CAD) and the UHPLC-HRMS signal of the OS-specific ions recorded in the AIF mode, and (d) same as (c), but with the mass spectrometric signal being divided by the methanol content to correct for the ionization efficiency. The peak numbering in (a, b) represents the eight spiked internal standards. The color bar of (c, d) shows the retention time (min).

For total OS quantification, we fitted the chromatographically unresolved broad peak as one large peak (Figure 7.3-5 a). The resulting integration showed that ~ 2.3 , ~ 2.8 , and $\sim 2.4 \mu\text{g}/\text{m}^3$ of OSs were chromatographically unresolved for the Handan 18.10.2018 daytime, 21.10.2018 daytime, and 21.10.2018 night-time samples, respectively. Figure 7.3-5 b indicates that the chromatographically resolved OSs of the Handan samples contributed ~ 0.7 -1% to the total organic matter (OM), while the overall area of the CAD chromatogram (representing the resolved and unresolved OSs) contributed 12-17% to the OM. Although the TO samples exhibited a lower total OM, we found an overall larger fractional contribution of OSs. The TO 2 (14.01.2022, night-time) sample showed the lowest concentration of OSs, at $\sim 0.04 \mu\text{g}/\text{m}^3$ that were chromatographically resolved. No chromatographically unresolved OSs were visible in this sample (Figure S 11.5-13). The contribution of the individually quantified OSs to the total OM was $\sim 34\%$, although the uncertainty of this value remains large due to the low concentration of OSs (Figure 7.3-5 b). The homologous series of aliphatic OSs in this sample suggests an anthropogenic origin (Figure S 11.5-2 e). Backward trajectories indicate a possible marine origin from the North Sea (Figure S 11.5-16) with aliphatic OSs being emitted by the shipping sector (Qi et al., 2021). The concentration of total OSs for TO 11.12.2021 daytime and TO 28.02.2022 night-time was ~ 0.6 and $\sim 0.8 \mu\text{g}/\text{m}^3$, hence, the total OSs contributed $\sim 21\%$ to the total OM for both samples (Figure 7.3-5 b). This large OS contribution to the total OM at TO is certainly an upper estimate since our sample selection for this field site was guided by a pre-evaluation of a full-year compositional analysis. Furthermore, we cannot rule out that a fraction of OSs is formed during aerosol filter sampling, although the SO_2 concentrations at this rural background station are usually below quantifications limits

for standard detectors. Hence, we infer that the majority of OSs observed at rural and remote stations forms during atmospheric transport. Analysis of the backward trajectories for TO 3 indicate that the air masses originated from eastern Germany, southern Poland and the northern Czech Republic, which are Europe's hotspots of coal combustion by power plants (Figure S 11.5-16)(Glasius et al., 2018a). The time of atmospheric transport from this source area of around one day is twice as long as the actual aerosol filter sampling period, which speaks against significant OS artifact formation for the TO aerosol filter samples.

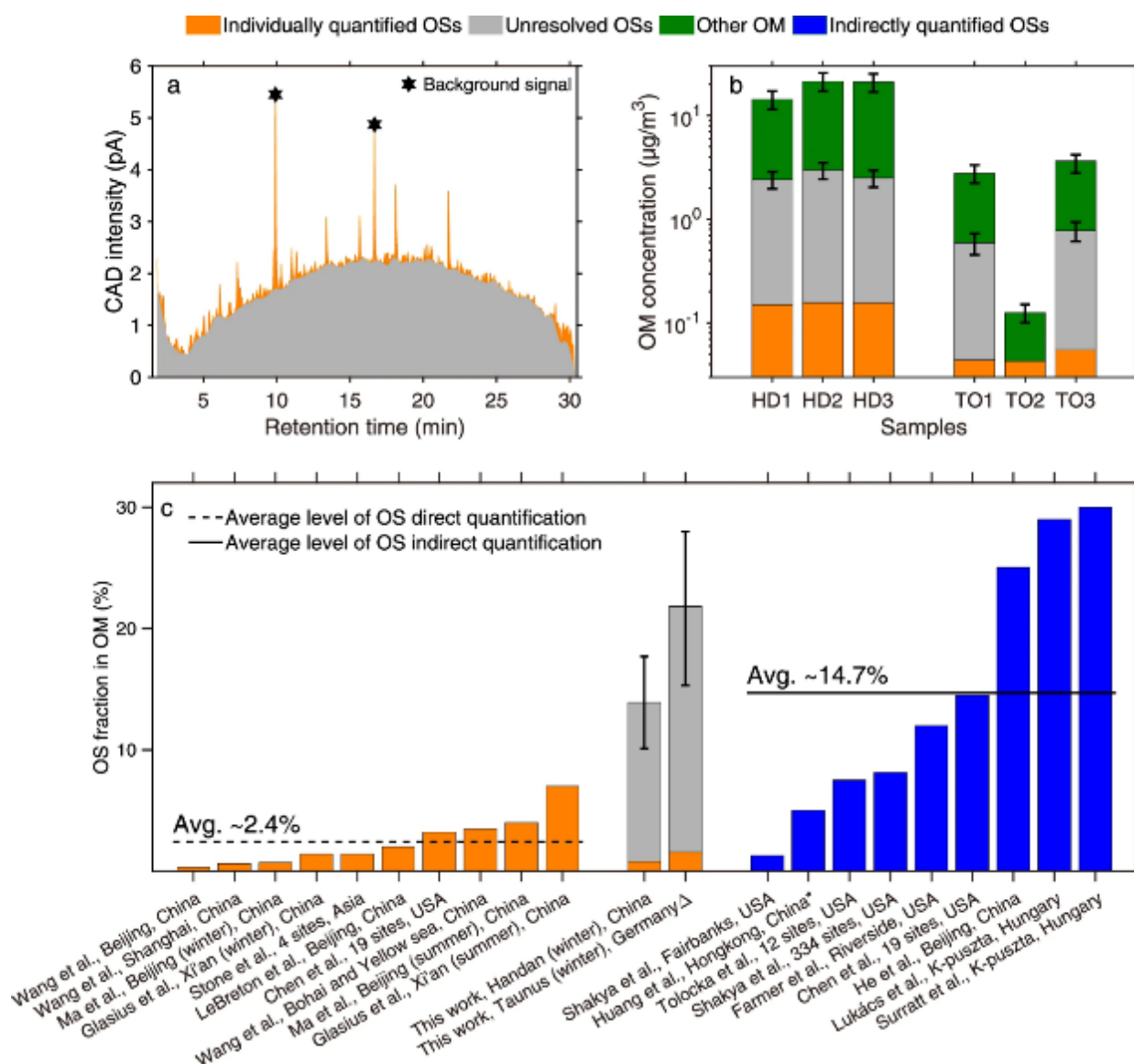


Figure 7.3-5: Integration of the chromatographically unresolved peak of the charged aerosol detector (CAD) measurements, its contribution to the total organic matter (OM), and its comparison with other studies. Graph a shows the integration of the CAD chromatogram (Handan 1, 18.10.2018 daytime): gray area and orange peaks show unresolved and resolved organosulfates (OSs), respectively, b shows the comparison of the concentration ($\mu\text{g}/\text{m}^3$) of resolved OSs (orange), unresolved OSs (gray) and other OM (dark green) for the six investigated samples (Handan 1, 18.10.2018 daytime; Handan 2, 21.10.2018 daytime; Handan 3, 21.10.2018 night-time; Taunus Observatory (TO) 1: 11.12.2021, daytime; TO 2: 14.01.2022, night-time; TO 3: 28.02.2022, night-time). The OM and OSs concentration error bars represent the uncertainty for the organic carbon-to-organic matter conversion, the SPE reproducibility, and CAD quantification. Graph c shows the comparison of the OS fraction obtained in the OM between different studies; directly quantified OS (orange and gray) vs. indirect quantification (blue) (See Table S 11.5-7). The dashed and solid lines are the averages of the OS fractions from the direct and indirect quantification studies, respectively. Error bars represent the combined error from solid phase extraction reproducibility, CAD quantification, and OC to OM conversion for each site. We note that the OS mass fraction includes the sulfate group. *Minimal estimation, Δ Only TO 1 and TO 3 being calculated.

To evaluate the quantitative contribution of OSs to total OM, we compared the major quantification studies that followed either the direct or the indirect approaches (Figure 7.3-5 c and Table S 11.5-7). The indirect methods determine a larger OS fraction contributing to the OM (on average ~15%), whereas the direct approaches reveal a smaller fraction of OSs in the OM (~2%) (Chen et al., 2021; Le Breton et al., 2018; Ma et al., 2022; Surratt et al., 2008; Wang et al., 2018; Wang et al., 2023c). Our method presented here enables the direct quantification of the hidden OS fraction and, consequently, suggests that the direct quantification of molecularly resolved OSs generally underestimates the total OS content in ambient aerosol samples by roughly a factor of five to ten. Thus, the described quantification approach for estimating OSs using SPE and UHPLC-CAD enables the direct quantification with lower uncertainties compared to the approaches that employ two different methods. Further assumptions, for example, about the average molecular weight of OSs, are no longer necessary.

Our observation of the high contribution of OSs at both locations, in urban China and rural Europe, calls for further investigation of the variability and seasonality of OSs in atmospheric aerosol across the globe. The described observations are in agreement with the indirect quantification methods of organic sulfur species. Due to the enrichment of individual OSs that enable a more detailed OS fingerprint (Figure S 11.5-2), we are now able to evaluate the fractions of OSs that are purely anthropogenic (e.g., saturated aliphatic OSs) or whether they can be seen as anthropogenically enhanced OSs (e.g., sulfate from anthropogenic sources with a carbon backbone from biogenic sources). Especially, isoprene-derived OSs might still be underestimated using the described method, as we found the SPE-recovery for these polar compounds is around 30% (Figure S 11.5-17). Interestingly, some of the OSs at the rural Taunus Observatory indicate the long-range transport of anthropogenic pollution. The low abundance of terpene-derived OSs can be explained by very low biogenic emissions of the investigated samples from the winter season. Further analysis of year-long aerosol filter analyses should reveal the pure anthropogenic and mixed biogenic/anthropogenic OS quantities, thus enabling a better understanding of pollution over whole seasons at different locations.

7.4 Methods

7.4.1 Aerosol filter sampling, organic carbon analysis, and solid-phase extraction

Six 12 h integrated PM_{2.5} filter samples were collected at two sampling sites. The first sampling site was located at Hebei University of Engineering (36.57°N, 114.50°E), an urban site in Handan, China. We collected three Handan samples on preheated quartz fiber filters (203.2 mm × 254 mm, QM-A Quartz Microfiber Filters, Whatman™, China) with a high volume sampler (TH-1000 C, Tianhong, China; sampling flow rate 1 m³/min) on 18.10.2018 (daytime, 08.00–19.30), 21.10.2018 (daytime, 08.00–19.30) and 21.10.2018 (night-time, 20.00–07.30). The second sampling site was located at the Taunus Observatory (TO; 50.22°N, 8.45°E, altitude 825 m), a mountaintop site at the Kleiner Feldberg in Hesse, Germany. We collected three TO samples on preheated glass fiber filters (Ø 150 mm, MG 160, Ahlstrom-Munksjö, USA) by using a high volume sampler (DHA-80, Digitel, Switzerland, air volume 500 L/min) on 11.12.2021 (daytime, 07.00–19.00), 14.01.2022 (night-time, 19.00–07.00) and 28.02.2022 (night-time, 19.00–07.00).

We took 1.45 cm² of each aerosol filter and performed the OC analysis by using a thermal/optical carbon analyzer (Model 4, Sunset Lab.). We deployed the NOISH 870 protocol for Handan aerosol filters (quartz fiber filter) and the Semi-Continuous OC/EC Analyzer with a program featuring a lower temperature setting of up to 500 °C for TO aerosol filters (glass fiber filter). We used an OC-to-OM conversion factor of 1.6 and 1.8 for Handan and TO, with the assumption of 20% relative uncertainty, respectively (Surratt et al., 2008; Wang et al., 2020b).

We sampled a 24.5 cm² and a 13.0 cm² filter punch from each Handan and TO ambient aerosol filter, respectively (we determined the area of the filter punch based on the amount of sampled air volume). We extracted the filter fragments by using an orbital shaker (Edmund Bühler GmbH, Germany) for

2 × 20 min, each time using 8 mL of a water/methanol mixture (98/2 (v/v); water: Milli-Q water, 18.2 MΩ·cm; Milli-Q® Reference A+ System with Millipak® Express 40 Filter (0.22 μm), Merck Millipore; methanol: UHPLC-MS grade, Thermo Scientific™). We combined the two consecutive native extractions, centrifuged at 4000 rpm for 40 min, and transferred ~14.5 mL of liquid supernatant to new vials. We saved an aliquot of the native extract for a direct measurement and used the remaining extract for the SPE separation.

After conditioning the SPE cartridge (Oasis MAX, 1cc/10 mg bed weight, Ø 30 μm particles, Waters™, Milford, MA, USA) with 1 mL each of (1) methanol, (2) Milli-Q water, (3) 5% NH₄OH in Milli-Q water, and (4) extraction solution (methanol/water mixture), we loaded the native aerosol filter extracts onto the cartridge and collected the flow through for further analysis. Omitting a drying step, we directly eluted the cartridge twice using (1) 6 mL of 2% formic acid in methanol, followed by (2) 3 mL of 5% formic acid and 0.5% hydrochloric acid in methanol (Figure S 11.5-18). The two elutions were collected separately. An aliquot of each elution was taken and diluted with the extraction solution to the same concentration level as the native extract.

We added 10 μL of dimethyl sulfoxide to the second elution as a preservative and to ensure the suspension of compounds before evaporating the sample under a gentle nitrogen flow to a volume of ~10 μL. After the evaporation, we used 50 μL methanol/water mixture (50/50 (v/v)) to re-dissolve the remaining sample for subsequent analysis.

7.4.2 UHPLC-CAD-HRMS analysis

We measured the native extract, the diluted first SPE elution, diluted second SPE elution and the flow-through via the Orbitrap HRMS (QExactive Focus™ Hybrid Quadrupol-Orbitrap Mass Spectrometer, Thermo Fisher Scientific™) equipped with a UHPLC system (Vanquish Flex UHPLC System, Thermo Fisher Scientific™). We operated a reversed-phase column (CORTECS T3, 120 Å, 2.7 μm, 3 mm × 15 mm, Waters) in the gradient mode (at 40 °C, still air) to achieve chromatographic separation. The eluents were Milli-Q water (eluent A) and methanol (eluent B), both containing 0.1% formic acid (v/v). The mobile phase gradient started with 1% eluent B (0–1 min) which was then increased linearly to 99% B (1–14 min), kept at 99% B (14–15.5 min), and then decreased to 1% B (15.5–16.5 min); the column remained at 1% B (16.5–20 min) for re-equilibration. The total method duration was 20 min with a flow rate of 0.4 mL/min and an injection volume of 4 μL. Ionization was conducted in the negative mode via a heated ESI (HESI-II Probe, Thermo Fisher Scientific™). Data acquisition for *m/z* was set from 75 to 750, with a resolving power of ~70,000 at *m/z* 200. The settings for the ion source were as follows: 8 psi auxiliary gas (nitrogen), 40 psi sheath gas (nitrogen), 3.5 kV spray voltage, and 350 °C gas temperature.

CAD has a sensitivity in the low-nanogram to high-microgram range (on column), which allows for the detection of trace levels of non-volatile compounds. Hence, we measured the concentrated second SPE elution using UHPLC-CAD/HRMS. The LC method was adjusted by increasing the column temperature to 50 °C and prolonging the total method duration to separate the detected compounds further. The mobile phase gradient started with 1% eluent B (0–1 min) increasing linearly to 99% B (1–34.5 min), and was kept at 99% B (34.5–36.5 min) and then decreased to 1% B (36.5–38 min), and remained at 1% B (38–40 min) to re-equilibrate the column. The total method duration was 40 min. We utilized a post-column flow splitter (Quicksplit 610, Analytical Scientific Instruments US) to direct 83.5% of the mobile phase flow (0.4 mL/min) into the CAD (0.334 mL/min) and the remaining flow into the MS (16.5%, 0.066 mL/min). Due to the split of the flow rate, the auxiliary and sheath gas pressures of the ion source were changed to 10 and 31.5 psi, respectively. The settings for the CAD were as follows: 25 °C evaporator temperature, 2 Hz data collection rate and 1.00 power function value. We subsequently measured the enriched second SPE elution in the all-ion fragmentation (AIF) mode via the UHPLC-HRMS with the same gradient as in the CAD measurement. AIF acquisitions were performed with a

resolving power of ~ 70000 at an m/z ratio of 200, using a stepped collisional energy of 30, 40, and 55 units, and an automatic gain control (AGC) target of 3×10^6 .

7.4.3 Data analysis

The non-target analysis software Compound Discoverer (CD; version 3.3, Thermo Fisher Scientific™) was used to identify the chromatographic peaks. By comparing the exact mass, isotopic matching score and MS/MS fragmentation pattern with the database mzCloud™ (Thermo Fisher Scientific™), molecular formulae could be assigned to the detected peaks. The detailed settings of the CD-workflow for the UHPLC-HRMS and UHPLC-CAD/HRMS sequences are provided in Table S 11.5-8 and Table S 11.5-9.

In brief, a threshold intensity of 1×10^4 and a peak rating of larger than five was applied to the two-dimensional coordinate system (UHPLC-HRMS sequence: y-axis RT 0–20 min, x-axis m/z 50–750; UHPLC-CAD/HRMS sequence: y-axis RT 0–40 min, x-axis m/z 50–750) for all measurements. Only chromatographic peaks exceeding these thresholds were analyzed. In addition, the maximum peak signal of a compound had to be three times higher than its signal in the blank sample to be considered in the ambient aerosol samples. Molecular formulae were calculated with the permitted elemental combinations of $C_{n1}H_{n2}Br_{n3}Cl_{n4}N_{n5}O_{n6}P_{n7}S_{n8}$ ($n1 = 1-90$, $n2 = 1-190$, $n3 = 0-3$, $n4 = 0-4$, $n5 = 0-4$, $n6 = 0-20$, $n7 = 0-1$, and $n8 = 0-3$) and with a mass tolerance of 2 ppm. We set the minimum and maximum H to C ratios as 0.1 and 4.5, respectively, to filter out the chemically unrealistic compounds. We used the software Fityk to fit the individual CAD peaks based on the RT of the EIC of the MS data. CAD quantification of the total OSs was obtained using 95% confidence intervals of the fit. The obtained data from the non-target analysis were further processed and plotted by using self-written scripts using Matlab (Matlab R2023b, Mathworks).

Data availability

All data used to generate figures are available under <https://zenodo.org/records/1460950268>.

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Contributions

J.M. did the data curation and analysis, and wrote the original manuscript. J.M. and N.R. did the SPE experiment. J.M. performed the UHPLC/CAD/HRMS measurements and nontarget analysis. C.Z., B.L., and H.N. collected the ambient filters from Handan. D.D., J.R., Y.Q., and Z.W. did the OC quantification experiment. A.B., J.D., S.H., and T.H. performed the oxidation flow reactor and HILIC experiment. Y.B.,

Y.L., Y.X., L.L., and Y.W. synthesized and purified the 2-hydroxy- α -pinene organosulfate. A.L.V., N.R., F.U., M.S., and L.D. edited and revised the manuscript. A.L.V. managed the project and supervised the experiment. All authors have contributed to the scientific discussion and have given approval to the final version of the manuscript.

Competing interests

The authors declare no competing interests.

8 Conclusion

This dissertation provides a comprehensive, multi-scale perspective on the molecular composition, formation mechanisms, and environmental and anthropogenic controls of organic aerosols by combining advanced high-resolution mass spectrometry with atmospheric, meteorological, and ecosystem observations. Organic aerosols are among the most complex and least constrained components of the atmospheric system, exerting strong influences on climate, cloud formation, precipitation, air quality, and human health. Addressing this complexity requires analytical approaches that can resolve molecular diversity across a wide range of sources, chemical regimes, and environmental contexts. The results presented here demonstrate that such an understanding can be achieved only by integrating methodological innovation with applications across contrasting natural and anthropogenically influenced environments.

The review in Chapter 1 outlines the conceptual and methodological framework of the thesis by critically evaluating the current status of molecular OA characterization. It points out that, despite significant advances in LC–MS and HR-MS techniques, a large portion of organic aerosol mass remains difficult to analyze due to low volatility, high oxidation levels, reactivity, and structural complexity. This work emphasizes that progress in aerosol science is closely tied to advances in analytical chemistry and highlights multidimensional chromatography, non-targeted high-resolution mass spectrometry, and better quantification strategies as key tools to address these challenges. This framework directly supports the experimental studies in the following chapters, which collectively show how these methods can be applied to real atmospheric and environmental systems.

Chapters 2 and 3 apply these concepts to organic aerosols in the Amazon rainforest, one of the most important yet least perturbed atmospheric environments on Earth. Non-targeted HR-MS measurements at the Amazon Tall Tower Observatory reveal a highly complex molecular composition dominated by biogenic secondary organic aerosols derived primarily from isoprene and monoterpene oxidation, with strong seasonal modulation driven by wet and dry conditions. The large number of isomeric compounds observed underscores the necessity of chromatographic separation even in non-targeted workflows and highlights the limitations of purely bulk or online measurements. These results demonstrate that background OA in the Amazon is shaped by a dynamic interplay between biogenic emissions, biomass burning, and long-range transport, with organosulfates emerging as a key molecular class linking biogenic and anthropogenic influences.

By extending the molecular analysis to a size- and height-resolved framework, Chapter 3 shows that particle size is a critical dimension for understanding OA sources, formation pathways, and aging processes. The results demonstrate that different biogenic precursors contribute preferentially to distinct particle size ranges and atmospheric layers, revealing contrasting roles of isoprene, monoterpenes, and sesquiterpenes in new particle formation, early growth, and accumulation-mode aerosol. The identification of significant contributions from primary biological material to ultrafine particles further challenges the traditional separation between primary and secondary organic aerosol. Together, these findings show that bulk aerosol composition masks key molecular information relevant for nucleation, growth, and aerosol–cloud interactions and that size-resolved molecular measurements are essential to constrain these processes in tropical environments.

Chapter 4 places these molecular observations into a dynamic environmental context by demonstrating that rainfall and canopy-related processes act as strong, recurring triggers for new particle formation in the Amazon. The observed bursts of sub-40 nm particles following precipitation events establish a direct mechanistic link between meteorology, trace gas chemistry, and particle formation. The results indicate that reductions in the condensation sink, combined with ozone injections into the canopy and subsequent oxidation of biogenic precursors, create favourable conditions for nucleation and growth.

These locally formed particles can supply sufficient cloud condensation nuclei to sustain the background population of Amazonian “green ocean” clouds. This work provides a crucial process-level bridge between the molecular composition of OA and its climatic relevance.

Chapter 5 expands the dissertation's scope beyond the atmosphere by situating aerosol precursor formation within the ecosystem context. Non-targeted HR-Orbitrap-MS analysis of dissolved organic matter in Amazonian soils reveals distinct nutrient limitations and processing pathways across contrasting forest types. The identification of phosphorus limitation in terra firme forests, potential nitrogen co-limitation, and unexpected sulfur limitation in white-sand ecosystems highlights the diversity of nutrient controls within the Amazon basin. These findings emphasize that soil chemistry and nutrient cycling influence the availability and composition of precursors for biogenic volatile organic compounds, thereby indirectly affecting secondary organic aerosol formation. This chapter demonstrates that understanding OA formation ultimately requires linking atmospheric chemistry to belowground ecosystem processes.

Finally, Chapter 6 examines anthropogenic influences on organic aerosols, focusing on organosulfates in urban and rural environments. By combining solid-phase extraction, HR-Orbitrap-MS, and charged aerosol detection, this study overcomes key limitations in quantifying chemically diverse organosulfates and reveals that a substantial fraction of these compounds remains chromatographically unresolved in conventional analyses. The results show that organosulfates contribute a much larger fraction to total organic aerosol mass than previously recognized and that sulfur emissions play a critical role in shaping both aerosol composition and climate-relevant properties. This work demonstrates the broader applicability of the methodological framework developed in this dissertation and highlights the importance of reducing sulfur emissions to mitigate organic aerosol pollution.

Taken together, this dissertation demonstrates that the complexity of organic aerosols can only be unraveled by integrating high-resolution molecular characterization with size-resolved, vertically resolved, environmental, and ecosystem-level observations. By linking molecules to particles, particles to environmental processes, and environmental processes to ecosystem and anthropogenic controls, this work advances a holistic understanding of organic aerosols across natural and polluted systems. The results emphasize the central role of high-resolution mass spectrometry not only as an analytical tool but as a unifying framework for connecting chemistry, physics, and ecology in atmospheric science. Future progress will depend on further methodological developments, closer integration of molecular and online measurements, and the explicit coupling of atmospheric observations with ecosystem processes to better represent organic aerosols in climate and air quality models.

9 Outlook

Future research on organic aerosols must move beyond static, offline molecular snapshots toward a dynamic, process-oriented understanding of aerosol formation and transformation. While this dissertation demonstrates the power of high-resolution mass spectrometry to resolve the molecular complexity of organic aerosols, it also reveals critical gaps that can only be closed by integrating molecular detail with temporal and size-resolved observations. One major challenge remains the quantitative and mechanistic understanding of primary organic aerosol (POA). Primary biological particles, soil-derived organics, and combustion-related POA contribute substantially to atmospheric organic matter, yet their molecular composition, volatility distribution, and role in new particle formation and early growth remain poorly constrained. Distinguishing POA from secondary organic aerosol at the molecular level, particularly in biogenically dominated environments, requires improved tracer concepts and analytical strategies that explicitly target primary emissions and their transformation pathways.

Progress in this direction will strongly depend on the development and application of high-resolution online mass spectrometric techniques. Offline analyses provide unparalleled molecular coverage, but they integrate over long sampling times and cannot resolve rapid changes driven by meteorology, emissions, or photochemistry. Online HR-MS approaches would enable the direct observation of transient formation pathways, short-lived intermediates, and fast aging processes, thereby linking molecular composition to atmospheric dynamics in real time. Such measurements are particularly critical for understanding episodic events such as rainfall-induced particle formation, biomass burning plumes, or urban pollution pulses, where chemical regimes change on timescales of minutes to hours.

Equally important is the expansion of online measurements toward particle size resolution. This dissertation shows that particle size is a key dimension for disentangling sources, formation pathways, and chemical aging. However, size-resolved molecular information is currently almost exclusively accessible through offline approaches. The development of online size-segregating inlets coupled with HR-MS would allow continuous tracking of molecular composition across nucleation, Aitken, and accumulation modes. This would provide unprecedented insight into how specific precursor classes and functionalized products contribute to new particle formation, early growth, and cloud condensation nuclei production under different chemical and meteorological regimes.

Finally, future studies should more strongly integrate molecular aerosol characterization with ecosystem and emission dynamics. The results of this work suggest that biogenic precursor supply is controlled not only by vegetation and atmospheric chemistry but also by belowground nutrient cycling and microbial processing. Coupling soil and plant chemistry with online aerosol and trace gas measurements will therefore be essential to constrain how changes in climate, land use, and nutrient availability affect aerosol formation in tropical and temperate ecosystems alike. At the same time, improved quantification of anthropogenically driven compound classes, such as organosulfates, highlights the need to better connect molecular observations with emission control strategies and air quality policies.

In summary, the next generation of organic aerosol research will require a convergence of methodological innovation and conceptual integration. High-resolution online mass spectrometry, combined with size-resolved sampling and an explicit focus on primary organic aerosol and ecosystem–atmosphere coupling, offers a pathway toward a more complete and mechanistic description of organic aerosol life cycles. Such advances are essential for improving the representation of aerosol processes in atmospheric models and for refining predictions of aerosol impacts on climate, air quality, and ecosystem feedbacks.

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Acknowledgements

11 Appendix

11.1 Supplementary material chapter 3

Table S11.1-1: Values of n_c^0 and b according to the compound class to calculate C0. The parameterization is obtained from the detailed study by Li et al. (2016).

Compound class	n_c^0	b_c	b_o	b_{co}	b_N	b_S
CHO	22.66	0.4481	1.656	-0.7790		
CHON	24.13	0.3667	0.7732	-0.0779	1.114	
CHOS	24.06	0.3637	1.327	-0.3988		0.7579
CHONS	28.50	0.3848	1.011	0.2921	1.053	1.3160

Table S11.1-2: Average values¹ of the detected background ions for the wet and dry seasons in 2018 and 2019. The listed molecules were detected in at least 75% of all corresponding samples. The signals are divided into four subgroups regarding their elemental composition. The relative contribution of the subgroups was calculated by dividing the number of compounds of the particular subgroup by the total number of compounds. Additionally, the average values¹ of molecular weight (MW), carbon oxidation state (OSC) and aromaticity index (Xc) are listed.

Season	Height m	Number of compoun ds detected	CHO %	CHON %	CHONS %	CHOS %	MW Da	OSC ²	Xc
WS18	42	36	89	0	0	11	170	0.031	0.060
	150	45	82	5	2	11	177	- 0.039	0.180
	320	28	82	0	0	18	174	0.040	0.024
DS18	80	211	90	4	1	5	191	- 0.404	0.724
	150	215	90	4	1	4	188	- 0.418	0.738
	320	209	89	4	1	5	188	- 0.407	0.755
WS19	80	51	94	0	2	4	197	- 0.497	0.696
	150	52	98	0	2	0	195	- 0.464	0.577
	320	60	97	0	2	2	196	- 0.499	0.606
DS19	0	72	94	4	1	0	196	- 0.367	0.424
	80	108	95	4	0	1	182	- 0.424	0.480
	320	75	97	3	0	0	191	- 0.398	0.279

¹ Average values are calculated based on the molecular composition of each compound.

² Only CHO compounds are considered in the calculation of OSC.

Table S 11.1-3: Number of active fires each month in the Amazon region since 1998 until 2020. The sampling periods are highlighted in yellow. Data retrieved by INPE - Instituto Nacional de Pesquisas Espaciais, 2020 (Portal do Monitoramento de Queimadas e Incêndios Florestais, <http://www.inpe.br/queimadas>).

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1998	-	-	-	-	-	1549	3192	20075	19214	8777	3833	2547
1999	160	358	130	70	449	1439	3675	21525	16106	12794	4449	1703
2000	87	182	405	92	930	3211	1510	12791	10062	10226	5497	3175
2001	165	699	1134	617	916	4227	1816	17679	15528	14292	8346	4256
2002	590	667	901	405	1490	5702	7529	43484	48549	27110	23660	9174
2003	3704	1573	1997	1038	1983	6848	15918	34765	47789	25341	19631	13813
2004	2178	805	1035	1012	3131	9179	19179	43320	71522	23928	26424	16924
2005	4314	1048	758	832	1746	2954	19364	63764	68560	26624	16790	6966
2006	1973	879	903	709	843	2522	6995	34208	51028	18309	17474	8579
2007	1918	1761	1431	760	1176	3519	6196	46385	73141	28731	16025	5437
2008	938	527	860	569	383	1248	5901	21445	26469	23518	15450	6145
2009	1095	354	584	435	673	1023	2327	9732	20527	19323	19104	6505
2010	1697	1147	1176	633	1026	1911	5868	45018	43933	14798	12167	5240
2011	771	271	427	465	528	1083	2445	8002	16987	9760	9815	7632
2012	1203	438	484	473	855	1875	3095	20687	24067	14814	13259	5469
2013	1181	374	738	518	796	1450	2531	9444	16786	10242	6615	8013
2014	1573	473	1010	632	673	1628	2766	20113	20522	13222	12169	7773
2015	2042	1047	572	762	407	1287	2817	20471	29326	19469	16935	11303
2016	4657	1559	2024	1075	895	1663	6120	18340	20460	14234	11610	5124
2017	796	379	736	618	805	1759	7986	21244	36569	14457	14105	7985
2018	1444	888	1359	513	772	1980	4788	10421	24803	10654	8881	1842
2019	1419	1368	3383	1702	854	1880	5318	30900	19925	7855	11297	3275
2020	1200	1196	1641	789	829	2248	6803	29307	32017	17326	6321	2498

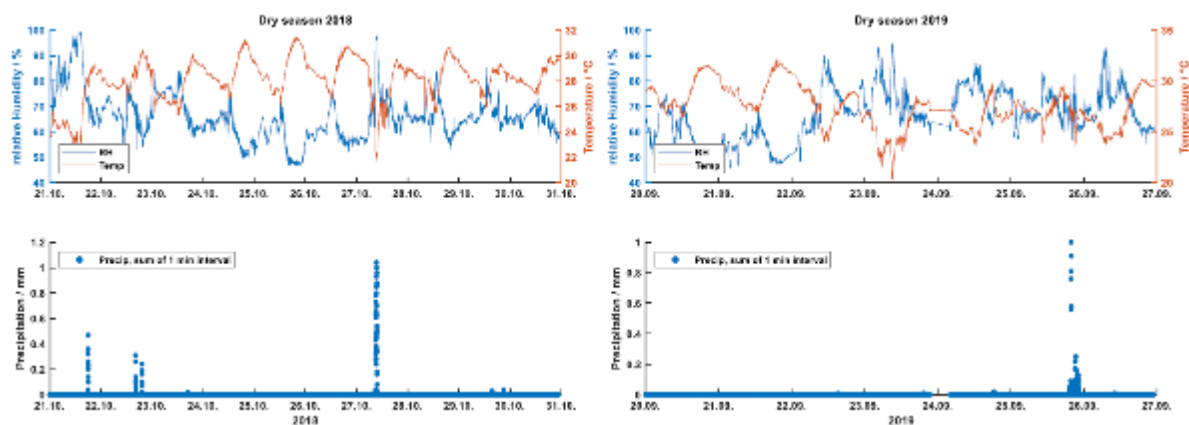


Figure S 11.1-1: The upper panel illustrates the relative humidity and temperature at ATTO for the dry season 2018 (left) and the dry season 2019 (right), respectively. The lower panel shows the precipitation as a sum of 1 min intervals. The instrument was located at 325 m.

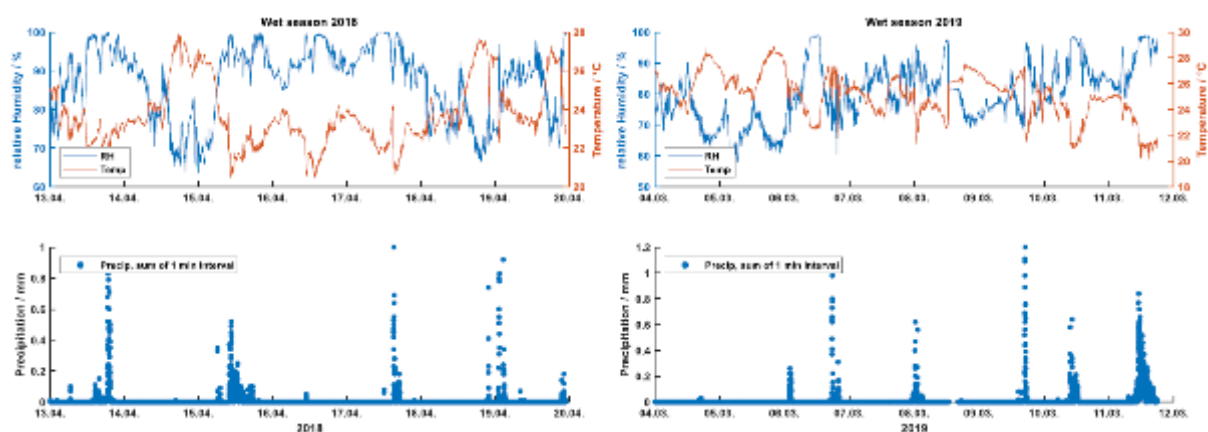


Figure S 11.1-2: The upper panel illustrates the relative humidity and temperature at ATTO for the wet season 2018 (left) and the wet season 2019 (right), respectively. The lower panel shows the precipitation as a sum of 1 min intervals. The instrument was located at 325 m.

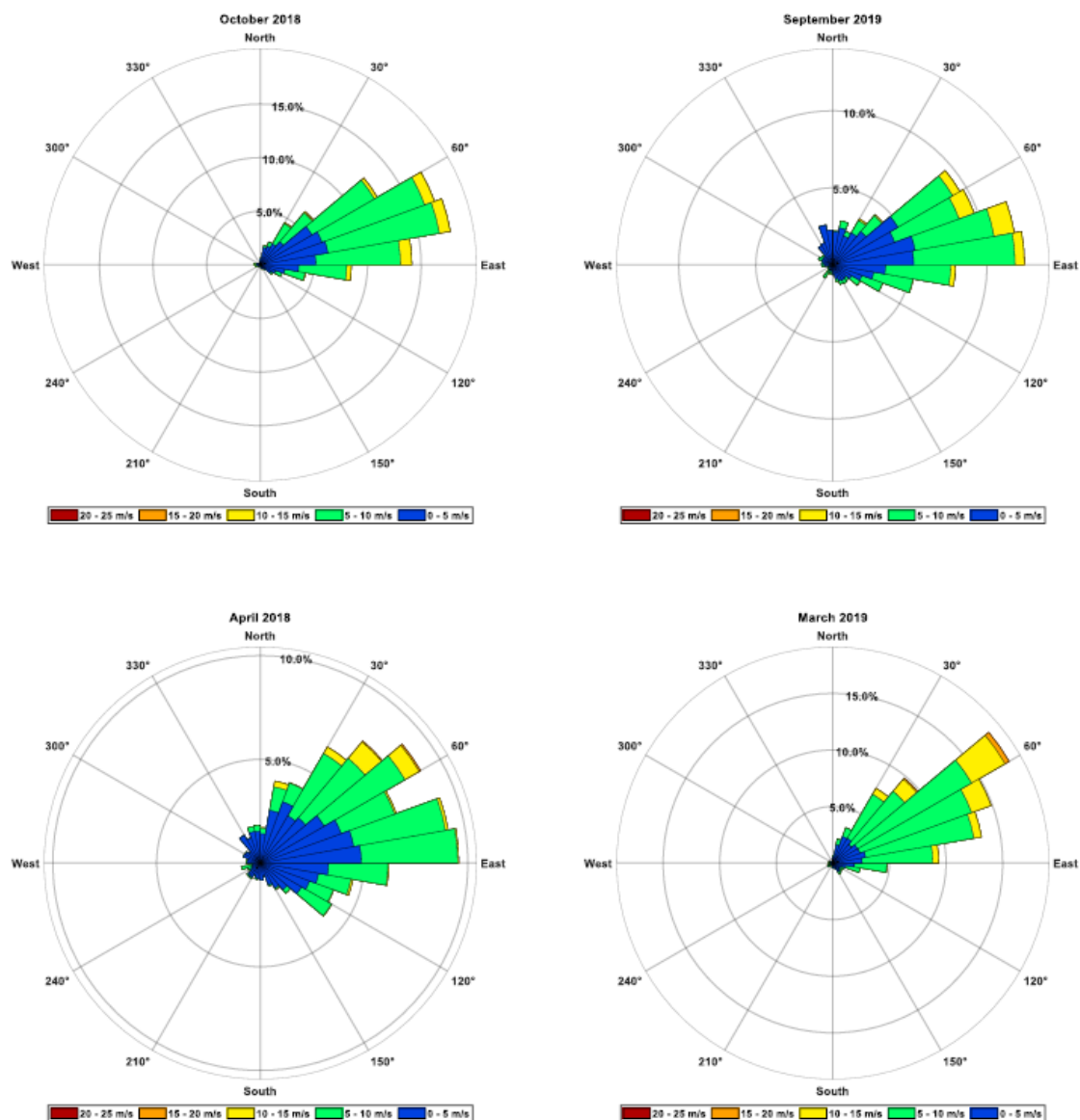


Figure S 11.1-3: Wind roses for the sampling period during the dry seasons in October 2018 and September 2019 (upper part) and during the wet seasons in April 2018 and March 2019 (lower part).

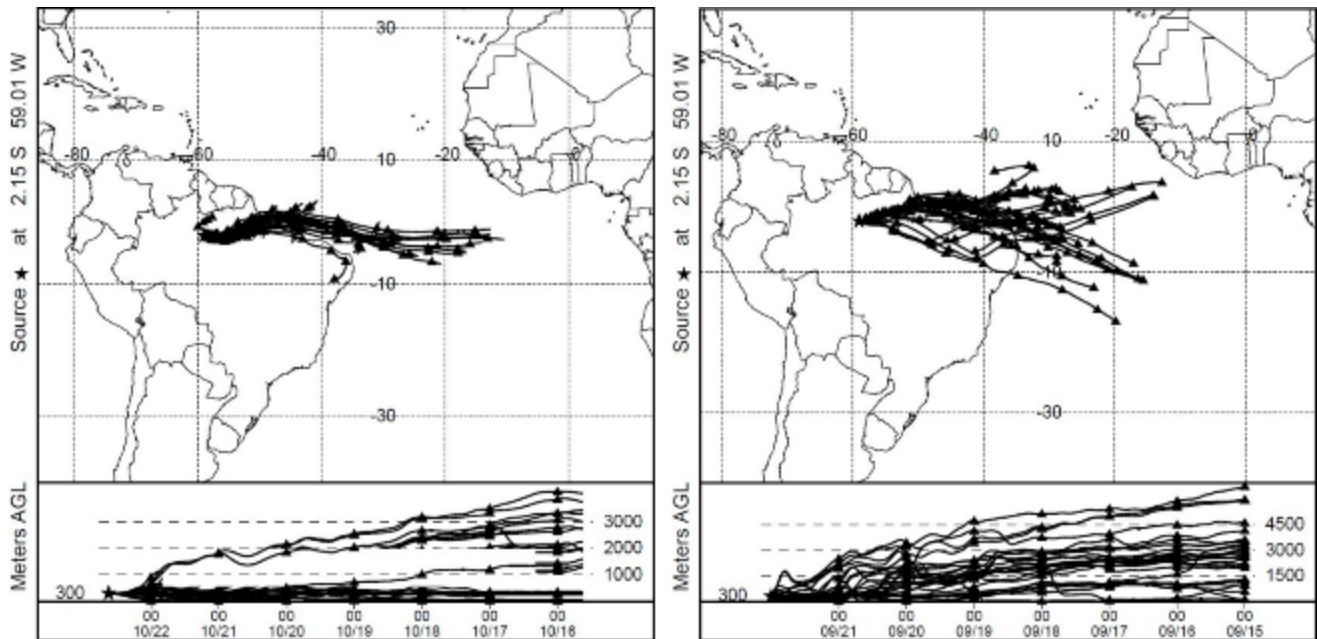


Figure S 11.1-4: The 7 d HYSPLIT backward trajectory ensembles starting at 300 m above ground level for the dry season 2018 (left) and dry season 2019 (right) (Stein et al., 2015).

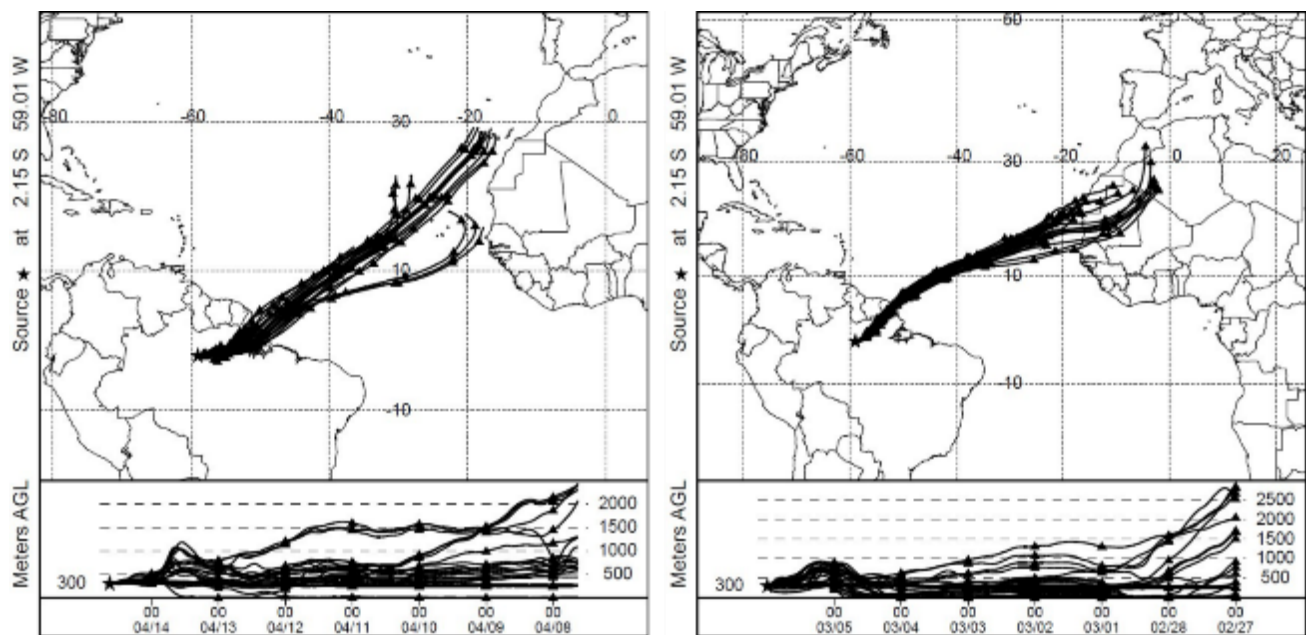


Figure S 11.1-5: The 7 d HYSPLIT backward trajectory ensembles starting at 300 m above ground level for the wet season 2018 (left) and the wet season 2019 (right) (Stein et al., 2015).

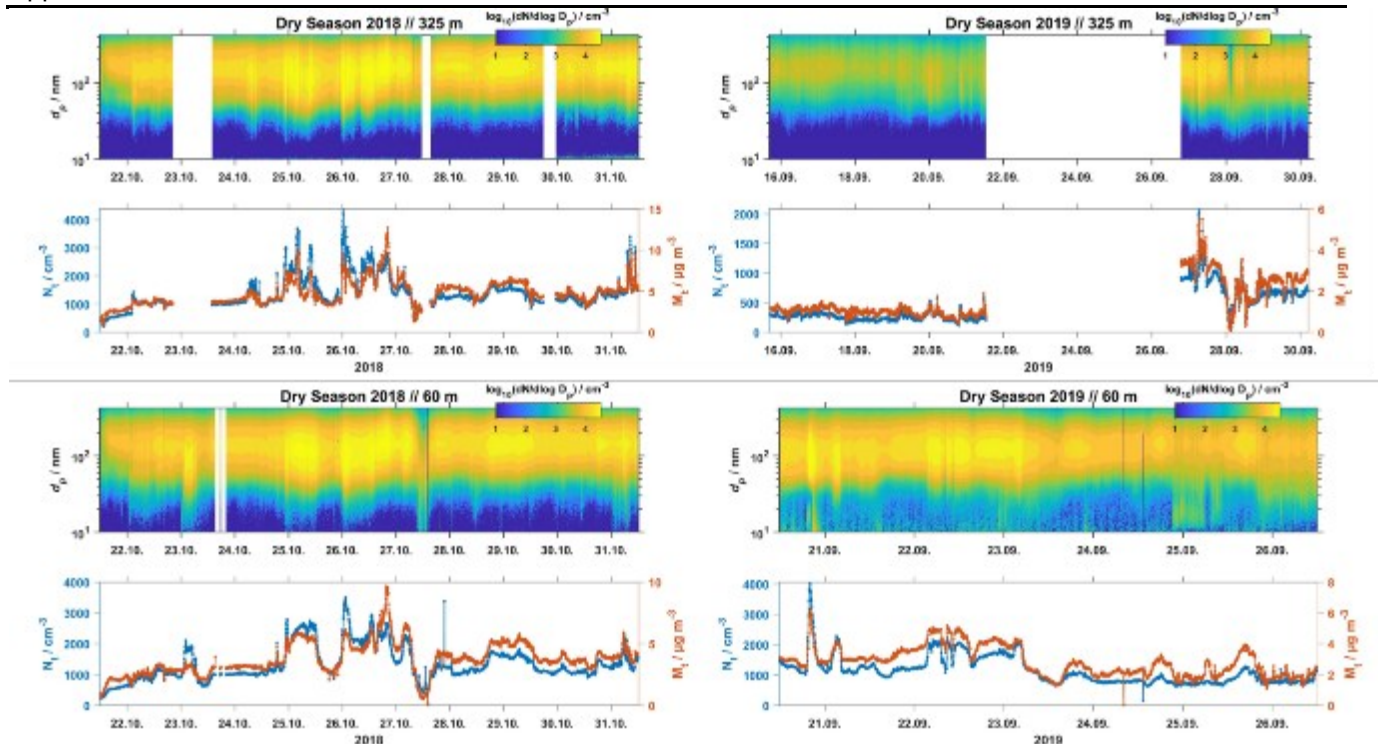


Figure S 11.1-6: SMPS data for the dry season 2018 and 2019 at 60 m and 325 m altitude. The calculated total particle numbers and total particle masses are illustrated in the lower panels, respectively. The instruments did not work during the 23., 27., and 30.10.2018 and during the 21.09.2019 and 27.09.2019. Thus, a longer period is displayed.

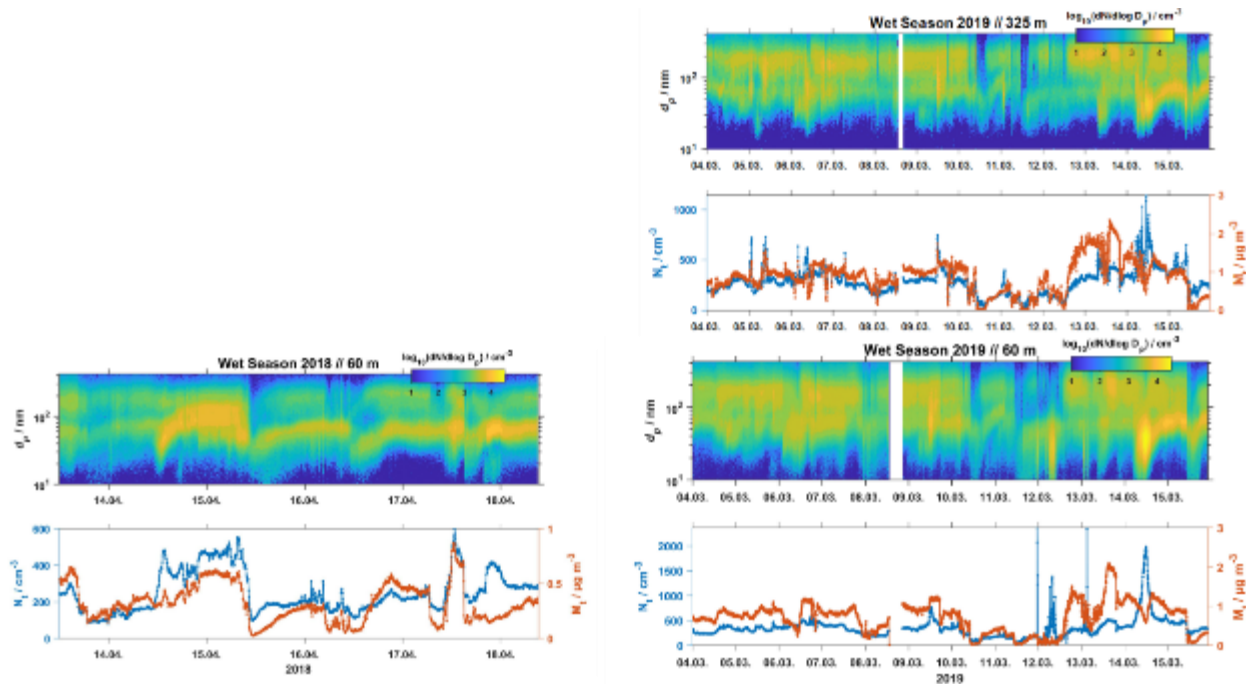


Figure S 11.1-7: SMPS data for the wet season 2018 and 2019 at 60 m and 325 m altitude. The calculated total particle numbers and total particle masses are illustrated in the lower panels, respectively. No data were collected at 325 m during the wet season 2018.

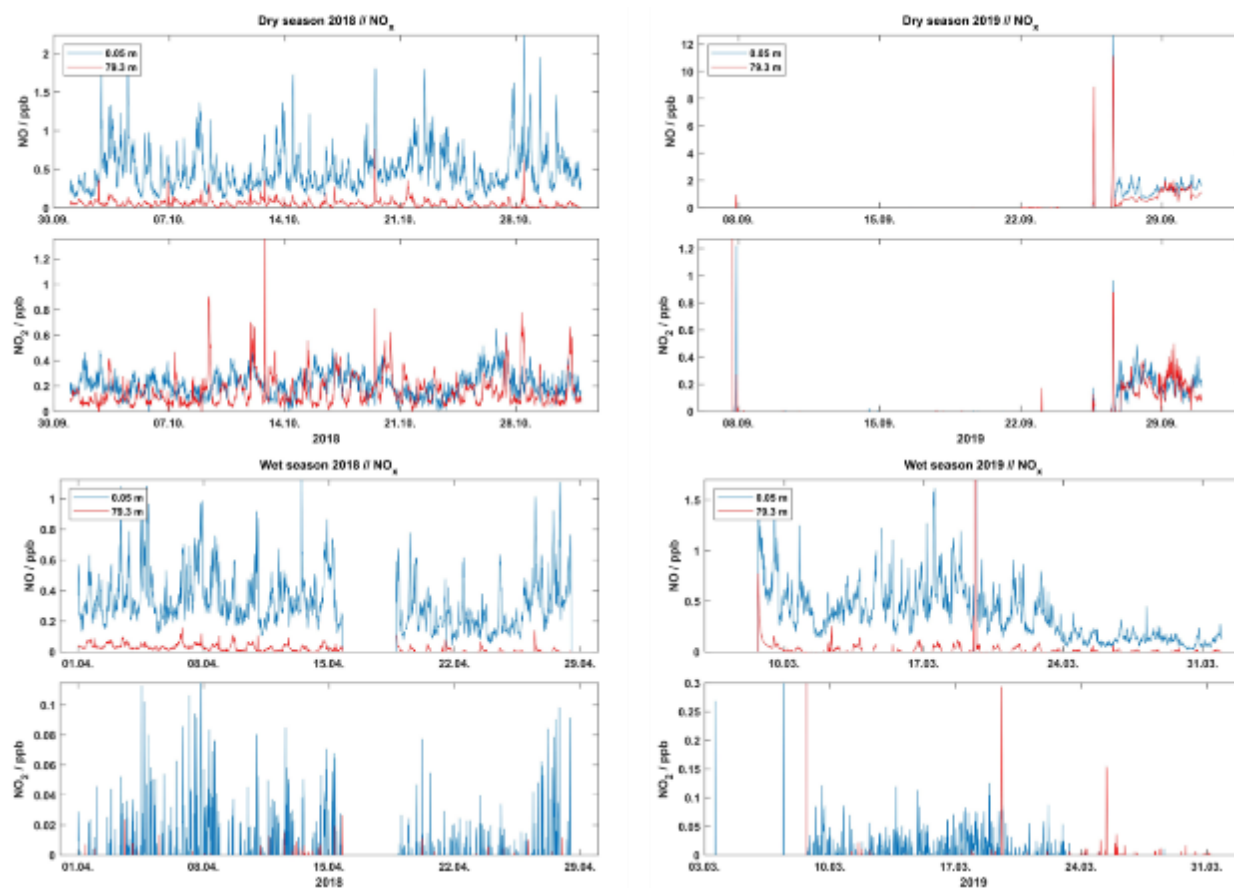


Figure S 11.1-8: NO and NO₂ concentrations at 0.05 m and 79.3 m height during the dry seasons 2018 and 2019 (upper part). The instrument was malfunctioning during the dry season 2019 resulting in few datapoints. The NO_x concentration for the wet seasons 2018 and 2019 are illustrated in the lower part.

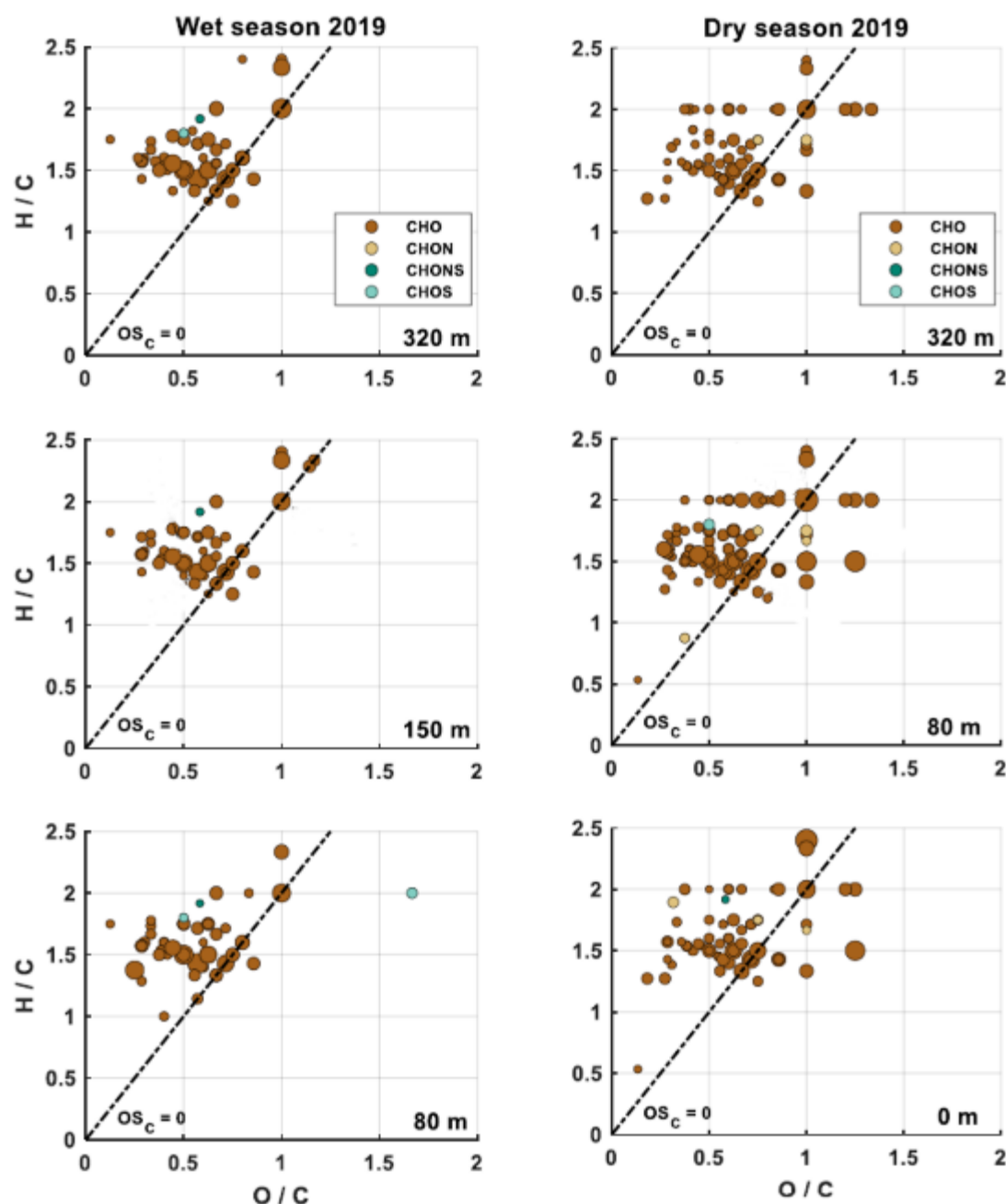


Figure S 11.1-9: Van Krevelen plots from the wet season 2019 (left panel; sampling heights: 320 m, 150 m, 80 m) and the dry season 2019 (right panel; sampling heights: 320 m, 80 m, 0 m). Included are only molecular formulae that were present in more than 75% of the samples, respectively. The size of the data points represents the signal intensity of the corresponding peak. The four subgroups are distinguished with different colors. Compounds located on the black dashed line have an average carbon oxidation state of 0 ($OSC = 0$).

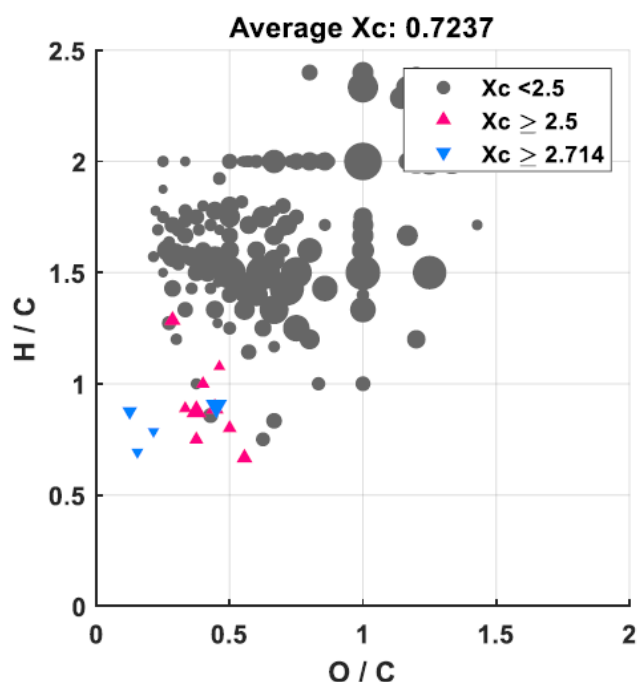


Figure S 11.1-10: Van Krevelen diagram illustrating the chemical background ions during the dry season 2018 at 80 m height. According to Yassine et al. (2014), all compounds were classified by the aromaticity equivalent X_c , highlighting unsaturated mono- and polycyclic structures.

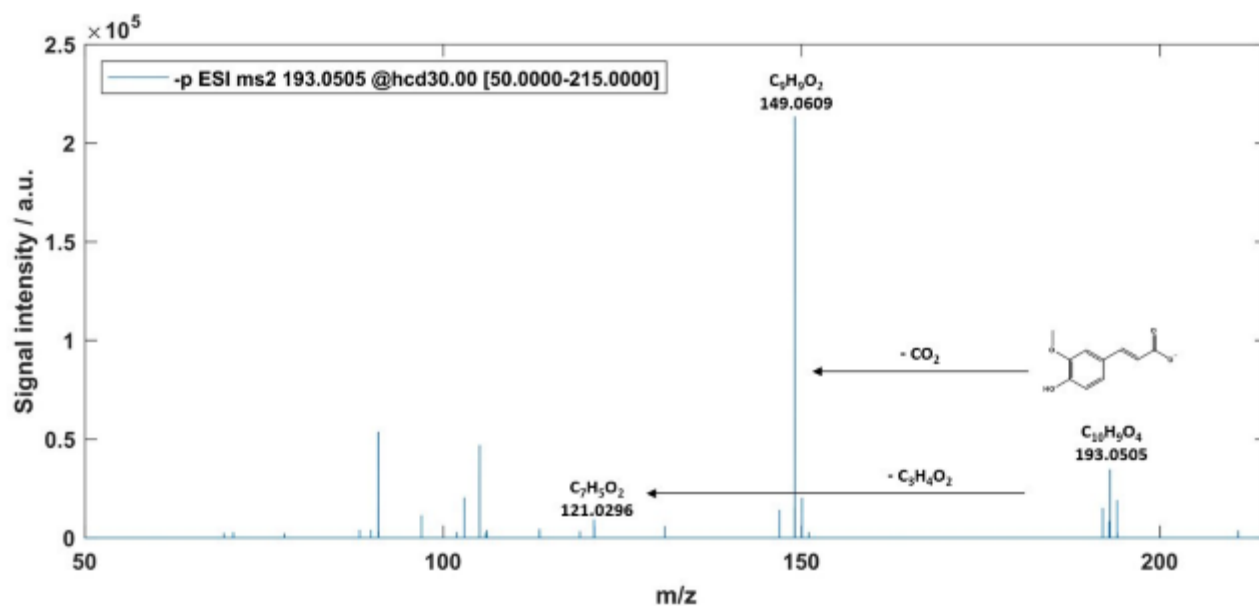


Figure S 11.1-11: MS2 of the background aromatic species with the molecular formula $C_{10}H_{10}O_4$ (m/z 193.0505) during the dry season 2018. Presumably, the detected ion might be ferulic acid according to the characteristic losses of carbon dioxide and acrylic acid.

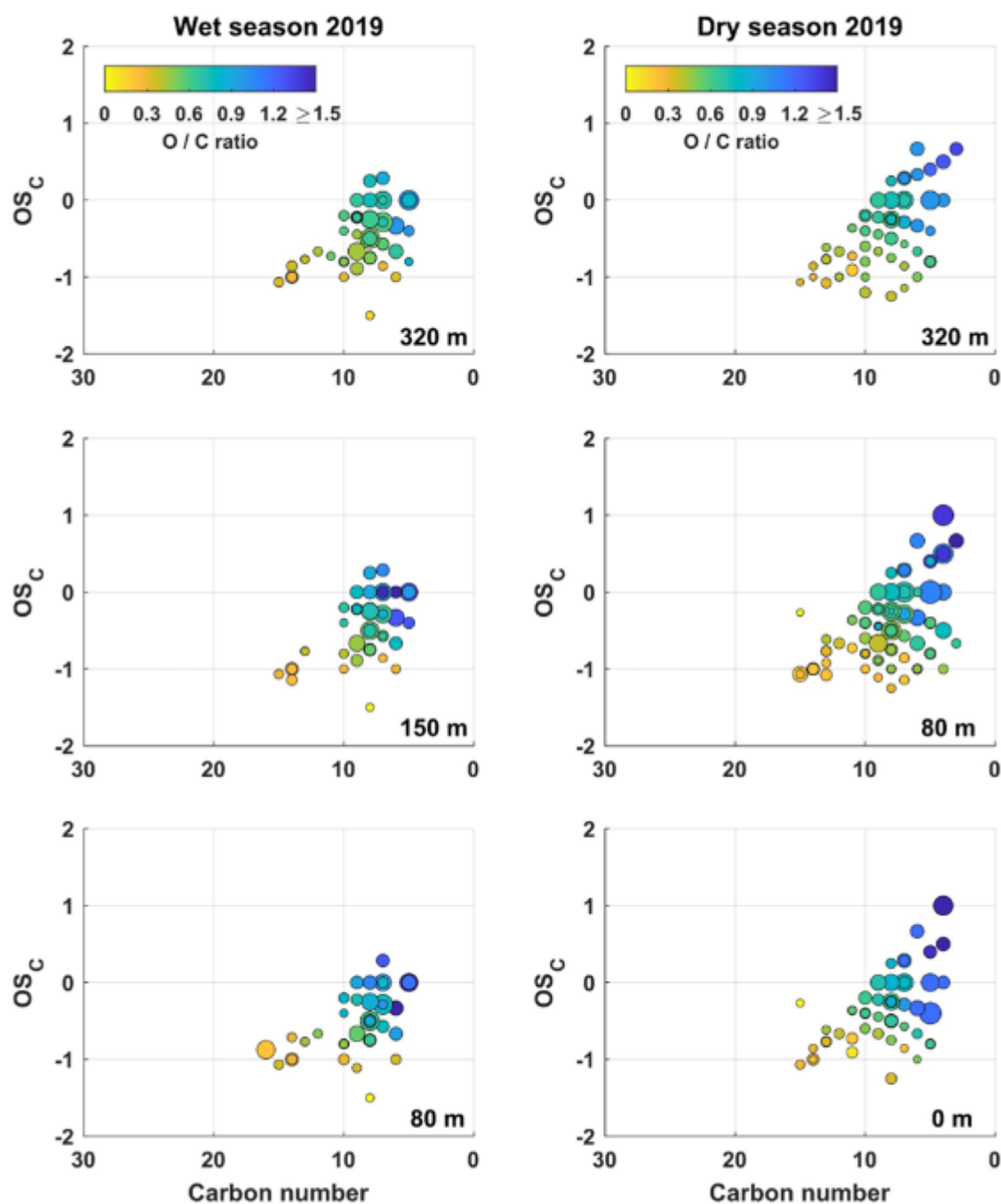


Figure S 11.1-12: Carbon oxidation state (OSC) plots for all detected CHO species during the wet season 2019 (left) and dry season 2019 (right) at different sampling heights. Only background ions are included. The size of the data points represents the signal intensity of the corresponding peak. The color code illustrates the degree of oxygenation.

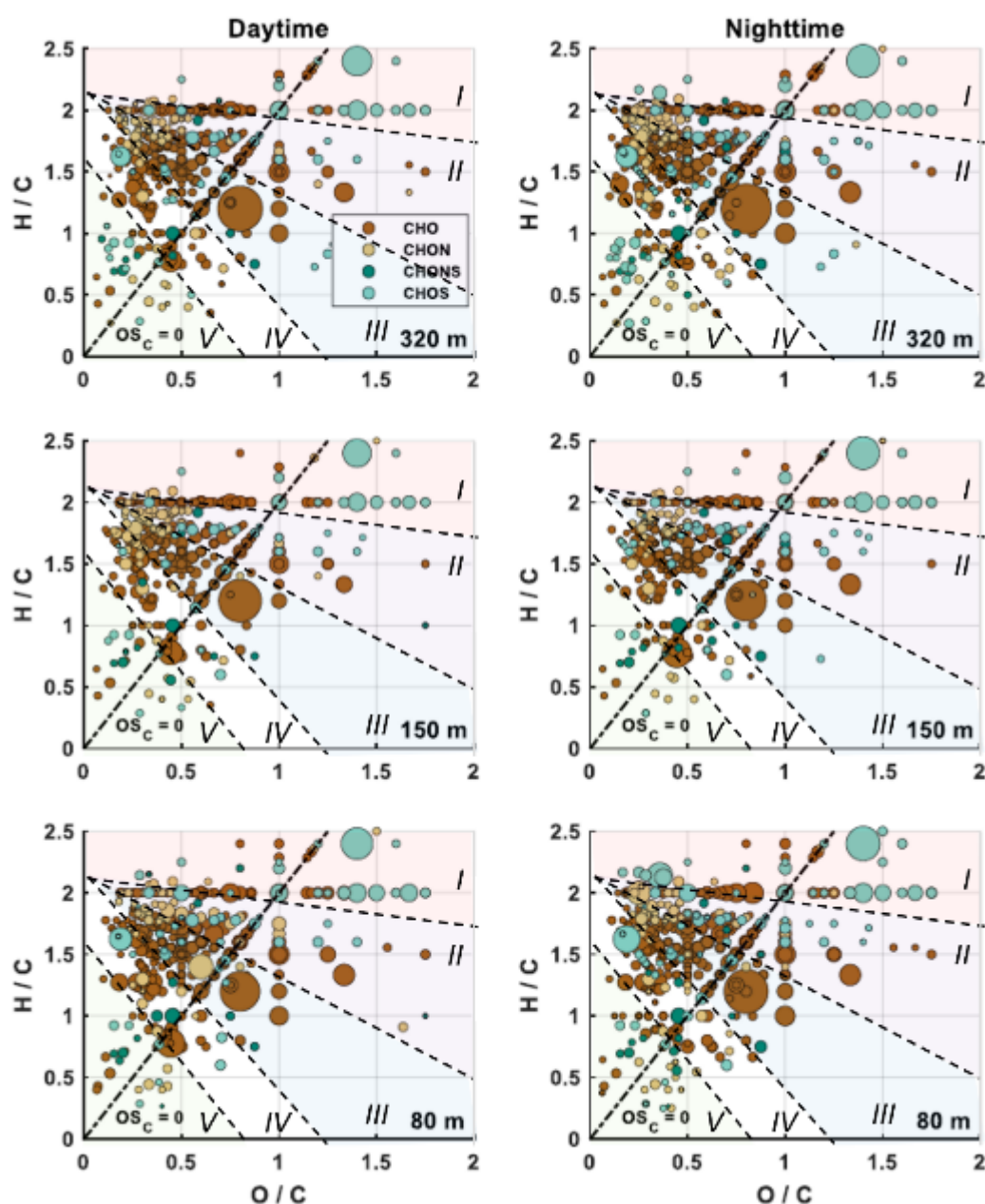


Figure S 11.1-13: Van Krevelen plots from the wet season 2019 (upper panel) during daytime (left panel) and nighttime (right panel) at 80 m, 150 m and 320 m height. Included are only molecular formulae that were present in more than one of the samples, respectively. The background signals are subtracted. The size of the data points represents the signal intensity of the corresponding peak. The four subgroups CHO, CHON, CHONS and CHOS are distinguished with different colors. Compounds located on the black dashed line have an average carbon oxidation state of 0 ($OSC = 0$).

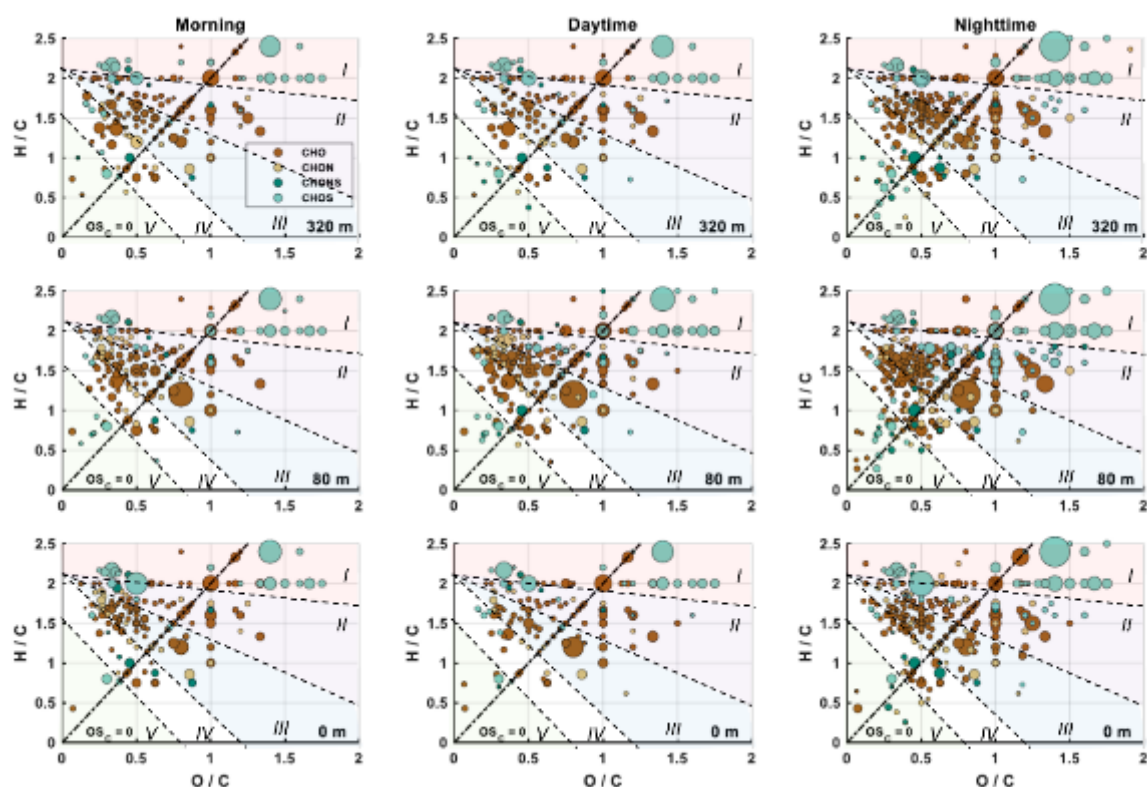


Figure S 11.1-14: Van Krevelen plots from the dry season 2019 during the morning (left panel), daytime (middle panel), and nighttime (right panel). Included are only molecular formulae that were present in more than one of the samples, respectively. The background signals are subtracted. The size of the data points represents the signal intensity of the corresponding peak. The four subgroups are distinguished with different colors. Compounds located on the black dashed line have an average carbon oxidation state of 0 (OSC = 0).

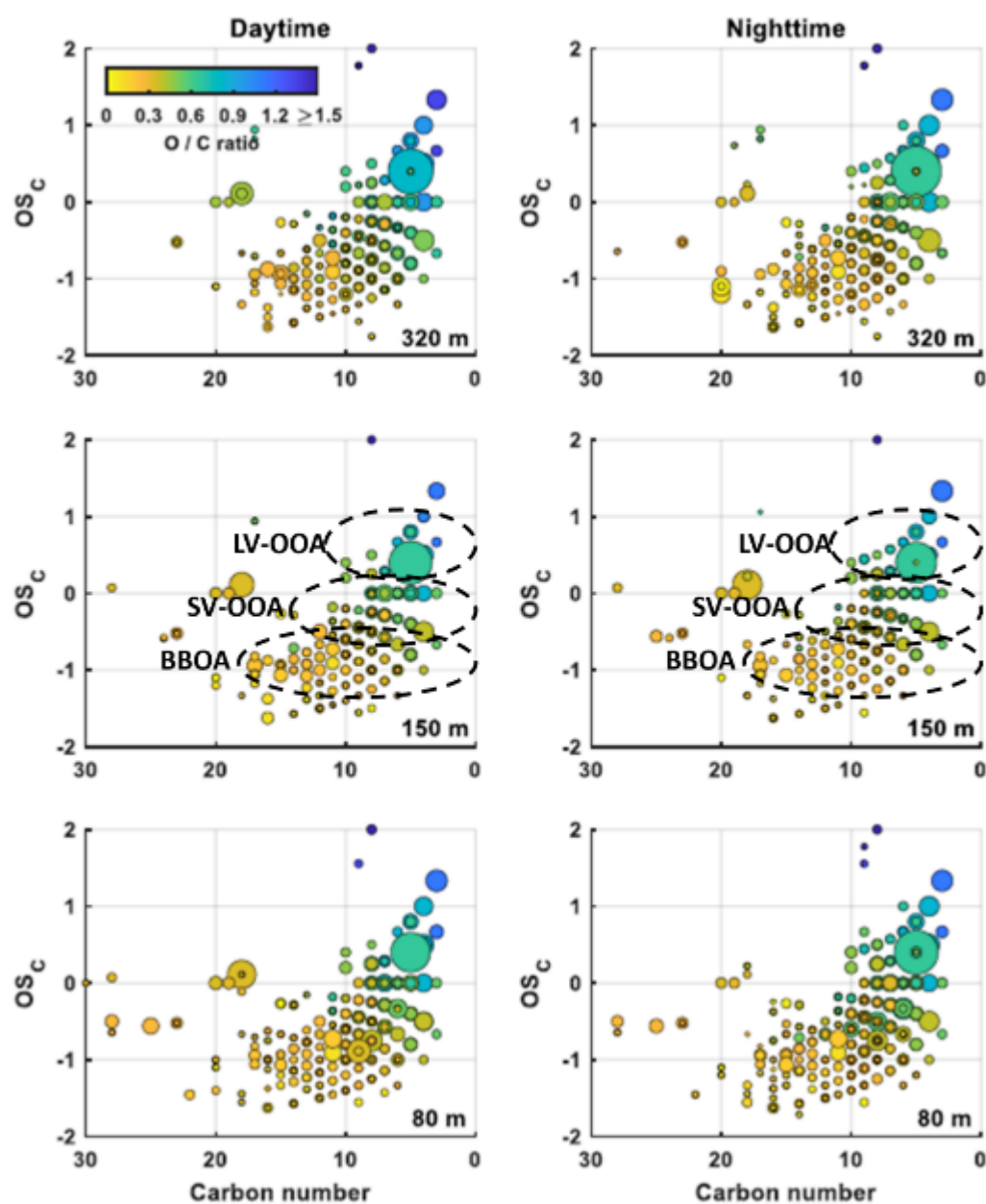


Figure S 11.1-15: Carbon oxidation state (OSC) plots for all detected CHO species during the wet season 2019 at daytime (left panel) and nighttime (right panel) at 80 m, 150 m and 320 m sampling height. Included are only molecular formulae that were present in more than one of the samples, respectively. The background signals are subtracted. The size of the data points represents the signal intensity of the corresponding peak. The color code illustrates the degree of oxygenation. The black dashed areas are related to low- volatility (LV-OOA), semivolatile (SV-OOA) oxygenated organic aerosol and biomass burning organic aerosol (BBOA).

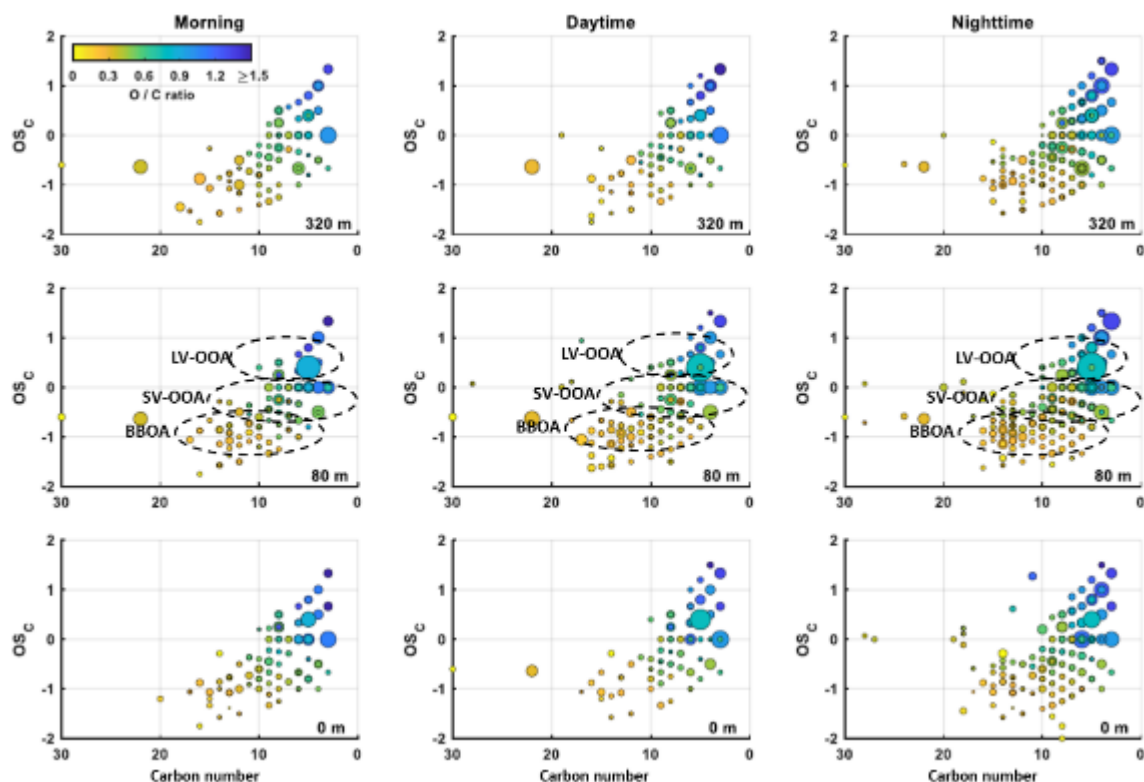


Figure S 11.1-16: Carbon oxidation state (OSC) plots for all detected CHO species during the dry season 2019 at morning (left), daytime (middle), and nighttime (right). Included are only molecular formulae that were present in more than one of the samples, respectively. The background signals are subtracted. The size of the data points represents the signal intensity of the corresponding peak. The color code illustrates the degree of oxygenation. The black dashed areas are related to low- volatility (LV-OOA), semivolatile (SV-OOA) oxygenated organic aerosol and biomass burning organic aerosol (BBOA).

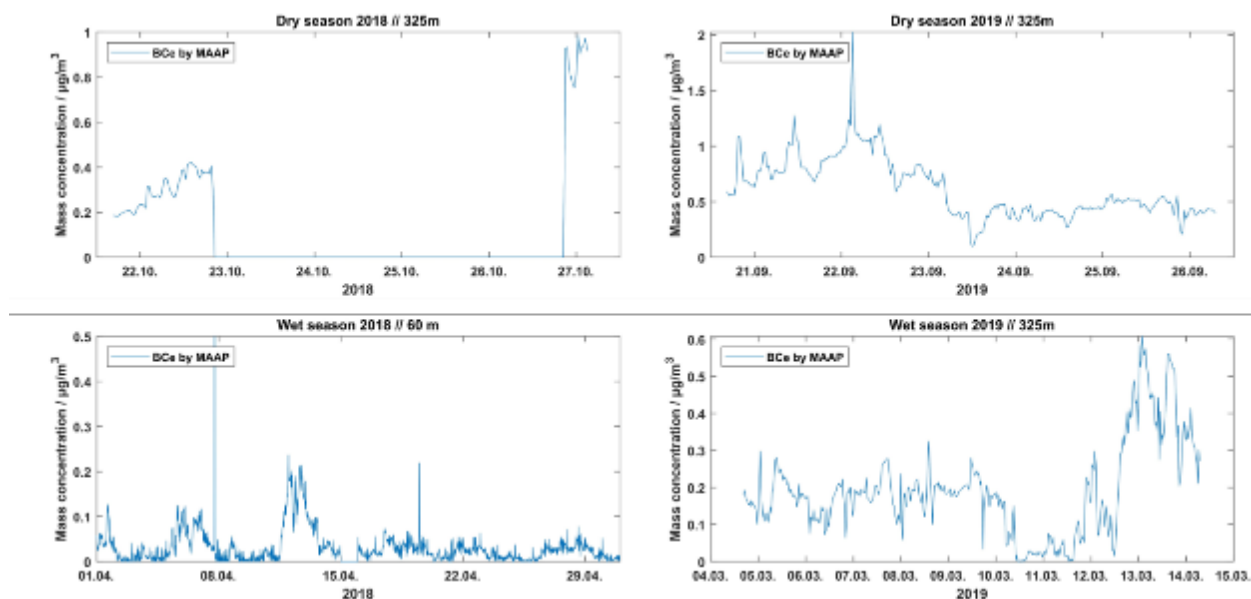


Figure S 11.1-17: Black carbon equivalent (BCe) mass concentrations during dry season 2018 and 2019 (upper part) and during the wet seasons 2018 and 2019 (lower part), respectively. Higher incidents of forest fires during the wet season 2019 are presumably responsible for increased BCe mass concentrations.

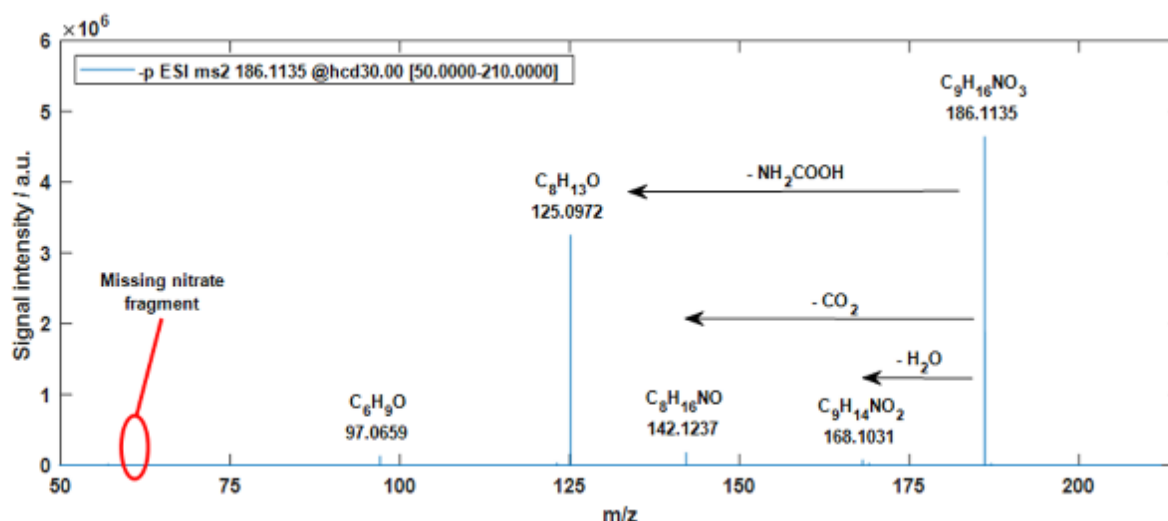


Figure S 11.1-18: MS2 of m/z 186.1135 ($C_9H_{17}NO_3$). A typical nitrate fragment was not observed. Consequently, a nitrooxy-species can be excluded. In contrast, the observed fragments indicate an amide and a hydroxy-functional group within the molecular structure.

Method Evaluation

This section covers important aspects of the LC method development. This study focused on a single and sophisticated approach for the trace analysis of specific marker species on aerosol filter samples. Characteristic marker species can be used to identify emission sources for biogenic SOA or biomass burning events (Robinson et al., 2006a, 2006b). However, marker compounds must fulfill certain criteria, such as chemical stability against atmospheric oxidation and low volatility. These properties provide increased molecular lifetimes so that the marker species can also be detected after long-range transportation. For instance, levoglucosan (1,6-anhydro- β -D-glucopyranose) has been established as marker species for biomass burning activities. It is emitted into the atmosphere by the combustion of cellulose-containing wood (Simoneit et al., 1999). Biogenic SOA markers include oxidation products of isoprene, monoterpenes, and sesquiterpenes. Appropriate tracers for isoprene-derived SOA are 2-methyltetrols (Claeys et al., 2004a; Claeys et al., 2004b; Kourtchev et al., 2005). However, these compounds are highly polar due to the four hydroxyl groups, which complicates the analysis by RP-HPLC. The most important marker compound for aged biogenic SOA from monoterpenes is 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) formed by OH radical-initiated oxidation of α - and β -pinene (Szmigielski et al., 2007; Müller et al., 2012). Earlier-generation oxidation products, such as pinonic acid and pinic acid, can then be used to distinguish between freshly formed and processed SOA. Additionally, sesquiterpene oxidation products, such as β -caryophyllinic acid and β -nocaryophyllonic acid, are suitable marker species because of their low volatility (van Eijck et al., 2013).

The marker species used in this study for method development are listed in Table S 11.1-4. Salicylic acid (99%), 3-oxoglutaric acid (96%), terebic acid (98%), pimelic acid (96%), levoglucosan (99%), *cis*-pinonic acid (98%), methyltricarballic acid ($\geq 88\%$), and camphoric acid (99%) were purchased from Sigma-Aldrich (Steinheim, Germany). D-malic acid ($\geq 99.5\%$) was obtained from Merck (Darmstadt, Germany). Vanillic acid was purchased from Alfa Aesar (Heysham, UK). Pinic acid was synthesized according to Moglioni et al. (2000). MBTCA was synthesized following the study by Dette et al. (2014). The sesquiterpene oxidation products β -caryophyllonic acid, β -caryophyllinic acid, and β -nocaryophyllonic acid were synthesized by van Eijck et al. (2013). Calibration solutions were prepared in a mixture of water and acetonitrile (9:1) (Fisher Scientific, Optima™ grade) with concentrations ranging from 0.5 ng mL^{-1} to 800 ng mL^{-1} . Blank solutions were prepared in the same manner.

Table S 11.1-4: Analytes used for method development. Also listed are the molecular formulae, m/z ratios and the calculated quantification limits (LOD).

Analyte	Molecular formula	m/z [M–H]–	LOD ¹ / ng mL ^{–1}
D-malic acid	C ₄ H ₆ O ₅	133.0142	9.98
2-methyltetrols	C ₅ H ₁₂ O ₄	135.0663	5.74
salicylic acid	C ₇ H ₆ O ₃	137.0244	2.11
3-oxoglutaric acid	C ₅ H ₆ O ₅	145.0142	2.71
terebic acid	C ₇ H ₁₀ O ₄	157.0506	3.09
pimelic acid	C ₇ H ₁₂ O ₄	159.0663	4.52
levoglucosan	C ₆ H ₁₀ O ₅	161.0455	29.68
vanillic acid	C ₈ H ₈ O ₄	167.0349	12.66
cis-pinonic acid	C ₁₀ H ₁₆ O ₃	183.1027	2.38
pinic acid	C ₉ H ₁₄ O ₄	185.0819	1.74
methyltricarballic acid	C ₇ H ₁₀ O ₆	189.0405	2.17
camphoric acid	C ₁₀ H ₁₆ O ₄	199.0976	3.32
MBTCA	C ₈ H ₁₂ O ₆	203.0561	3.25
β-caryophyllonic acid	C ₁₅ H ₂₄ O ₃	251.1653	7.87
β-caryophyllinic acid	C ₁₄ H ₂₂ O ₄	253.1445	2.67
β-nocaryophyllonic acid	C ₁₄ H ₂₂ O ₄	253.1445	3.06

¹Instrumental detection limits calculated according to DIN 32645.

Each measurement was calibrated externally by six- to eight-point linear regression, which provided calibration functions for all analytes. The unknown concentrations of the filter samples were quantified after the determination of the signal areas and background subtraction. The limits of detection (LOD) were calculated according to DIN 32645.

Furthermore, the filter extraction method was evaluated to assess the extraction efficiency. Therefore, blank filters were spiked with 50 ng mL^{–1} and 500 ng mL^{–1} of α-pinene oxidation products, i.e., pinic acid and MBTCA, respectively. The experiments were performed in triplicates. The calibration functions are illustrated in Figure S 11.1-19. Based on the linear regression, extraction efficiencies of (93.6 ± 3.9)% and (92.5 ± 5.5)% were calculated for pinic acid and MBTCA, respectively. Thus, a quantitative extraction of SOA constituents from filter samples was assumed for all measurements.

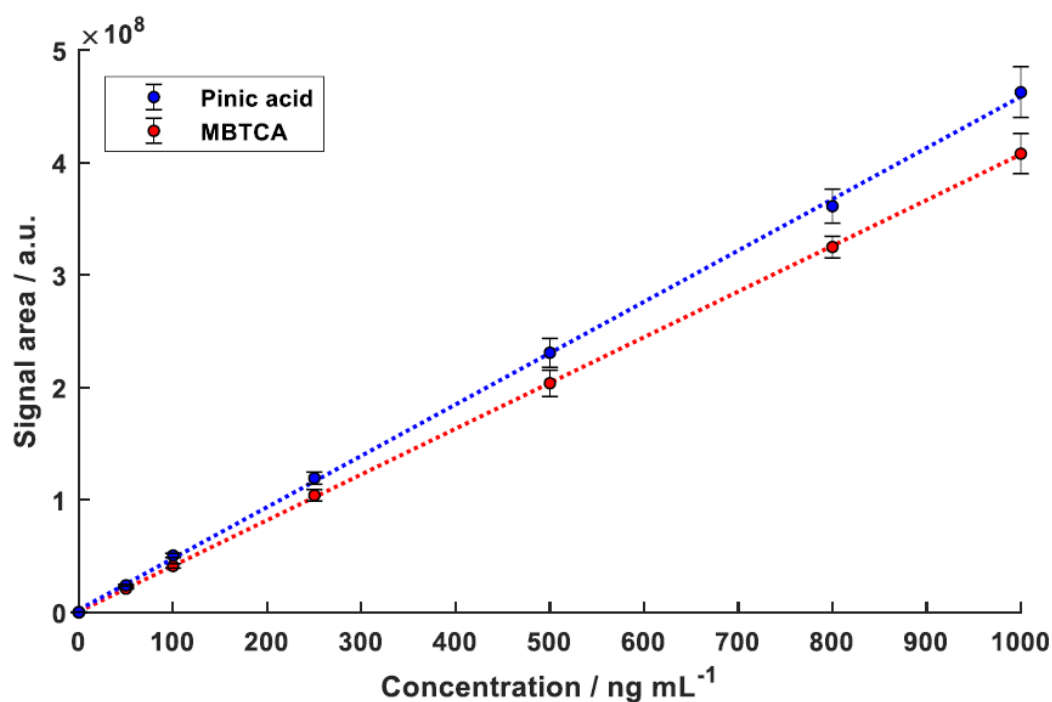


Figure S 11.1-19: External calibration functions of pinic acid (blue) and MBTCA (red) used for the validation of filter extraction efficiencies.

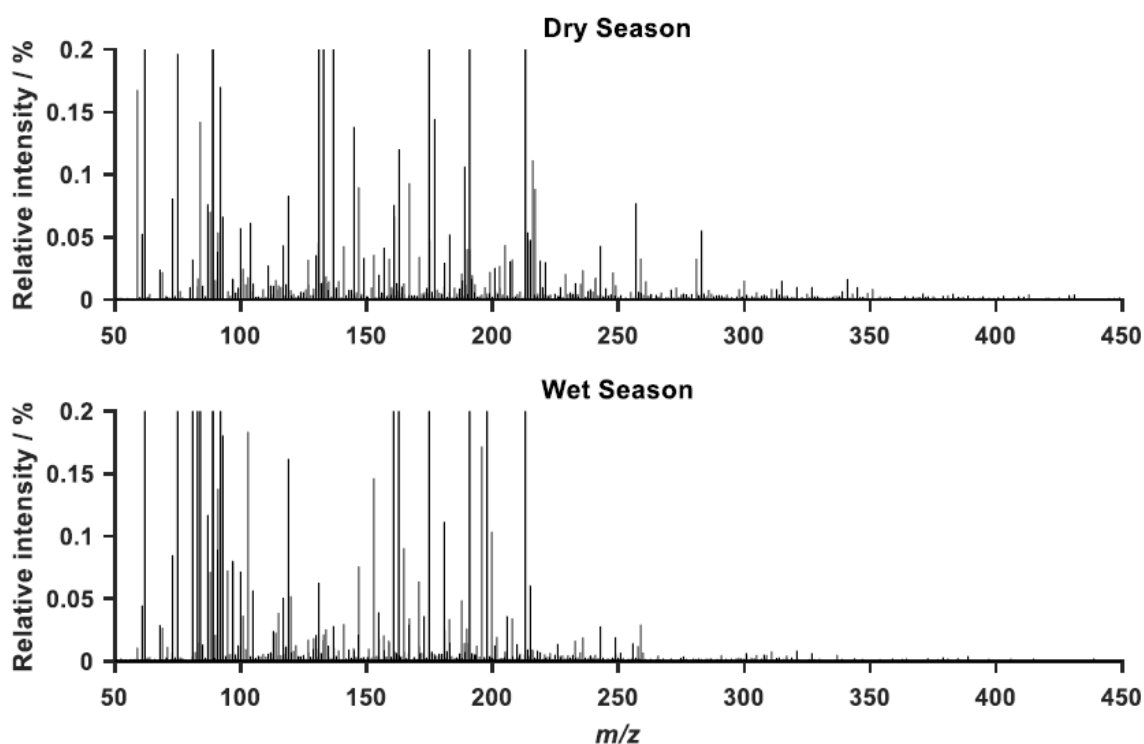


Figure S 11.1-20: Typical high-resolution mass spectra obtained in the negative ESI mode from filter samples of the dry season 2018 and wet season 2019, respectively. A UHPLC system separated the compounds before the injection into the mass spectrometer. The most intense ion signal at m/z 91.0036 was omitted for clarity reasons. It was attributed to the deprotonated formic acid dimer ($\text{C}_2\text{H}_3\text{O}_4$), which was added to the aqueous LC solvent.

Data Processing by MZmine 2.30

A non-targeted approach was developed and applied to the high-resolution mass spectra obtained from the analysis of each filter sample. Therefore, MZmine2.30 was used for data processing including toolboxes for peak detection, filtering for shoulder peaks and duplicates, chromatogram builder, deconvolution and smoothing, alignment, adduct and complex search, and formula prediction (Pluskal et al., 2010; Wang et al., 2017). The following optimized parameterization was used in this study:

1. For each scan, only masses with signal intensities above 5000 were included for further processing. Signal intensities below 5000 were treated as noise and consequently not considered. Afterward, a shoulder peak filtering was applied with a mass resolution of 140 000 at m/z 200.
2. Chromatograms were built for each mass by using the ADAP Chromatogram Builder Module (Myers et al., 2017). The minimum intensity required to start a new chromatogram was set to 15 000 with a mass tolerance of 2 ppm.
3. The chromatograms were smoothed (filter width of 5) and deconvoluted by the ADAP Wavelet algorithm (Myers et al., 2017) (S/N threshold of 9; coefficient/area threshold of 110; peak duration of 0.03 – 1.00; retention time wavelet range of 0.01 – 0.17).
4. Isotopic peaks were removed (mass tolerance of 2 ppm; 0.1 min retention time tolerance; maximum charge of 1).
5. Adducts were removed (retention time tolerance of 0.1 min; mass tolerance of 2 ppm; maximum relative peak height of 50%; mass difference: m/z 41.0266 $[M-H+ACN]^-$, m/z 46.0055 $[M-H+CH_2O_2]^-$, m/z 67.9874 $[M-H+CH_2ONa]^-$). Ion complexes were also removed with the parameters mentioned above.
6. Peaks detected in different samples were aligned, based on the mass and retention time tolerances (mass tolerance of 2 ppm; weight for m/z of 5; retention time tolerance of 0.1 min; weight for retention time of 4). A minimum score of 85% for isotope patterns was required.
7. The formula prediction was based on $[M-H]^-$ ions with a mass tolerance of 2 ppm. Tentative molecular formulae with an elemental composition of CHONS were determined according to the following constraints: C2-40H2-100O0-40N0-4S0-2; $0.1 \leq H/C \leq 6$; $N/C \leq 4$; $O/C \leq 3$; $S/C \leq 3$; multiple- element counts according to Kind and Fiehn (2007); double bond equivalents (DBE) integer and between 0 – 30. Finally, all peaks were filtered for isotope pattern with a mass tolerance of 5 ppm. Therefore, the software was used in a batch mode with decreasing minimum scores for the isotope pattern match starting at 99% to 85%.
8. Peak duplicates were removed (mass tolerance of 2 ppm; retention time tolerance of 0.1 min)

The resulting peak lists contained m/z ratios, molecular formulae, retention times, and signal areas of each detected organic species. The mass spectra of blank samples were processed accordingly. All

peak lists were further computed by Matlab R2017b (The MathWorks Inc., Natick, USA). Background subtraction was performed to only retain signals with sample-to-blank ratios ≥ 3 . Afterward, further elemental constraints were applied (H/C ratio of 0.3 – 3; N/C ratios of 0 – 0.5; S/C ratios of 0 – 0.2) to remove molecular formulae unlikely to be observed in nature (Wozniak et al., 2008; Fuller et al., 2012; Wang et al., 2017).

Table S 11.1-5: Confirmed species due to comparison with authentic standard substances. Also listed are the molecular formulae, m/z ratios and the retention time. The standard substances used are described in the section “method evaluation” in the supporting information. The shown species could be unambiguously assigned by comparing the exact masses and retention times.

Confirmed species	Molecular formula	m/z [M–H]–	Retention time /min
D-malic acid	C ₄ H ₆ O ₅	133.0142	1.07
2-methyltetrols	C ₅ H ₁₂ O ₄	135.0663	0.99
terebic acid	C ₇ H ₁₀ O ₄	157.0506	5.81
levoglucosan	C ₆ H ₁₀ O ₅	161.0455	1.13
pinic acid	C ₉ H ₁₄ O ₄	185.0819	7.63
MBTCA	C ₈ H ₁₂ O ₆	203.0561	6.01
β-caryophyllonic acid	C ₁₅ H ₂₄ O ₃	251.1653	12.94
β-caryophyllinic acid	C ₁₄ H ₂₂ O ₄	253.1445	12.59
β-nocaryophyllonic acid	C ₁₄ H ₂₂ O ₄	253.1445	11.43

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11.2 Supplementary material chapter 4

Table S 11.2-1: Sampling periods of the chosen MOUDI runs, including information about the height of the MOUDI inlet, with quartz filters equipped MOUDI stages, and actual sampling flow.

MOUDI run	Start date	Start time (UTC)	End date	End time (UTC)	Height	Equipped stages	Flow [L/min]
Case 1_1_60	19.04.2022	22:25	23.04.2022	13:00	60 m	S13-S5 (10 nm-1000 nm)	9.50
Case 1_1_320	21.04.2022	10:36	24.04.2022	14:05	325 m	S13-S5 (10 nm-1000 nm)	28.50
Case 1_2_60	16.06.2023	13:30	20.05.2023	19:41	60 m	S13-S1 (10 nm- 10 µm)	9.33
Case 1_2_320	16.06.2023	13:29	20.05.2023	19:41	320 m	S13-S1 (10 nm- 10 µm)	28.75
Case 2_1_60	21.05.2022	20:24	24.05.2022	14:00	60 m	S13-S5 (10 nm-1000 nm)	8.50
Case 2_1_320	19.05.2022	21:01	24.05.2022	13:03	320 m	S13-S5 (10 nm-1000 nm)	25.05
Case 2_2_60	08.12.2022	21:45	12.12.2022	11:30	60 m	S13-S3 (10 nm – 3.2 µm)	9.50
Case 2_2_320	08.12.2022	21:45	12.12.2022	11:30	320 m	S13-S3 (10 nm – 3.2 µm)	32.5
Case 2_3_60	11.05.2023	22:08	15.05.2023	20:33	60 m	S13-S1 (10 nm -10 µm)	9.10

Case 2_3_320	11.05.2023	21:56	15.05.2023	20:38	320 m	S13-S1 (10 nm -10 µm)	29.92
Case 3_1_60	24.09.2022	19:37	27.09.2022	21:53	60 m	S13-S1 (10 nm -10 µm)	8.30
Case 3_1_320	24.09.2022	19:37	27.09.2022	21:53	320 m	S13-S1 (10 nm -10 µm)	25.00
Case 3_2_60	01.10.2022	18:47	04.10.2022	11:11	60 m	S13-S1 (10 nm -10 µm)	8.56
Case 3_2_320	01.10.2022	18:48	04.10.2022	11:13	320 m	S13-S1 (10 nm -10 µm)	24.54
Case 3_3_60	30.09.2023	22:12	02.10.2023	12:22	60 m	S13-S1 (10 nm -10 µm)	7.88
Case 3_3_320	30.09.2023	22:12	02.10.2023	12:22	320 m	S13-S1 (10 nm -10 µm)	28.50

Table S 11.2-2: Mass concentrations M calculated by logarithmic integration across bin boundaries, assuming spherical particles with densities $\rho = 1.47 \text{ g cm}^{-3}$. OPS bin boundaries were first corrected for particle refractive index using the TSI AIM software. Refractive indices of $1.33 - 0.006i$ were applied for cases 1 and 2 (wet-season conditions; Franco et al., 2024), and $1.41 - 0.013i$ for Case 3 (biomass burning conditions; Guyon et al., 2003). The optical particle diameter measured by the OPS was treated as equivalent to the particle's volume-equivalent (geometric, shape-factor 1) diameter (Peters et al., 2006). To ensure comparability with MOUDI measurements, the geometric diameters d_p were converted to aerodynamic diameters d_a using Equation 4.3-4. The mass concentrations within the size ranges corresponding to the MOUDI stages were determined using partial bin integration.

Case	Diameter	Refractive Index	M (0.32-0.56 µm)	M (0.56-1.00 µm)	M (1.0-1.8 µm)	M (1.8-3.2 µm)	M (3.2-5.6 µm)	M (5.6-10 µm)
			[µg/m ³]	[µg/m ³]	[µg/m ³]	[µg/m ³]	[µg/m ³]	[µg/m ³]
1_1_60	opt	1.33-0.006i	56.833	43.954	119.699	729.221	2065.866	2259.617
	aero	1.33-0.006i	73.051	66.271	135.760	848.709	2796.720	5481.356
1_2_60	opt	1.33-0.006i	39.225	22.025	41.837	247.609	630.516	665.374
	aero	1.33-0.006i	51.805	37.907	53.602	311.286	848.557	1631.519

2_1_60	opt	1.33- 0.006i	536.983	154.340	231.088	1500.346	3539.832	3252.803
	aero	1.33- 0.006i	728.809	396.195	291.953	1791.312	5033.498	8182.646
2_2_60	opt	1.33- 0.006i	823.010	355.047	797.411	3261.433	4161.616	3396.670
	aero	1.33- 0.006i	1182.068	587.698	975.047	5130.397	6067.247	8862.153
2_3_60	opt	1.33- 0.006i	299.440	105.474	175.452	1189.558	3278.488	3032.060
	aero	1.33- 0.006i	407.589	229.082	228.640	1398.394	4435.589	7702.369
3_1_60	opt	1.47- 0.013i	5324.940	1851.229	981.003	3705.348	4402.772	4017.498
	aero	1.47- 0.013i	7009.922	4796.981	1849.308	5683.386	6654.453	10155.567
3_2_60	opt	1.47- 0.013i	1736.302	621.131	552.291	2251.869	3128.744	3184.865
	aero	1.47- 0.013i	2361.016	1440.809	877.850	3422.526	4377.688	7972.136
3_3_60	opt	1.47- 0.013i	4944.732	2332.974	1180.314	3656.101	3098.892	3567.878
	aero	1.47- 0.013i	6171.527	5419.487	2482.995	5969.613	4898.920	8530.270

Table S 11.2-3: Inlet transmission loss corrected mass concentrations M_{corr} and calculated particle loss correction factor determined by the ratio of corrected M_{corr} to calculated M in Table S 11.2-2.

Case	Diameter	Refractive Index	M_{corr} (0.32-0.56 μm) [$\mu\text{g}/\text{m}^3$]	M_{corr} (0.56-1.00 μm) [$\mu\text{g}/\text{m}^3$]	M_{corr} (1.0-1.8 μm) [$\mu\text{g}/\text{m}^3$]	M_{corr} (1.8-3.2 μm) [$\mu\text{g}/\text{m}^3$]	M_{corr} (3.2-5.6 μm) [$\mu\text{g}/\text{m}^3$]	M_{corr} (5.6-10 μm) [$\mu\text{g}/\text{m}^3$]
1_1_60	aero loss corrected	1.33-0.006i	73.446	66.634	137.203	871.320	3025.387	6594.241
		correction factor	1.005	1.005	1.011	1.027	1.082	1.203
1_2_60	aero loss corrected	1.33-0.006i	52.085	38.109	54.092	318.725	910.712	1944.660
		correction factor	1.005	1.005	1.009	1.024	1.073	1.192
2_1_60	aero loss corrected	1.33-0.006i	732.753	398.278	294.651	1835.075	5394.651	9723.649
		correction factor	1.005	1.005	1.009	1.024	1.072	1.188
2_2_60	aero loss corrected	1.33-0.006i	1188.470	590.829	984.148	5248.341	6496.624	10500.558
		correction factor	1.005	1.005	1.009	1.023	1.071	1.185
2_3_60	aero loss corrected	1.33-0.006i	409.795	230.292	230.724	1432.356	4760.160	9143.761
		correction factor	1.005	1.005	1.009	1.024	1.073	1.187
3_1_60	aero loss corrected	1.47-0.013i	7047.358	4822.011	1865.232	5818.303	7107.137	12092.944
		correction factor	1.005	1.005	1.009	1.024	1.068	1.191

3_2_60	aero loss corrected	1.47-0.013i	2373.625	1448.338	885.797	3503.989	4681.329	9493.660
		correction factor	1.005	1.005	1.009	1.024	1.069	1.191
3_3_60	aero loss corrected	1.47-0.013i	6204.486	5447.885	2503.822	6109.076	5221.500	10214.070
		correction factor	1.005	1.005	1.008	1.023	1.066	1.197

Table S 11.2-4: Calculated inlet transmission loss factors for mass concentrations determined by filter sampling and UHPLC-ESI-HR-Orbitrap-MS analysis. The correction factors were calculated by the mean and standard deviation of the correction factors determined by the OPS data in Table S 2.1.3. For PM₁₀, the correction factors of all particle size ranges of the specific case were averaged between all respective subcases. For PM₁, only the correction factors of M_{corr} (0.32-0.56 μm) and M_{corr} (0.56-1.00 μm) of the specific case were considered and averaged between all respective subcases. For PM_{0.056}, only the correction factors of M_{corr} (0.32-0.56 μm) of the specific case were considered and averaged between all respective subcases.

	Case 1 “clean conditions”		Case 2 “mixed conciditons”		Case 3 “polluted conditions”	
	Particle loss correction factor	Δ Particle loss correction factor	Particle loss correction factor	Δ Particle loss correction factor	Particle loss correction factor	Δ Particle loss correction factor
PM₁₀	1.05349	0.07222	1.05042	0.06711	1.05061	0.06925
PM₁	1.00540	0.00006	1.00535	0.00007	1.00528	0.00006
PM_{0.056}	1.00541	0.00001	1.00541	0.00001	1.00534	0.00001

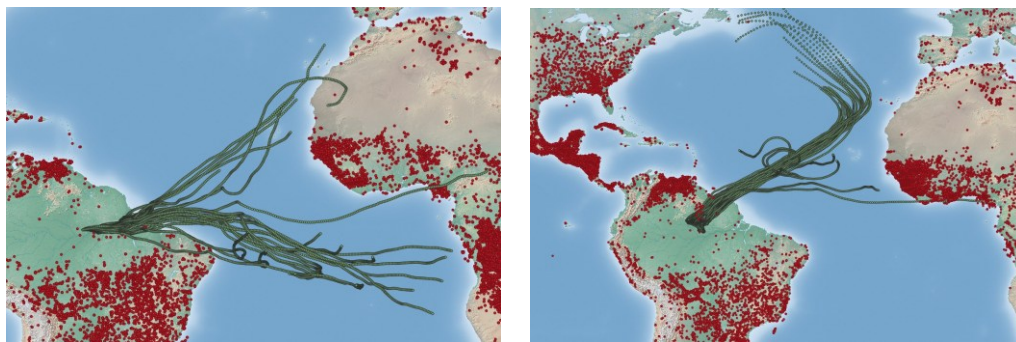


Figure S 11.2-1: The 11 d HYSPLIT backward trajectory ensembles starting at 300 m above ground level for subcase 1_1 (left) and subcase1_2 (right) (clean conditions) (Stein et al., 2015). Fire information was downloaded from NASA FIRMS (2026) <https://firms.modaps.eosdis.nasa.gov/> and combined with HYSPLIT trajectories by using the software QGIS.



Figure S 11.2-2: The 11 d HYSPLIT backward trajectory ensembles starting at 300 m above ground level for subcase 2_1 (left), subcase 2_2 (middle), and subcase 2_3 (right) (mixed conditions) (Stein et al., 2015). Fire information was downloaded from NASA FIRMS (2026) <https://firms.modaps.eosdis.nasa.gov/> and combined with HYSPLIT trajectories by using the software QGIS.

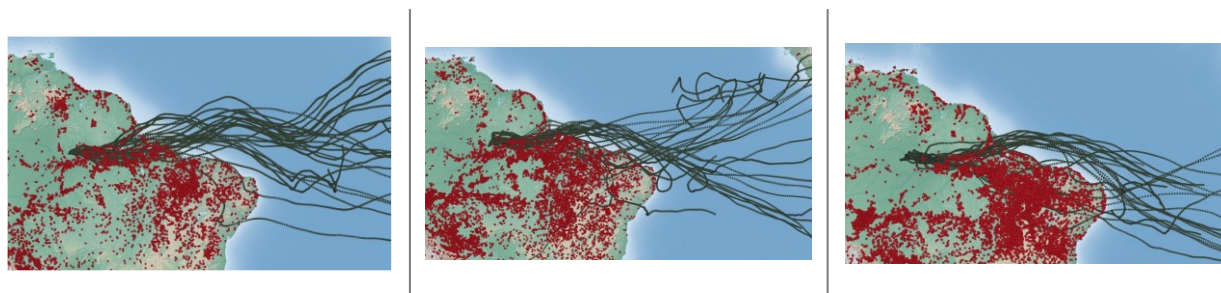


Figure S 11.2-3: The 11 d HYSPLIT backward trajectory ensembles starting at 300 m above ground level for subcase 3_1 (left), subcase 3_2 (middle), and subcase3_3 (right) (polluted conditions) (Stein et al., 2015). Fire information was downloaded from NASA FIRMS (2026) <https://firms.modaps.eosdis.nasa.gov/> and combined with HYSPLIT trajectories by using the software QGIS.

Table S 11.2-5: Means and standard deviations of the black carbon concentrations of the individual MOUDI runs at 60 m and 320 m determined by the MAAP by default measuring the light absorption and converting it to eBC using the default mass absorption efficiency of 11.4 m²/g (637 nm) for the periods 1-10 and 12.3 m²/g (637 nm) for the periods 11-16 according to the findings of (Saturno et al., 2018b). The data were normalized to standard conditions (STP).

Period	Sample_name	Start date & time (UTC)	End date & time (UTC)	Height (m)	BC (µg/m ³)	
					Mean	Std
1	Case1_1_60	19.04.2022 22:00	23.04.2022 13:00	60	0.008	0.008
2	Case1_2_60	16.05.2023 13:30	20.05.2023 20:00	60	0.013	0.010
3	Case1_1_320	21.04.2022 10:30	24.04.2022 14:30	320	0.003	0.008
4	Case1_2_320	16.05.2023 13:30	20.05.2023 20:00	320	0.016	0.013
5	Case2_1_60	21.05.2022 20:00	24.05.2022 14:00	60	0.105	0.023
6	Case2_2_60	08.12.2022 21:30	12.12.2022 11:30	60	0.135	0.072
7	Case2_3_60	11.05.2023 22:00	15.05.2023 20:30	60	0.021	0.009
8	Case2_1_320	19.05.2022 21:00	24.05.2022 13:00	320	0.106	0.070
9	Case2_2_320	08.12.2022 21:30	12.12.2022 13:00	320	0.139	0.076
10	Case2_3_320	11.05.2023 22:00	15.05.2023 21:00	320	0.026	0.017
11	Case3_1_60	24.09.2022 19:30	27.09.2022 22:00	60	0.476	0.105
12	Case3_2_60	01.10.2022 18:30	04.10.2022 11:30	60	0.264	0.121
13	Case3_3_60	30.09.2023 22:00	02.10.2023 12:30	60	1.067	0.304
14	Case3_1_320	24.09.2022 19:30	27.09.2022 22:00	320	0.508	0.148
15	Case3_2_320	01.10.2022 18:30	04.10.2022 11:30	320	0.307	0.138
16	Case3_3_320	30.09.2023 22:00	02.10.2023 12:30	320	0.897	0.100

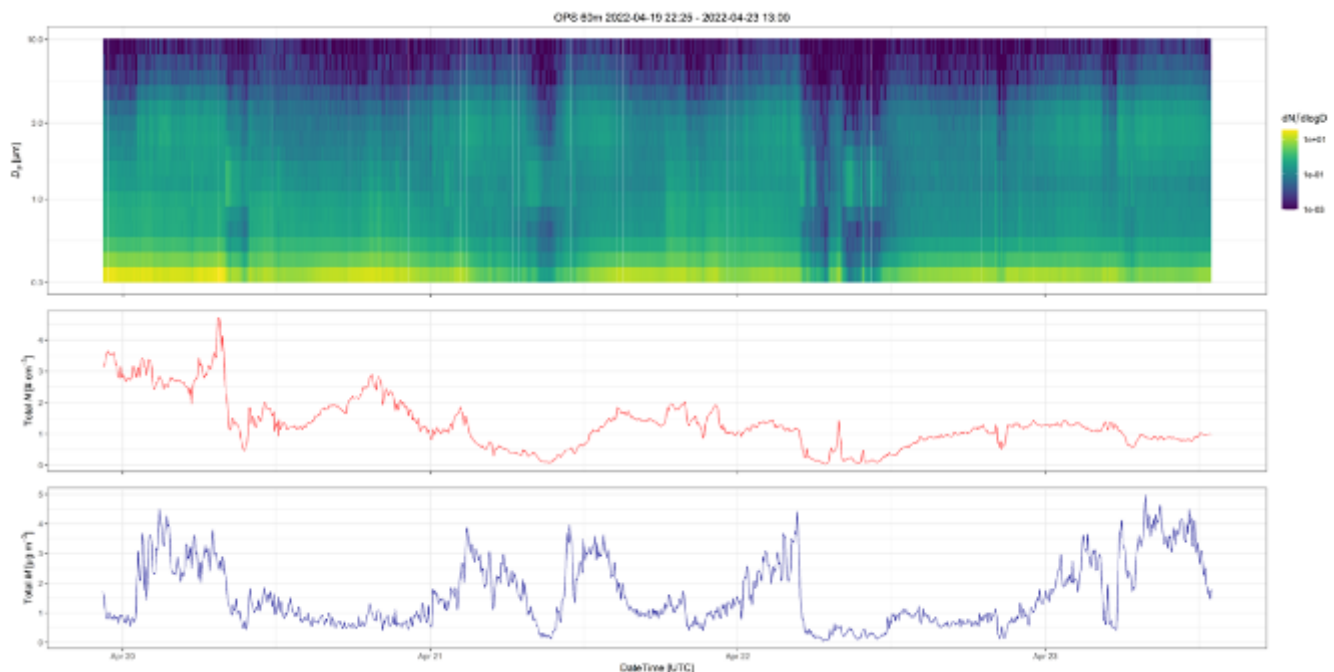


Figure S 11.2-4: Total particle number concentration N [# cm⁻³], total mass concentration M [µg m⁻³], and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 1_1 at 60 for particle diameters ranging from 300 nm to 10 µm, determined by OPS data.

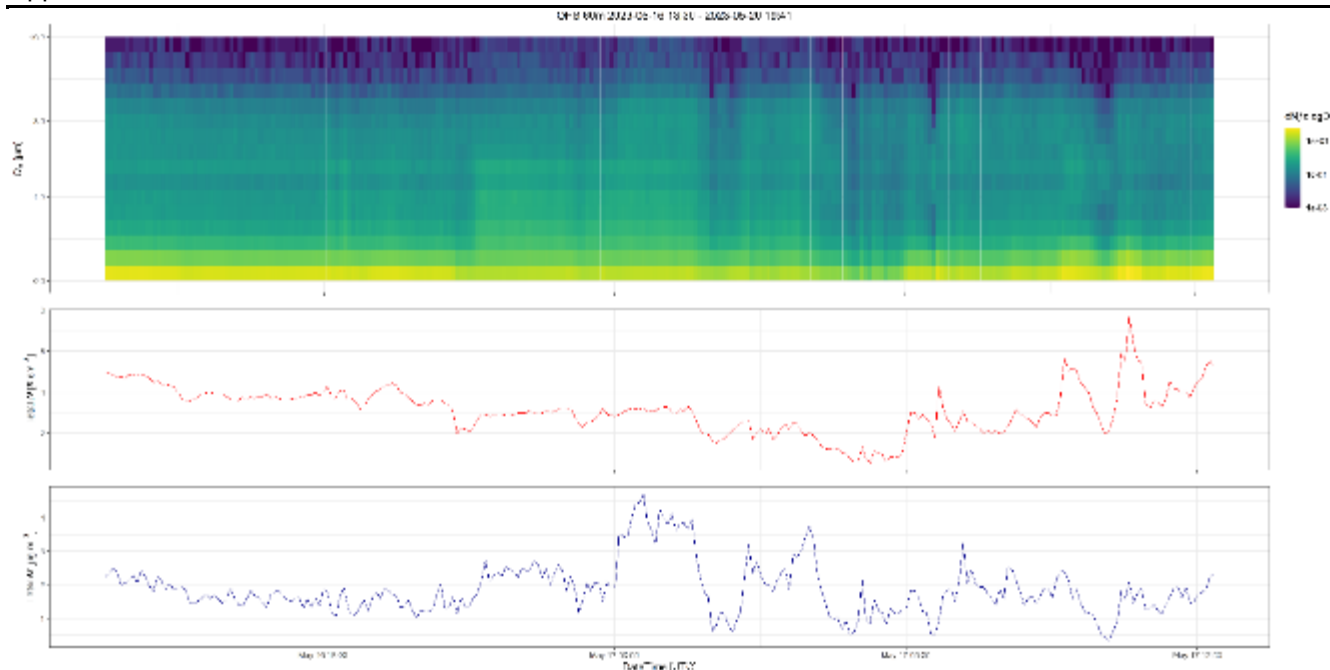


Figure S 11.2-5:Total particle number concentration N [$\# \text{ cm}^{-3}$], total mass concentration M [$\mu\text{g m}^{-3}$], and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 1_2 at 60 m for particle diameters ranging from 300 nm to 10 μm , determined by OPS data.

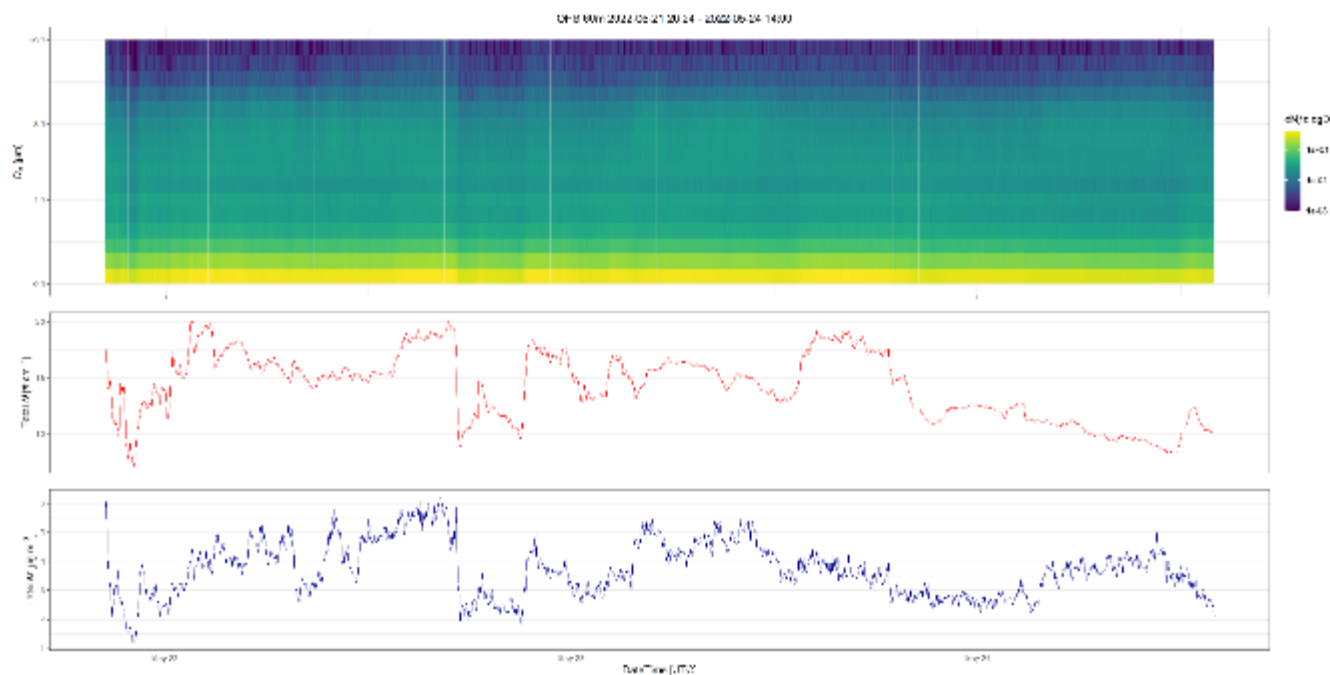


Figure S 11.2-6:Total particle number concentration N [$\# \text{ cm}^{-3}$], total mass concentration M [$\mu\text{g m}^{-3}$], and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 2_1 at 60 m for particle diameters ranging from 300 nm to 10 μm , determined by OPS data.

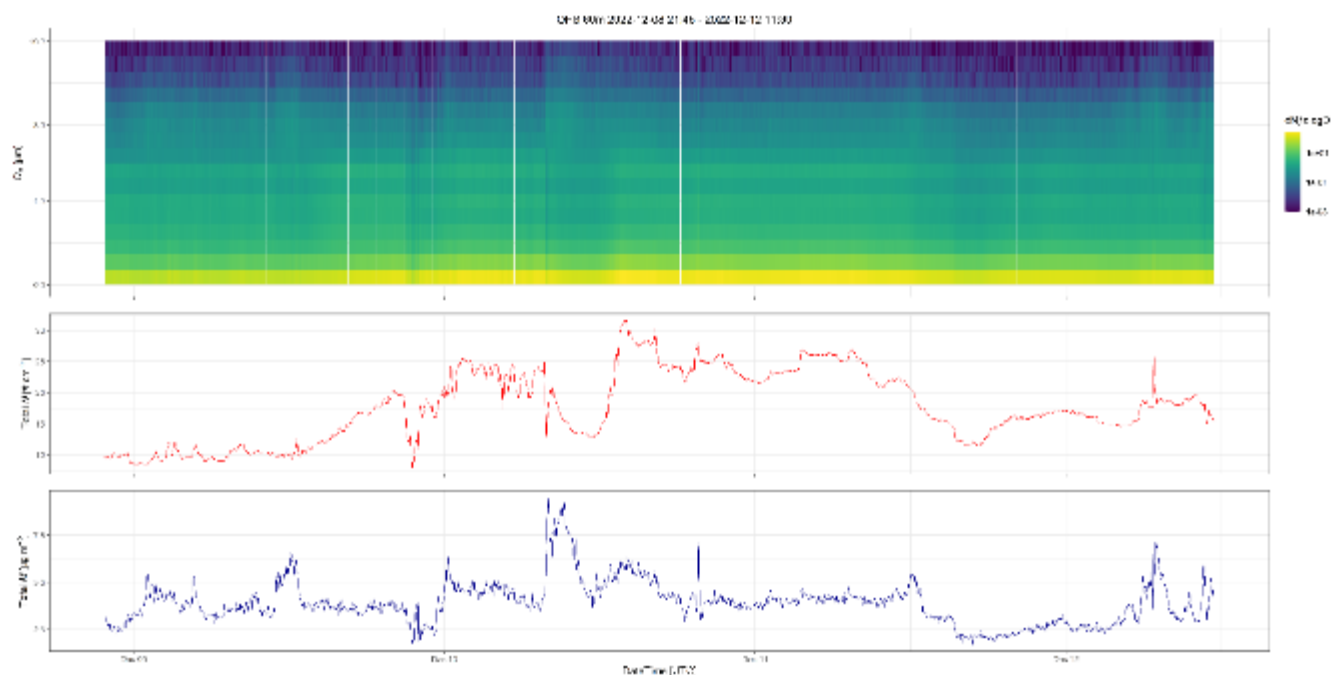


Figure S 11.2-7:Total particle number concentration N [$\# cm^{-3}$], total mass concentration M [$\mu g m^{-3}$], and particle number concentration per logarithmic particle diameter $dN/d \log D$ over the MOUDI sampling time period of case 2_2 at 60 m for particle diameters ranging from 300 nm to 10 μm , determined by OPS data.

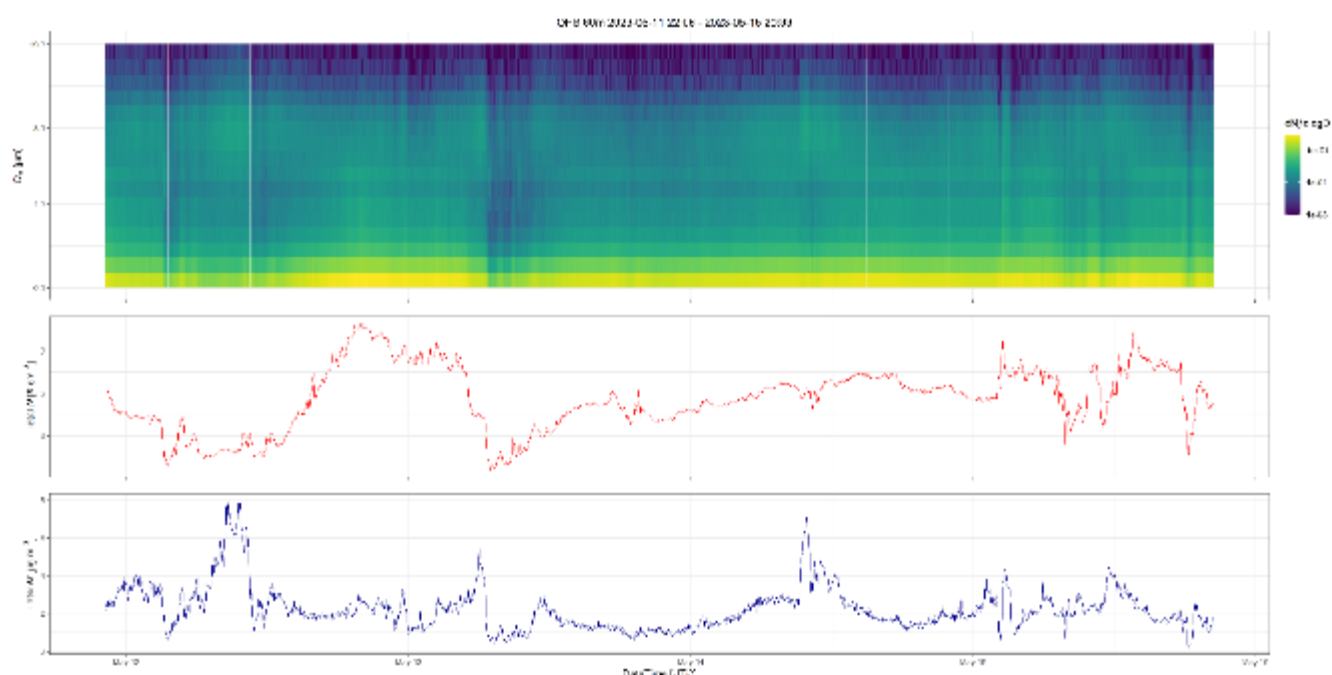


Figure S 11.2-8:Total particle number concentration N [$\# cm^{-3}$], total mass concentration M [$\mu g m^{-3}$], and particle number concentration per logarithmic particle diameter $dN/d \log D$ over the MOUDI sampling time period of case 2_3 at 60 m for particle diameters ranging from 300 nm to 10 μm , determined by OPS data.

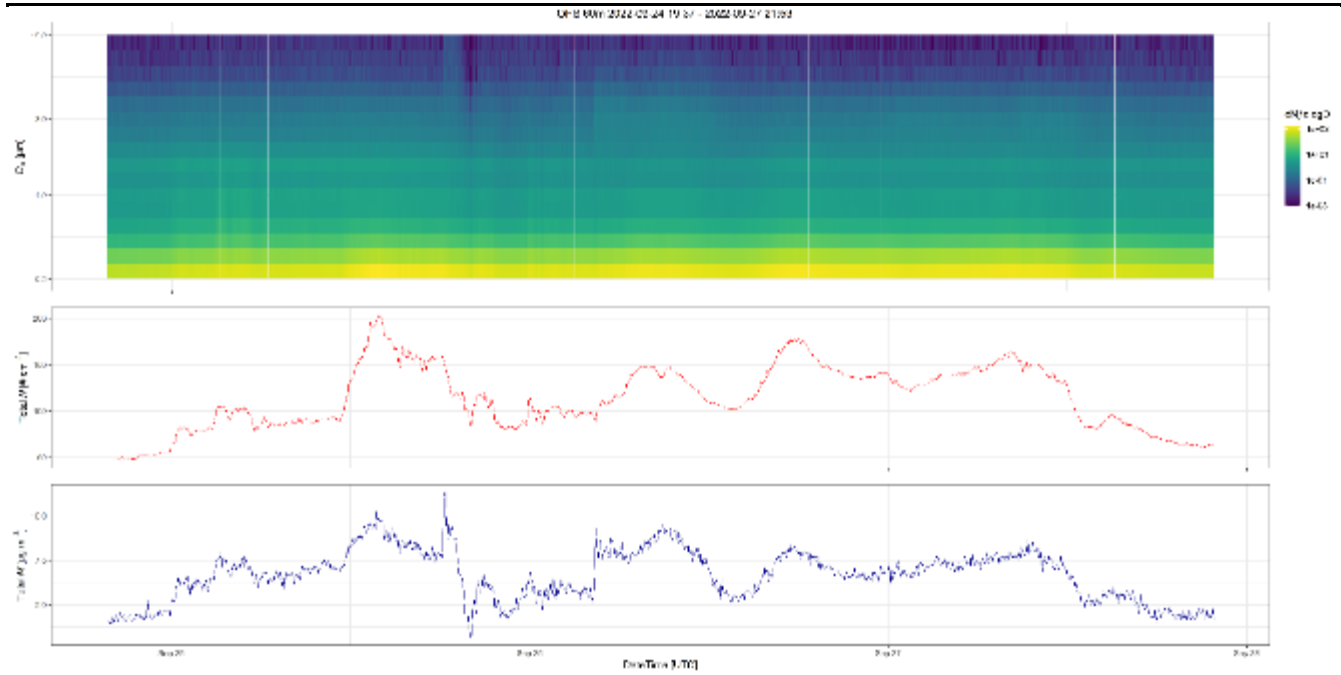


Figure S 11.2-9:: Total particle number concentration N [$\# cm^{-3}$], total mass concentration M [$\mu g m^{-3}$], and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 3_1 at 60 m for particle diameters ranging from 300 nm to 10 μm , determined by OPS data.

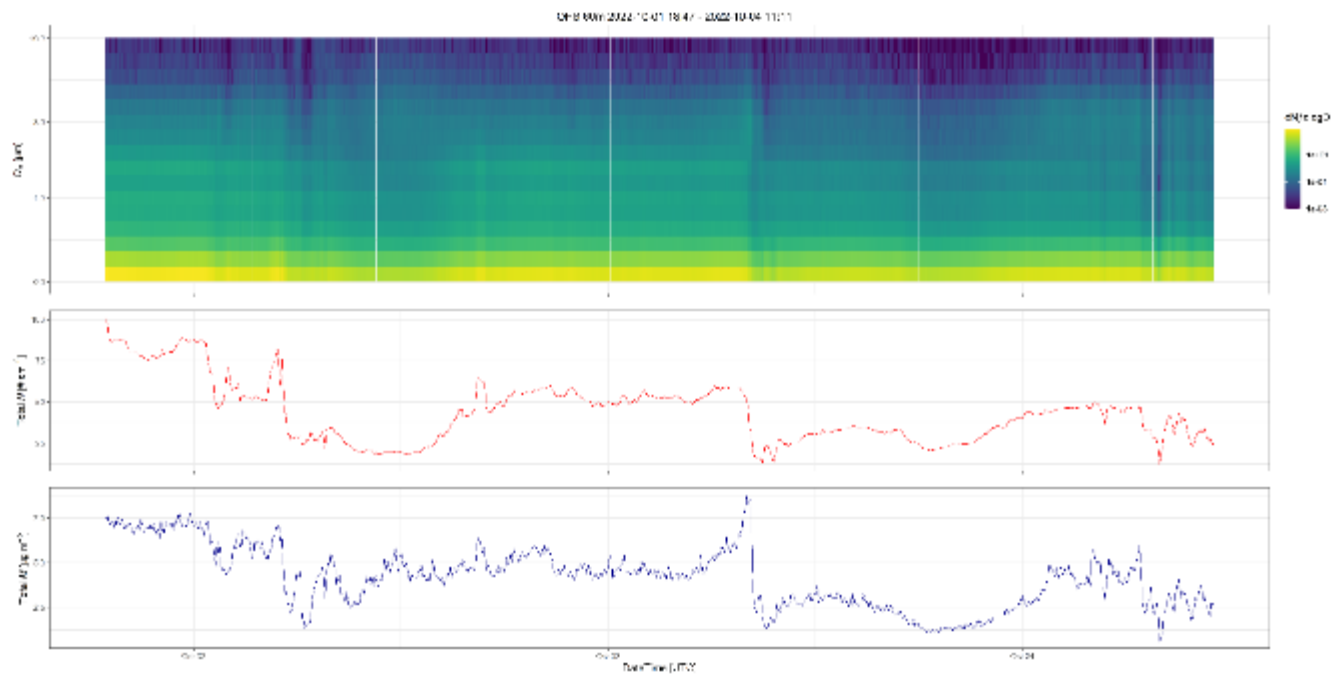


Figure S 11.2-10: Total particle number concentration N [$\# cm^{-3}$], total mass concentration M [$\mu g m^{-3}$], and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 3_2 at 60 m for particle diameters ranging from 300 nm to 10 μm , determined by OPS data.

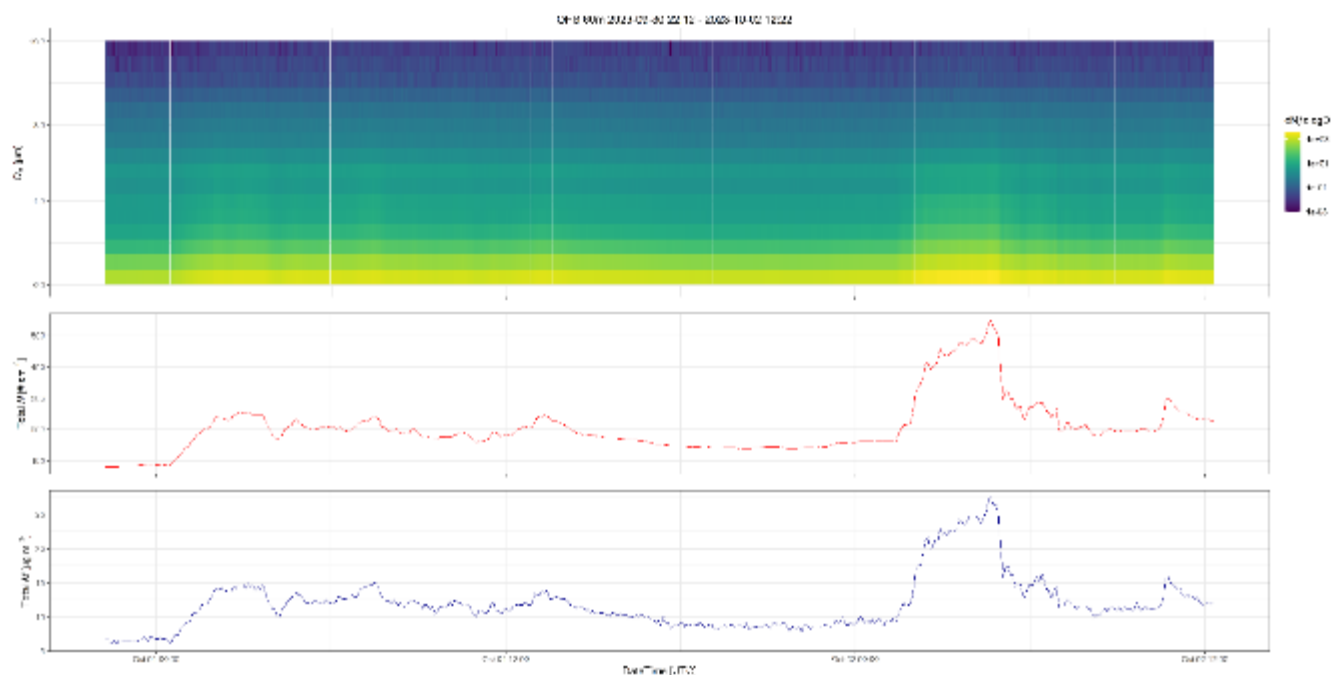


Figure S 11.2-11: Total particle number concentration N [# cm^{-3}], total mass concentration M [$\mu\text{g m}^{-3}$], and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 3_3 at 60 m for particle diameters ranging from 300 nm to 10 μm , determined by OPS data.

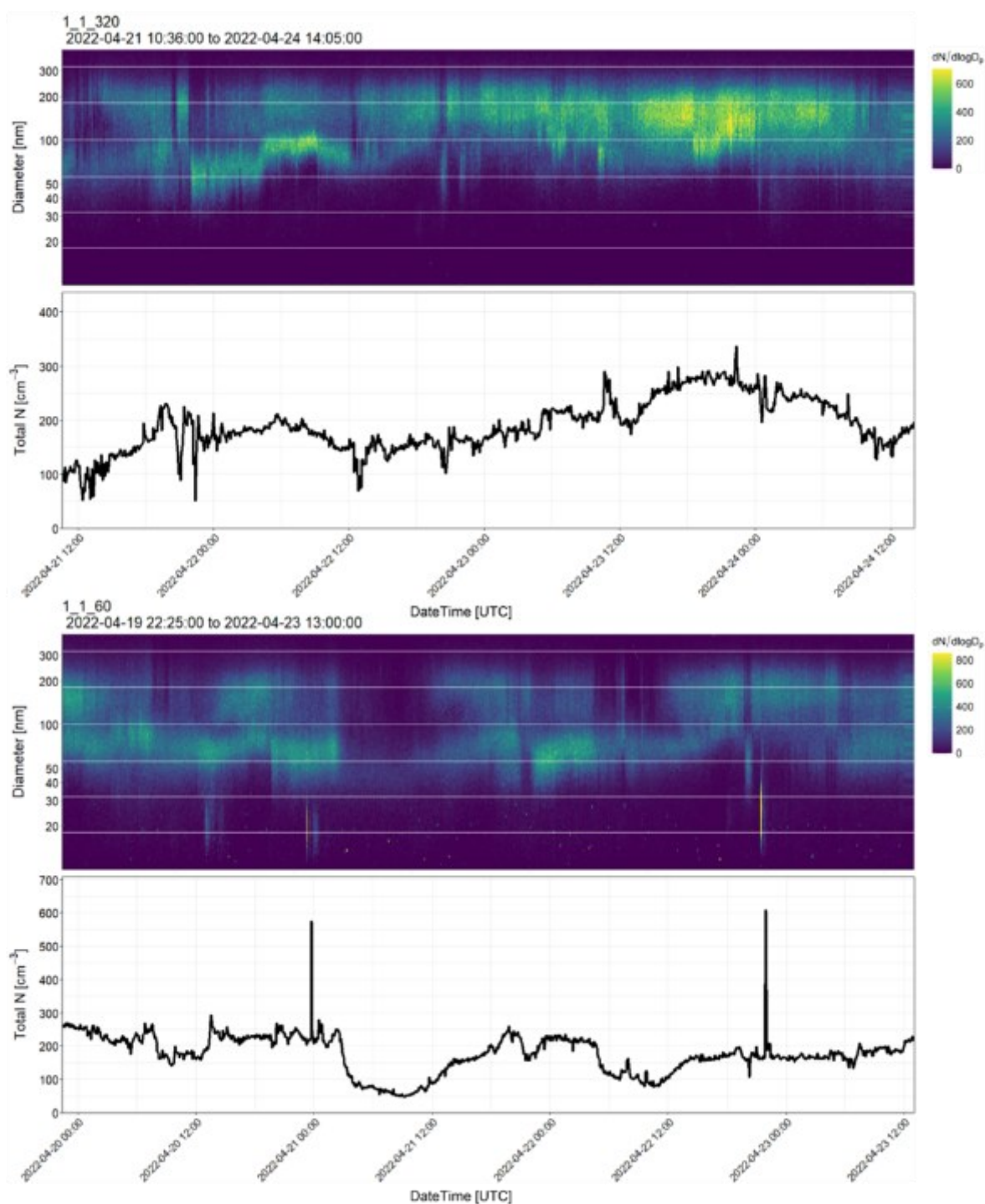


Figure S 11.2-12: Total particle number concentration N [$\# \text{ cm}^{-3}$] and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 1_1 at 60 m and 320 m for particle diameters ranging from 10 nm to 300 nm, determined by SMPS data. Periods during which the device malfunctioned were meticulously documented and subsequently filtered out.

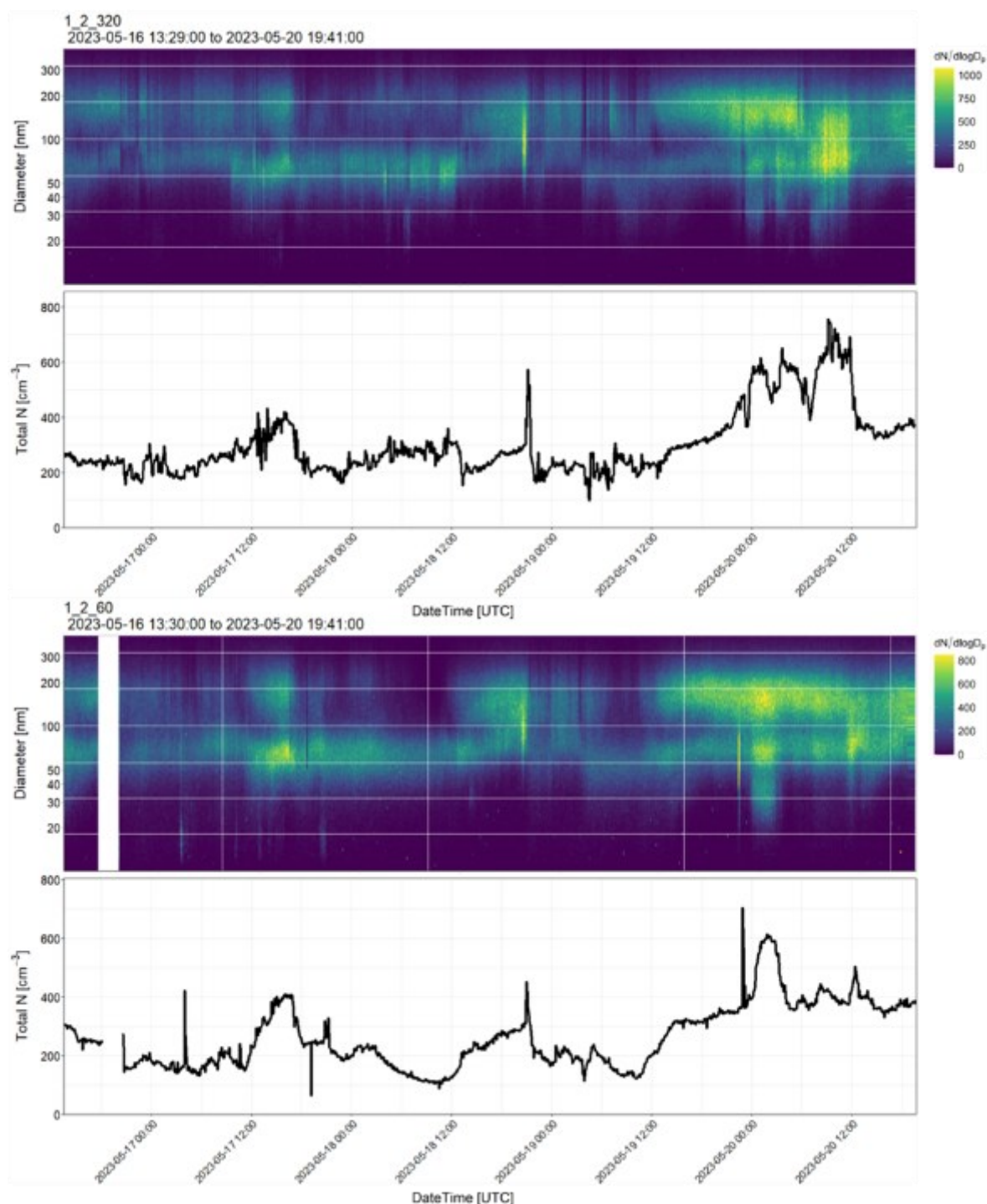


Figure S 11.2-13: Total particle number concentration N [# cm⁻³] and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 1_2 at 60 m and 320 m for particle diameters ranging from 10 nm to 300 nm, determined by SMPS data. Periods during which the device malfunctioned were meticulously documented and subsequently filtered out.

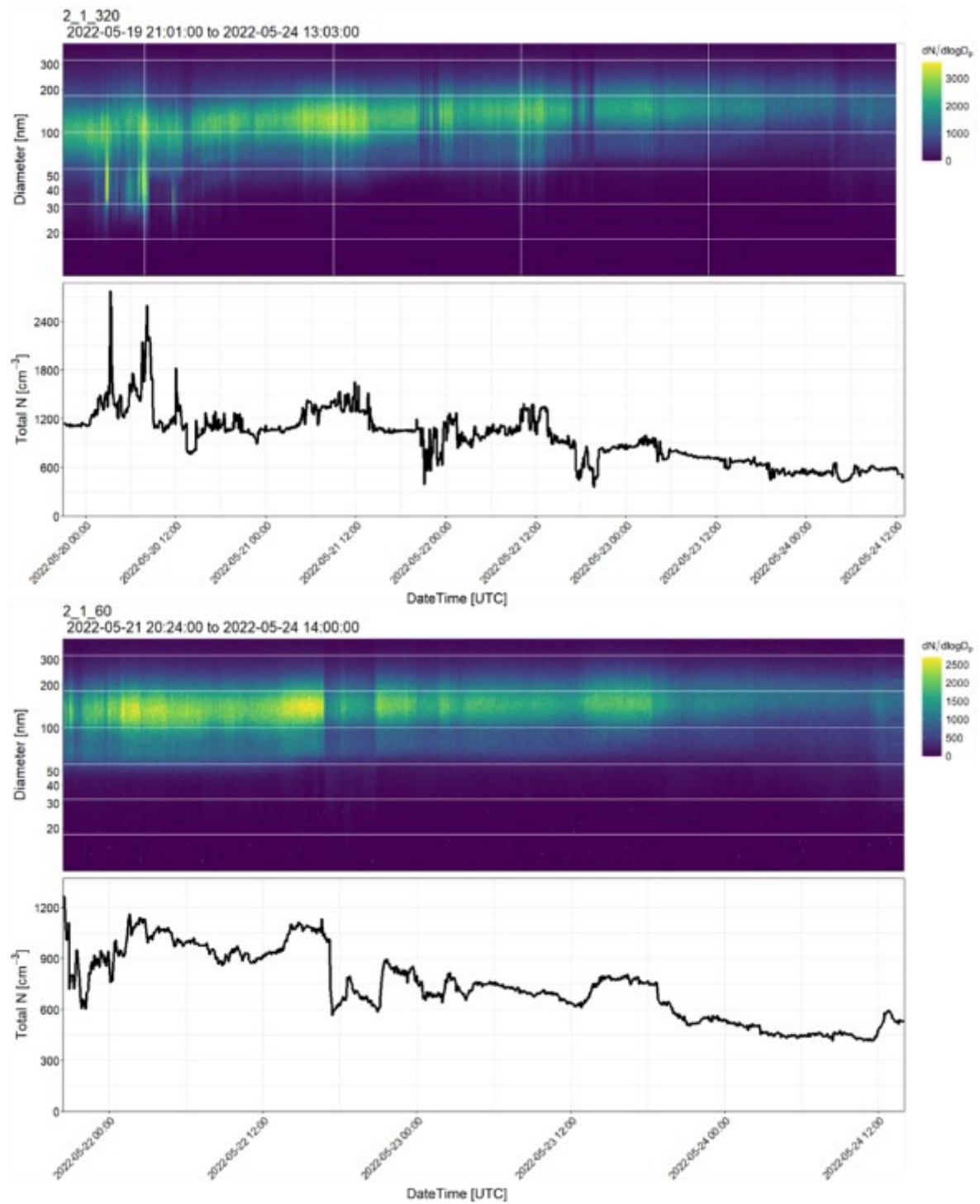


Figure S 11.2-14: Total particle number concentration N [$\# \text{ cm}^{-3}$] and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 2_1 at 60 m and 320 m for particle diameters ranging from 10 nm to 300 nm, determined by SMPS data. Periods during which the device malfunctioned were meticulously documented and subsequently filtered out.

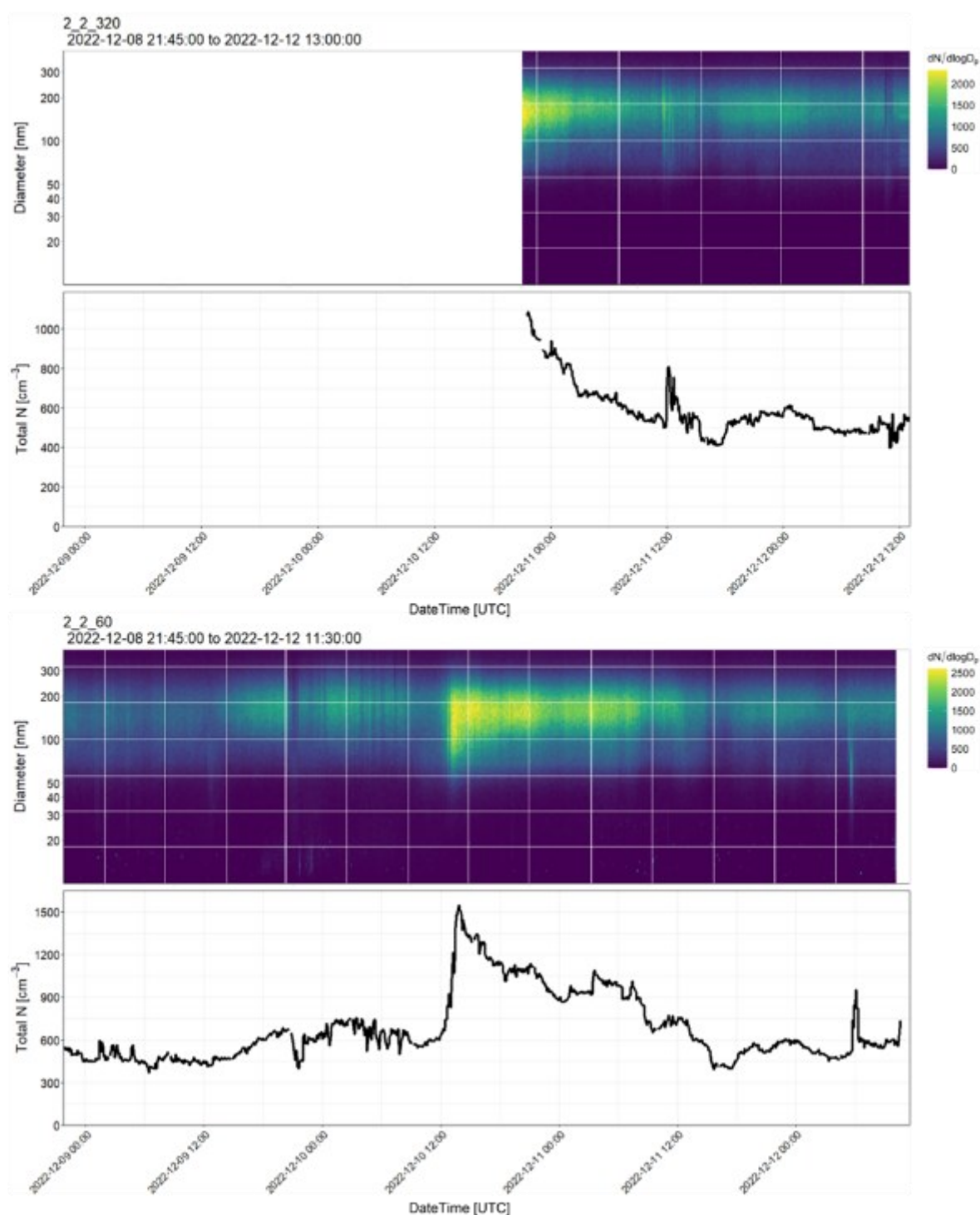


Figure S 11.2-15: Total particle number concentration N [cm^{-3}] and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 2_2 at 60 m and 320 m for particle diameters ranging from 10 nm to 300 nm, determined by SMPS data. Periods during which the device malfunctioned were meticulously documented and subsequently filtered out.

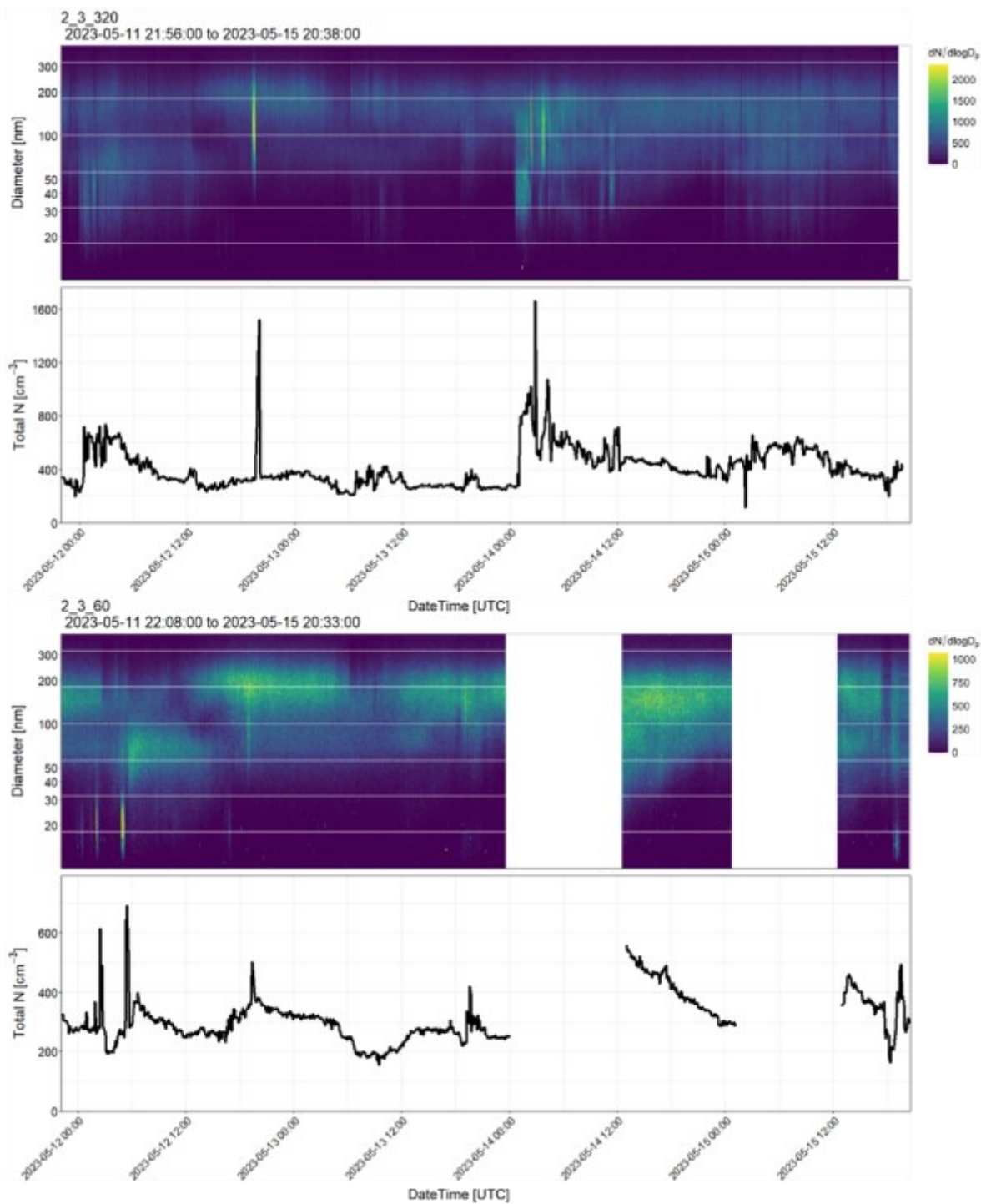


Figure S 11.2-16: Total particle number concentration N [$\# \text{ cm}^{-3}$] and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 2_3 at 60 m and 320 m for particle diameters ranging from 10 nm to 300 nm, determined by SMPS data. Periods during which the device malfunctioned were meticulously documented and subsequently filtered out.

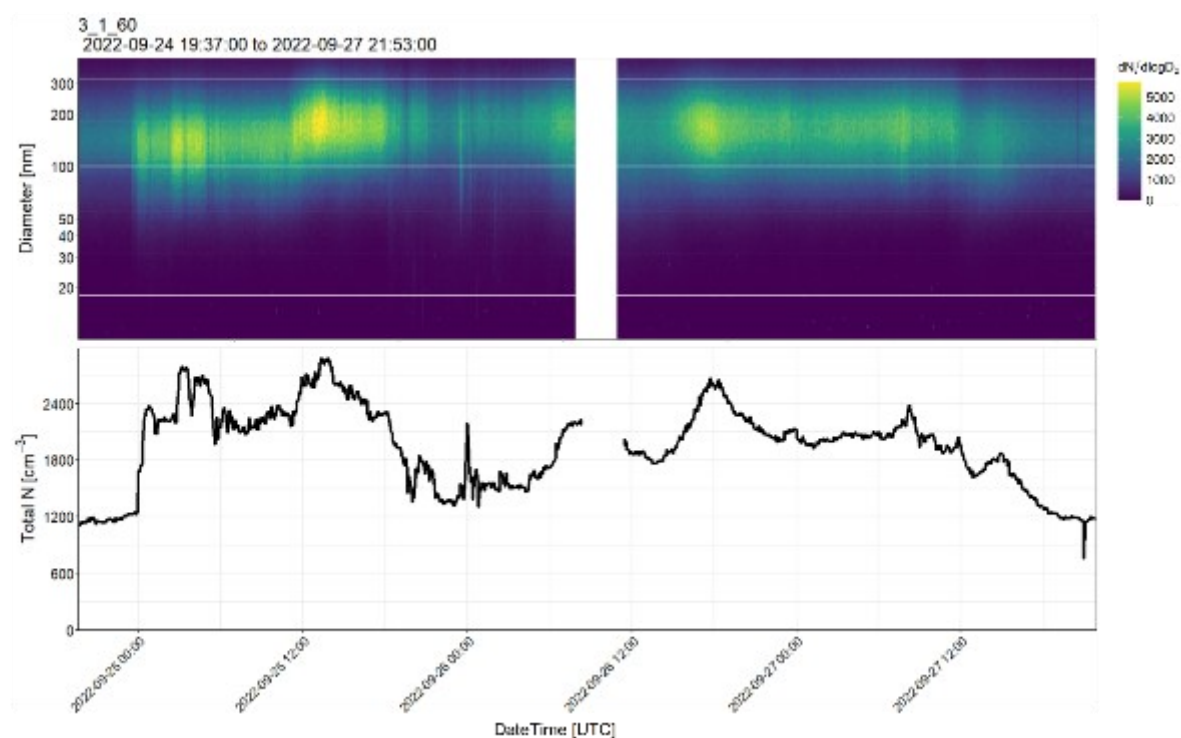


Figure S 11.2-17: Total particle number concentration N [cm^{-3}] and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 3_1 at 60 m for particle diameters ranging from 10 nm to 300 nm, determined by SMPS data. Periods during which the device malfunctioned were meticulously documented and subsequently filtered out (320 m data filtered out completely).

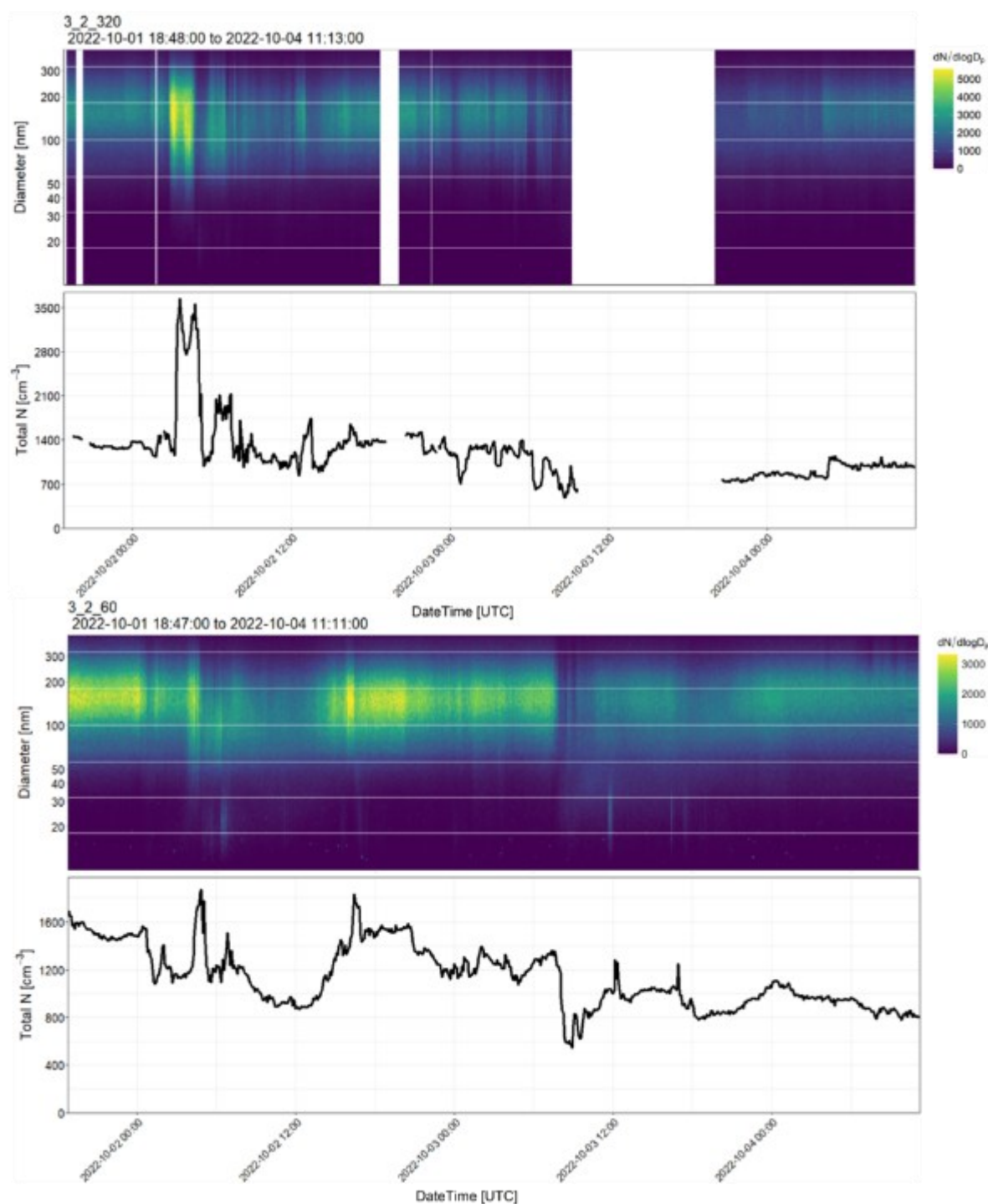


Figure S 11.2-18: Total particle number concentration N [$\# \text{ cm}^{-3}$] and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 3_2 at 60 m and 320 m for particle diameters ranging from 10 nm to 300 nm, determined by SMPS data. Periods during which the device malfunctioned were meticulously documented and subsequently filtered out.

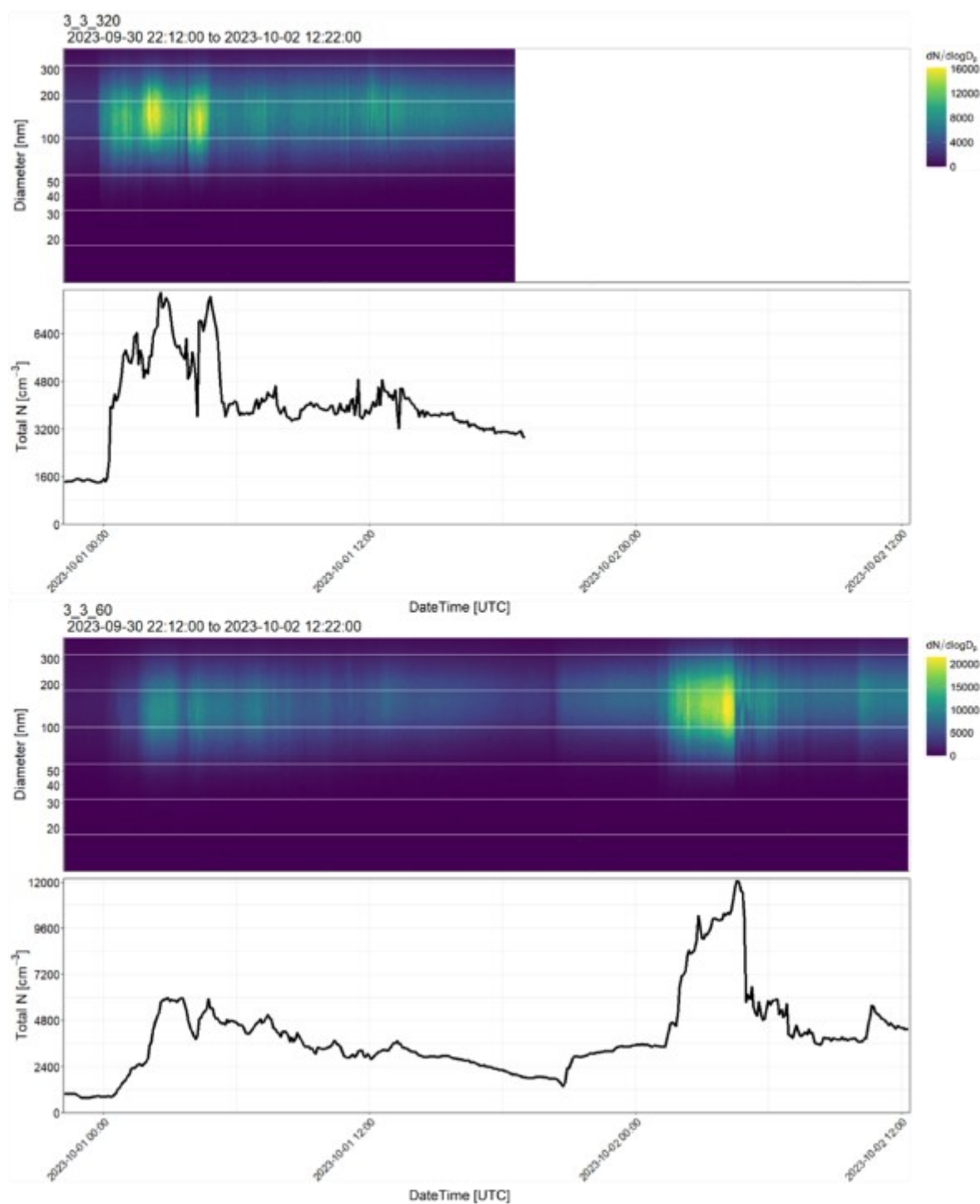


Figure S 11.2-19: Total particle number concentration N [$\# \text{ cm}^{-3}$] and particle number concentration per logarithmic particle diameter $dN/d\log D$ over the MOUDI sampling time period of case 3_3 at 60 m and 320 m for particle diameters ranging from 10 nm to 300 nm, determined by SMPS data. Periods during which the device malfunctioned were meticulously documented and subsequently filtered out.

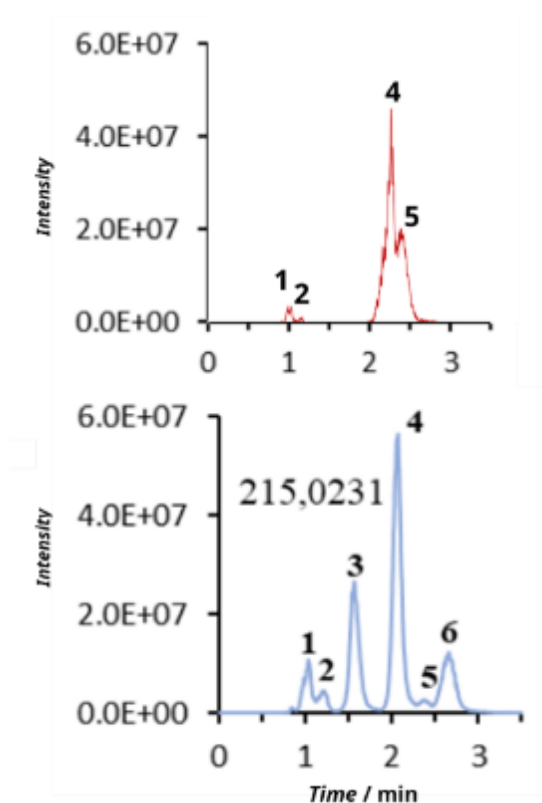


Figure S 11.2-20: Extracted ion chromatograms of OS-215 with $m/z = 215.0231$ in negative ionization mode using HILIC-ESI-HR-Orbitrap-MS. The upper panel shows the chromatogram of the in-house synthesized OS-215 standard, representing an isomeric mixture of 3-methyltetrol sulfate ester (peaks 4,5) and 2-methyltetrol sulfate ester (peak 1,2). The lower panel shows the chromatogram of OS-215 in an air sample of the Amazon rainforest, showing six different isomers, and having in common 4 of them with the authentic standard

11.3 Supplementary material chapter 5

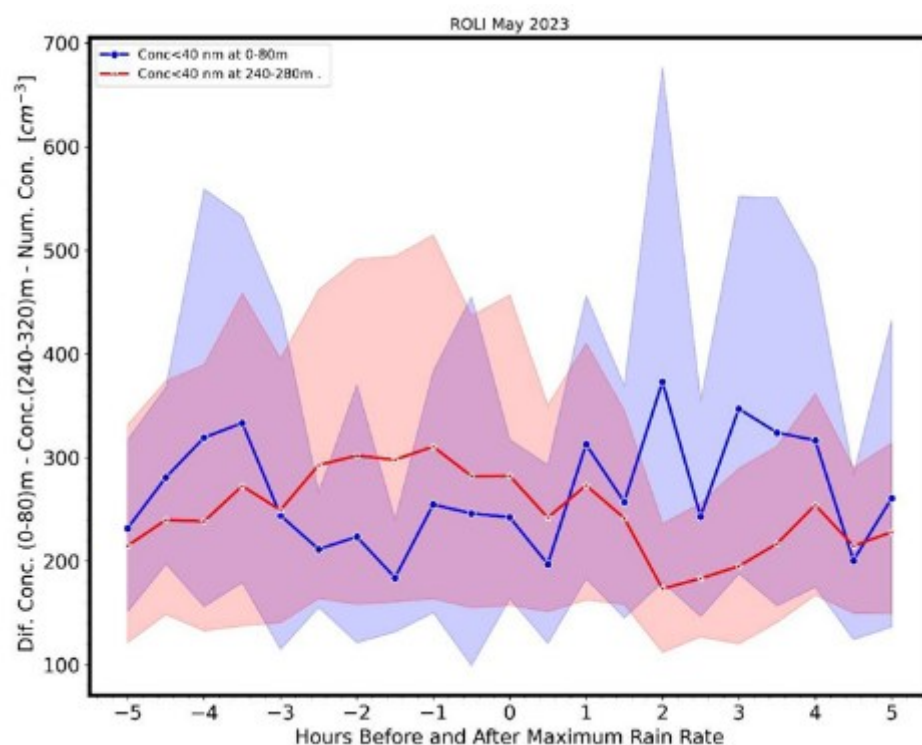


Figure S 11.3-1: Median concentration of particles with size smaller than 40 nm per cm^{-3} for ATTO in May 2023, measured by the elevator (ROLI), for the layer 0-80 m and 240-320 m, five hours before to five hours after the maximum rainfall event. The data was resampled to 30-minute time steps, which include one upward and one downward measurement. The 30-minute concentrations at (0-80 m) and (240-320 m) were analyzed as a function of the rainfall events (37 events) following the same methodology employed in the other composites. Shadow are 95% confidence intervals. The concentration of particles smaller than 40 nm near canopy is larger than at the upper levels after rain events.

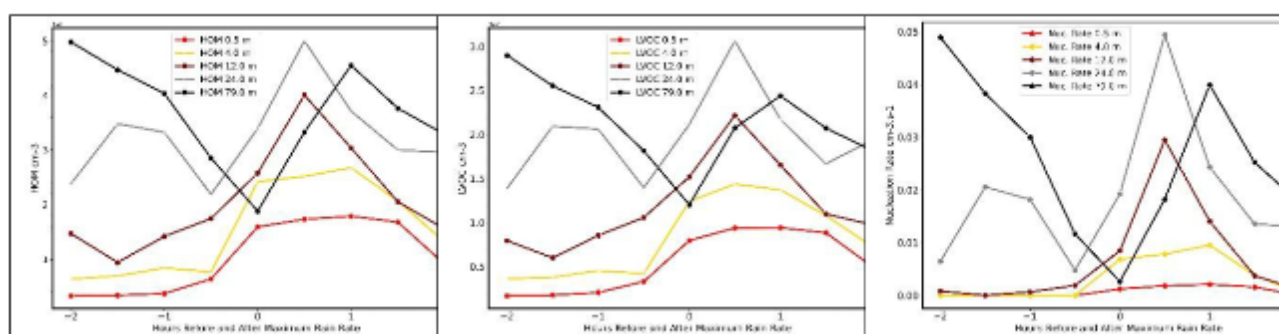


Figure S 11.3-2: Box Model Simulations for HOM, LVOC, and the pure biogenic nucleation rate for typical Amazonian wet season 2 hours before to 2 hours after rain events.

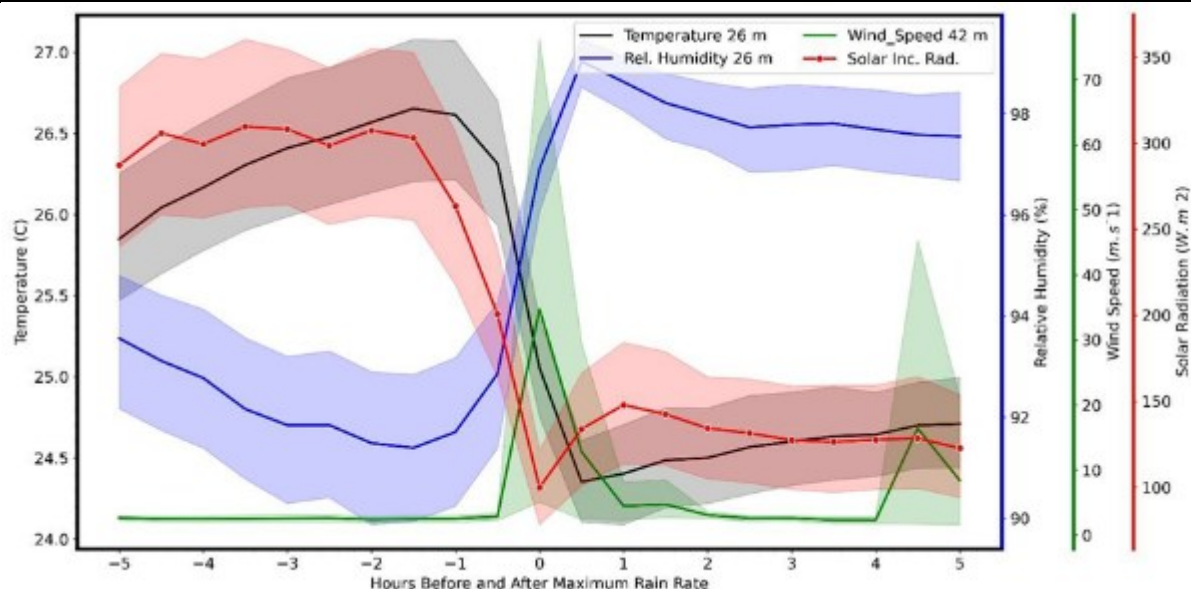


Figure S 11.3-3: Average and 95% confidence interval (Shadow) for air temperature, specific humidity at 26 m, wind speed at 4, and incoming solar radiation at 79 m, on the instant tower, between 2018-2020, February-May, five hours before to five hours after the maximum rainfall event. The data were averaged over 391 rain events with rain rates $>0.5 \text{ mm h}^{-1}$.

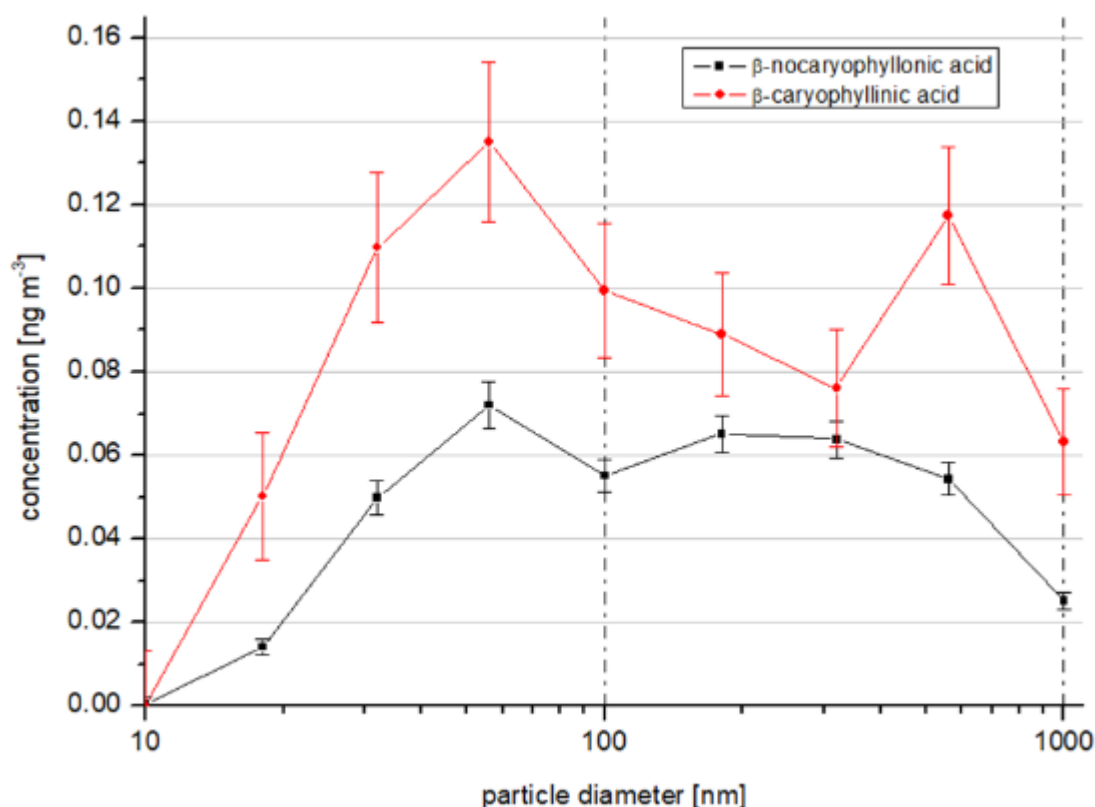


Figure S 11.3-4: Concentration profiles of β -nocaryophyllonic acid and β -caryophyllinic acid at 60 m heights during 5 days in May 2022 as a function of the particle size.

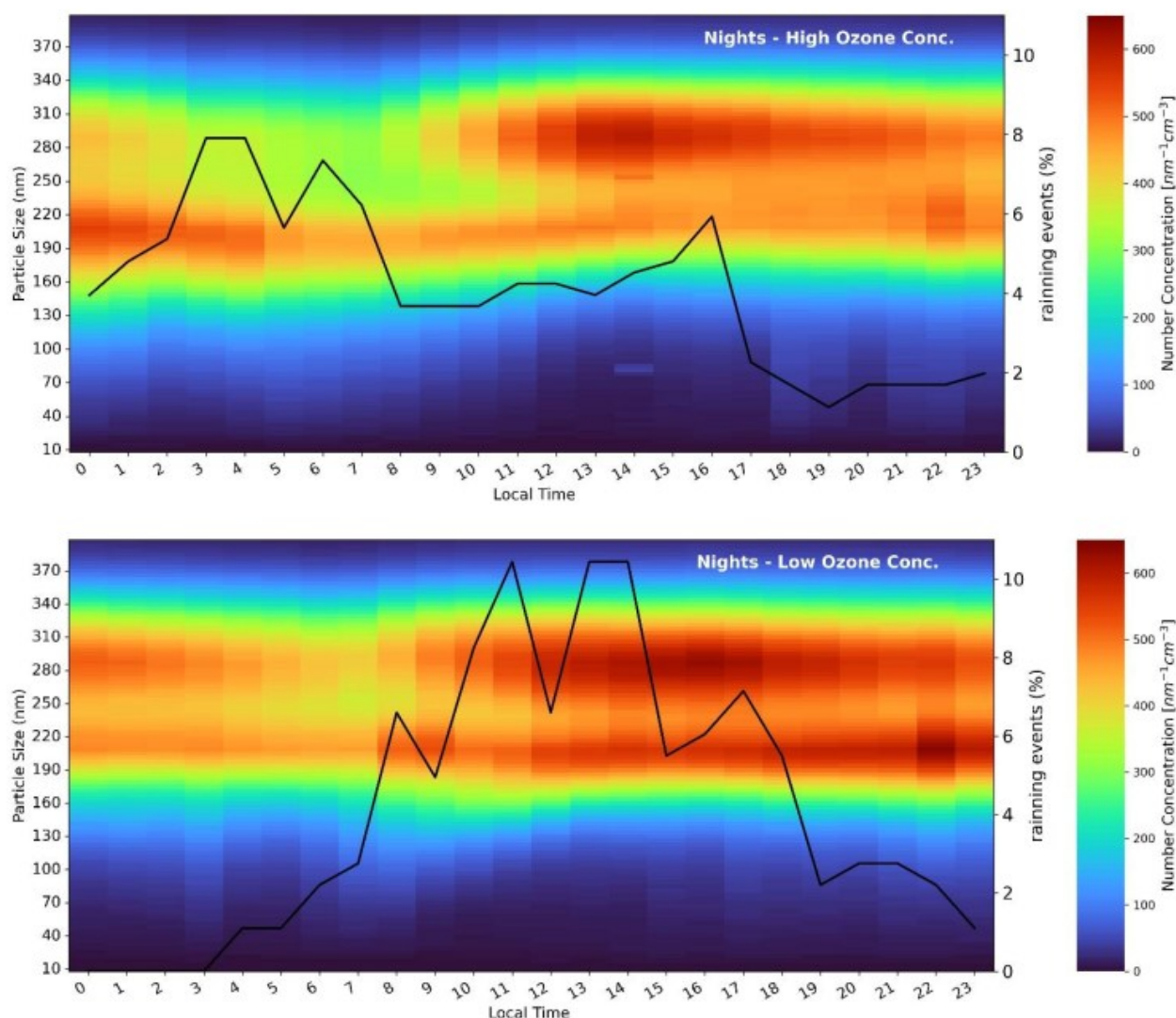


Figure S 11.3-5: Diurnal cycle of the particle size distribution at ATTO at 60 m during February to May 2018-2020, for (A) nights with O₃ concentration above the 75% quantile and (B) nighttime O₃ below the 25% quantile. The right axis shows the frequency of rain events each half hour. Nights with higher O₃ concentrations show a clear growth process beginning at sunrise and continuing up to early afternoon. The average were made with 85 days.

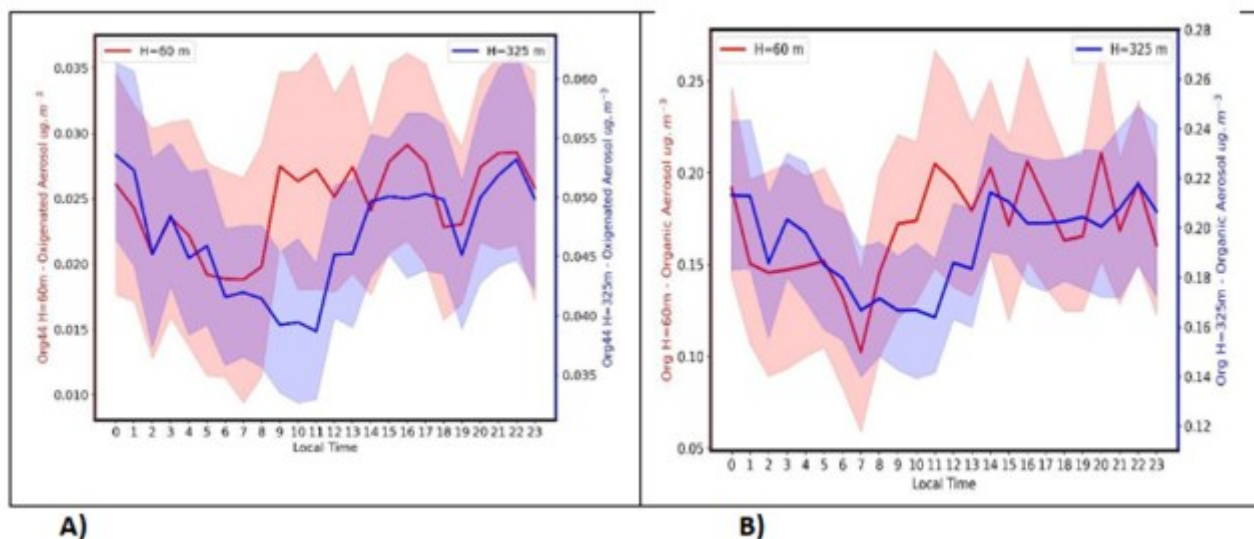


Figure S 11.3-6: Diurnal cycle of the A) mass concentration of oxygenated aerosol ($\mu\text{g m}^{-3}$) and B) the organic aerosol mass ($\mu\text{g m}^{-3}$) measured by ACSM at ATTO at 60 m and 325 m during February-May 2021 and 2022. The data was collected in a dedicated campaign and was not measured continuously. At 60 m, the oxygenated aerosol increases mass at sunrise; only 2-3 hours after this increase is observed at 325 m. The early increase in the mass of the oxygenated aerosol indicates a process occurring near the canopy before the turbulent mixing of the convective boundary layer.

11.4 Supplementary material chapter 6

Table S 11.4-1: Classification of DOM categories as described in Section 2.6 (Rivas-Ubach et al., 2018).

DOM categories	O/C	H/C	N/C	P/C	N/P
Lipid-like	≤ 0.6	≥ 1.32	≤ 0.126	< 0.35	≤ 5

Table S 11.4-2: Overview of intensity-weighted DOM parameters for all four research sites, separated for the individual nutrient pools of DOM. CHO-DOM = molecular formulas with only C, H and O assignment, N-DOM = molecular formulas with N-assignment, P-DOM = molecular formulas with P-assignment, S-DOM = molecular formulas with S-assignment. Number of samples (n): CD = 60, CW = 62, PL = 42, TE = 37. Site abbreviations: CD = *Campina*, CW = *Campinarana* (white-sand sites), PL = Plateau, TE = Terrace (*terra firme* sites).

Data subset	Site	Aromatic [%]	Aliphatic [%]	Lipid-like [%]	m/z [Da]	H/C ratio	O/C ratio	NOSC
All formulas	CD	48 ± 6.2	13 ± 4.0	5.2 ± 1.9	370 ± 10.2	0.89 ± 0.04	0.51 ± 0.02	0.23 ± 0.07
	CW	49 ± 5.5	14 ± 2.1	5.2 ± 1.4	370 ± 14.2	0.88 ± 0.03	0.51 ± 0.01	0.25 ± 0.03
	PL	6.8 ± 4.1	47 ± 5.8	21 ± 2.1	416 ± 14.6	1.18 ± 0.03	0.45 ± 0.02	-0.18 ± 0.07
	TE	15 ± 7.9	35 ± 6.3	14 ± 1.9	414 ± 19.2	1.10 ± 0.05	0.46 ± 0.01	-0.07 ± 0.08
CHO-DOM	CD	46 ± 6.4	14 ± 4.3	5.8 ± 2.0	381 ± 9.4	0.88 ± 0.04	0.51 ± 0.02	0.20 ± 0.07
	CW	47 ± 5.7	15 ± 2.3	5.8 ± 1.5	381 ± 13.0	0.88 ± 0.03	0.52 ± 0.01	0.22 ± 0.04
	PL	4.5 ± 3.5	49 ± 6.1	22 ± 2.2	427 ± 10.6	1.18 ± 0.03	0.46 ± 0.02	-0.22 ± 0.07
	TE	12 ± 7.2	38 ± 6.4	15 ± 1.9	430 ± 15.5	1.11 ± 0.05	0.47 ± 0.01	-0.11 ± 0.08
N-DOM	CD	63 ± 3.6	6.6 ± 1.0	0.6 ± 0.2	278 ± 13.6	0.88 ± 0.02	0.44 ± 0.02	0.5 ± 0.05
	CW	65 ± 3.8	6.4 ± 1.5	0.7 ± 0.3	278 ± 17.1	0.87 ± 0.02	0.44 ± 0.02	0.52 ± 0.05
	PL	27 ± 7.6	24 ± 4.8	5.4 ± 1.5	340 ± 31.4	1.07 ± 0.03	0.41 ± 0.02	0.11 ± 0.05
	TE	35 ± 11.0	16 ± 4.2	2.6 ± 1.0	327 ± 32.9	1.01 ± 0.04	0.40 ± 0.02	0.18 ± 0.06

P-DOM	CD	30 ± 3.1	0.2 ± 0.6	0.2 ± 0.6	410 ± 13.1	1.61 ± 0.07	0.73 ± 0.03	-0.78 ± 0.06
	CW	32 ± 3.0	0.1 ± 0.2	0.1 ± 0.2	417 ± 13.8	1.57 ± 0.07	0.71 ± 0.03	-0.73 ± 0.06
	PL	10 ± 6.2	37 ± 22.2	23 ± 18.7	471 ± 22.2	1.27 ± 0.1	0.43 ± 0.04	-0.62 ± 0.11
	TE	17 ± 6.8	12 ± 13.5	7.5 ± 9.6	476 ± 19.5	1.35 ± 0.1	0.50 ± 0.09	-0.65 ± 0.05
S-DOM	CD	56 ± 3.1	6.6 ± 0.6	4.2 ± 0.6	448 ± 13.1	0.95 ± 0.07	0.37 ± 0.03	-0.12 ± 0.06
	CW	60 ± 3.0	4.5 ± 0.2	2.6 ± 0.2	457 ± 13.8	0.92 ± 0.07	0.37 ± 0.03	-0.11 ± 0.06
	PL	2.0 ± 6.2	78 ± 22.2	58 ± 18.7	409 ± 22.2	1.37 ± 0.1	0.47 ± 0.04	-0.27 ± 0.11
	TE	2.2 ± 6.8	74 ± 13.5	45 ± 9.6	428 ± 19.5	1.31 ± 0.1	0.48 ± 0.09	-0.18 ± 0.05

Table S 11.4-3: Overview of intensity-weighted DOM parameters for groundwater data of plateau (*terra firme*) and *Campina* (white-sand) sites from (Simon et al., 2021) (piezometers, sampling depth < 2 m). Number of samples (n): *Campina* = 5, Plateau = 2.

Data subset	Site	Aromatic [%]	Aliphatic [%]	Lipid-like [%]	m/z [Da]	H/C ratio	O/C ratio	NOSC
All formulas	<i>Campina</i>	35 ± 2.2	21 ± 1.4	7.7 ± 1.0	427 ± 4.0	1.0 ± 0.02	0.50 ± 0.01	0.11 ± 0.03
	Plateau	3.3 ± 1.2	63 ± 2.0	27 ± 2.7	418 ± 20.5	1.2 ± 0.02	0.39 ± 0.02	-0.36 ± 0.01

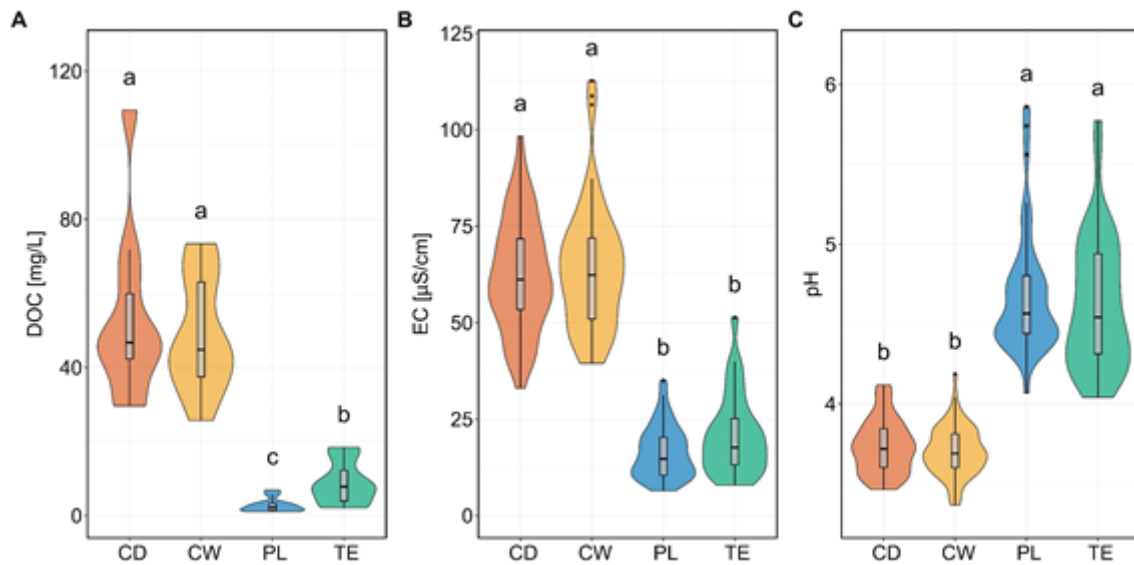


Figure S 11.4-1: Water chemistry of all research sites. DOC (dissolved organic carbon in mg/L; A), EC (electrical conductivity in $\mu\text{S/cm}$, B) and pH (C). Letters indicate significant differences between the sites (Kruskal Wallis test, $p < 0.05$). CD = *Campina*, CW = *Campinarana* (white-sand sites), PL = Plateau, TE = Terrace (*terra firme* sites).

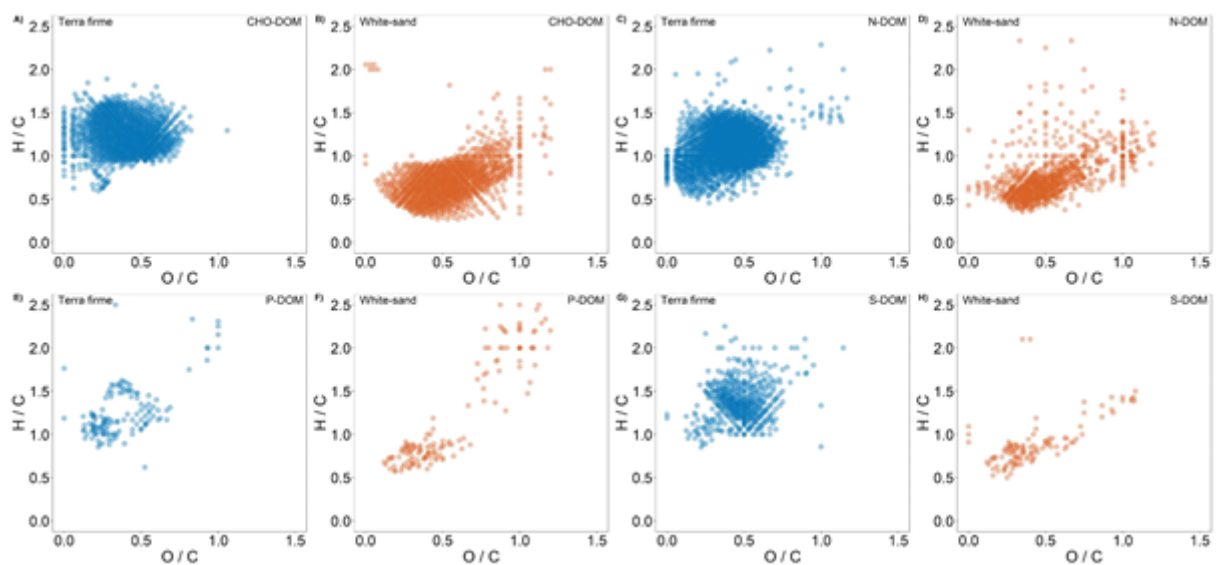


Figure S 11.4-2: Molecular formulas that were significantly enriched in DOM of *terra firme* or white-sand sites (Spearman's rank correlation based on relative ion intensities, $p < 0.05$). *Terra firme* markers include formulas that correlated with the ecosystem type (*terra firme*) and the sites (PL or TE), white-sand markers include formulas that correlated with the ecosystem type (white-sand) and the sites (CD or CW). Data are displayed for DOM pools: CHO-DOM (molecular formulas with only C, H and O assigned; A and B), N-DOM (molecular formulas that contain N; C and D), P-DOM (molecular formulas that contain P; E and F) and S-DOM (molecular formulas that contain S, G and H). Hydrogen / carbon (H/C) and oxygen / carbon (O/C) ratios are depicted for the individual pools of DOM.

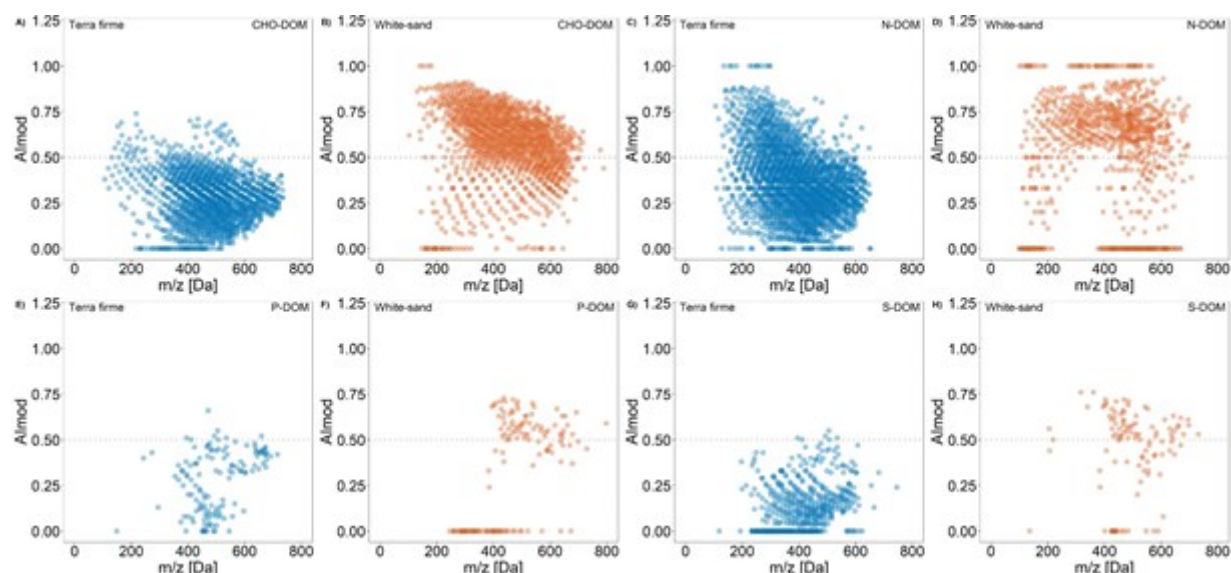


Figure S 11.4-3: Molecular formulas that were significantly enriched in DOM of *terra firme* or white-sand sites (Spearman's rank correlation based on relative ion intensities, $p < 0.05$). *Terra firme* markers include formulas that correlated with the ecosystem type (*terra firme*) and the sites (PL or TE), white-sand markers include formulas that correlated with the ecosystem type (white-sand) and the sites (CD or CW). Data are displayed for DOM pools: CHO-DOM (molecular formulas with only C, H and O assigned; A and B), N-DOM (molecular formulas that contain N; C and D), P-DOM (molecular formulas that contain P; E and F) and S-DOM (molecular formulas that contain S, G and H). The mass to charge ratio (m/z) and the modified aromaticity index (Al_{mod}) are depicted for the individual pools of DOM. Al_{mod} values >0.5 indicate aromatic compounds.

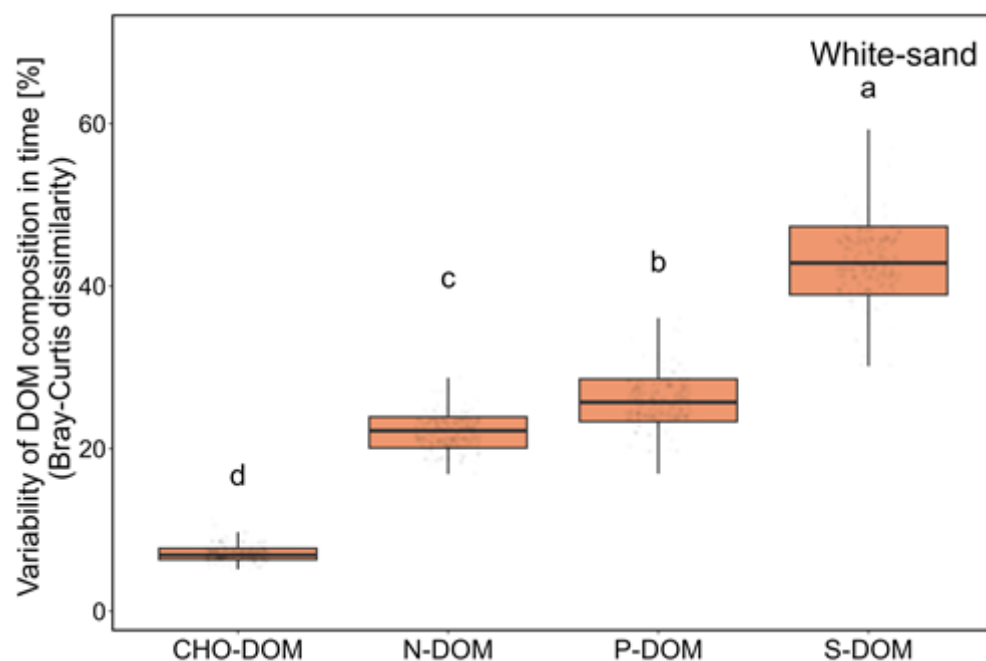


Figure S 11.4-4: Temporal variability of the DOM composition in % for 0 cm soil depth in white-sand sites, calculated as Bray-Curtis dissimilarity between all replicate samplings of the same site in 0 cm soil depth compared against each other. Data are displayed for DOM pools: CHO-DOM (molecular formulas with only C, H and O assigned), N-DOM (molecular formulas that contain N), P-DOM (molecular formulas that contain P) and S-DOM (molecular formulas that contain S). Letters indicate significant differences between the DOM pools (Kruskal Wallis test, $p < 0.05$).

Supporting Text S1. Additional information on molecular formula assignment and data processing

Masses were first aligned across all spectra using the fast join algorithm with 0.4 ppm tolerance. Then blank correction was performed before molecular formula assignment by removing peaks from the aligned mass list that comprised the top 95% of relative ion intensity in each blank. We applied the “NSP rule” to exclude unlikely formulas (formulas with the following elemental combinations: $N > 1$ and $(S + P) > 0$; $N = 1$ and $S \geq 1$ and $P \geq 1$; $S + P > 2$; $N = 1$ and S or $P > 1$) (Merder et al., 2020). Formulas that occurred in less than 3 samples were not considered. Lastly, a quality check was performed to identify false assignments of ^{31}P due to potential ambiguity with assignment of ^{35}Cl instead of ^{31}P . This was tested by a secondary formula assignment process. Molecular formulas were assigned to the same data with the same specifications as described above, but additionally chlorine was allowed (^{35}Cl 0-2). The second assignment was used to identify which of the original masses assigned P displayed formula assignment with Cl in the secondary assignment process. This was the case for 9 masses that were subsequently removed from the original data because of ambiguous assignments. The data from the secondary assignment were only used as quality control to remove ambiguous P assignments from the original data.

Based on the molecular formula data, the following DOM parameters were calculated for each molecular formula: hydrogen to carbon ratio (H/C), oxygen to carbon ratio (O/C), nitrogen to carbon ratio (N/C), phosphorus to carbon ratio (P/C), sulfur to carbon ratio (S/C), modified aromaticity index (AI_{mod}) (Koch & Dittmar, 2006, 2016) and the nominal oxidation state of carbon (NOSC) (Boye et al., 2017). Molecular subgroups were assigned as follows (Riedel et al., 2016): “Aromatic” compounds ($\text{AI}_{\text{mod}} \geq 0.5$) include polyphenolic and condensed aromatic structures as well as polycyclic condensed aromatics. “Highly unsaturated” compounds are non-aromatic but can contain phenols with aliphatic side-chains ($\text{AI}_{\text{mod}} < 0.5$, $\text{H/C} < 1.5$) and “aliphatic” formulas were defined as $\text{H/C} > 1.2$ and $\text{O/C} < 0.6$ (Khatami et al., 2019). The DOM category “lipid-like” was assigned based on O/C, H/C, N/C, P/C, and N/P ratios (Rivas-Ubach et al., 2018); see supplementary Table S1 for detailed specifications).

Supporting Text S2. Annotation of molecular formulas in ChEBI database

The groundwater samples from similar *terra firme* plateau and white-sand forest sites (Simon et al., 2021) were used to define compounds that were probable to be microorganism-derived. We set the conditions that formulas 1) must occur simultaneously in *terra firme* DOM of 30 cm soil depth and the plateau groundwater DOM, and 2) must not occur in *terra firme* DOM of 5 cm soil depth, because the latter were more likely to be derived from plant matter. The molecular formulas that were kept after applying these conditions were matched with the ChEBI database to characterize molecular entities using structural suggestions (Hastings et al., 2016) (“get_chebiid” function, “webchem” 1.2.0). The level “kingdom” was thereby excluded because it yields very broad classifications.

The compounds that were defined as probable to be microbially derived yielded 103 markers for N-DOM, 30 for S-DOM and 8 for P-DOM in the *terra firme* sites (see Online Resource 2 for list of the markers and database annotations). The chemical and ChEBI annotation-based characterization of the microbial markers supported the findings of a greater contribution of aliphatic and lipid-like compounds in the deeper soil and groundwater of *terra firme* forests. None of the N-containing markers were classified as aromatic, 81 as aliphatic and 55 as lipid-like. 51 N-formulas were annotated using the ChEBI database. Of these, 27 were classified in categories related to amino groups, such as peptides, amino acids and derivatives,

aminoglycosides or acylaminobenzoic acid and derivatives. For S-DOM, 21 of the 30 markers were aliphatic and lipid-like and none were aromatic. Nine of them were annotated in ChEBI. One was annotated in amino acid-related categories such as amino acids and derivatives. Others were categorized as sulfated steroids, benzenesulfonamides or broader as organosulfonic acids, phenylsulfate or benzenesulfonic acids and derivatives. None of the P-DOM markers were annotated in the ChEBI database. No P-DOM marker was classified as aromatic, and seven of the eight were classified as aliphatic and lipid-like. In the white-sand sites, slightly fewer microbial markers were found, with 75 for N-DOM, 23 for S-DOM and 14 for P-DOM. The chemical characterization and ChEBI annotations of these markers also aligned with the findings that white-sand DOM was less aliphatic and lipid-like than those *terra firme* DOM. The microbial markers in white-sand sites were generally more aromatic and less aliphatic than in the *terra firme* sites, and ChEBI annotations were much fewer. 34 of 75 N-containing markers were classified as aromatic, and none as aliphatic or lipid-like. Only one was annotated in ChEBI as a tetracycline and phenylpropanoid. Five of the S-containing markers were aromatic and only two were aliphatic and lipid-like. Two of them were annotated in flavonoid and phenylpropanoid categories. Also in white-sand sites, none of the P-containing microbial markers were annotated in ChEBI. Six of them were aromatic, and none of them were aliphatic or lipid-like.

The chemical characterization and ChEBI database annotation of probable microorganism-derived markers supported our findings of a higher degree of DOM processing in *terra firme* soils. Microbial markers in *terra firme* sites reflected a microbial processing signature with abundant aliphatic and lipid-like and no aromatic compounds in all nutrient pools. ChEBI annotations yielded many classifications in amino group-related categories, which supports the notion of a high microbial contribution to DOM in deeper soils because amino- and peptide-related compounds are more abundant in microbial biomass than in plant matter. The white-sand microbial markers reflected a more ambiguous signature and were more aromatic and less aliphatic or lipid-like compared to *terra firme* sites. This suggests that the compounds occurring in deeper soil solution and the white-sand groundwater were still less microorganism-derived than in *terra firme* soils, and that DOM was overall less processed. However, the low fraction of markers with ChEBI annotation shows that most of the compounds found in DOM are not yet covered in chemical libraries (Simon et al., 2022).

Supporting Text S3. Supporting data on soil volatile organic compounds

Volatile organic compounds (VOCs) were sampled from soil at two sites: a white-sand (CW, *Campinarana*) and a *terra firme* site (TE, Terrace). Sampling employed a VOC-Mole soil probe (Markes International) with a pre-conditioned sorption tube. Following a 15-minute adjustment period, soil gas was pumped into the sorption tube for 10 minutes. VOCs were measured with thermal desorption coupled with gas chromatography-mass spectrometry (Thermo Scientific Trace GC 1610, Orbitrap Exploris 60). Mass spectrometric measurements were performed in full-scan mode with electron impact ionization and a mass accuracy of 10 ppm. Untargeted data analysis and molecular formula assignment were performed using MzMine 3.9.0 and PyCharm V5, considering the elements C, H, O, N, S, P, Cl, Br, and F.

CHO and CH compounds were the most abundant groups at both sites, comprising 57% and 84% of total signal intensity in CW and TE, respectively (Table S4). The CW site exhibited a high proportion (38%) of compounds without formula assignment. CHON compounds were the third most abundant category with formula assignment in both sites. CHOS and CHONS compounds were detected at both locations, while CHS formulas were absent. S-containing

species showed ~2.5-fold higher intensities in the CW site, accounting for 2% of all detected compounds. CHOS species exhibited 7-fold higher intensities in the CW, whereas CHONS peaks were slightly more abundant in the TE. Compounds with P-assignment were extremely low abundant in both sites.

Table S 11.4-4: Signal intensities (%) of DOM groups based on molecular formula assignment of soil VOC (volatile organic compound) samples.

	<i>Campinarana</i> (CW)	Terrace (TE)		<i>Campinarana</i> (CW)	Terrace (TE)
DOM group	% signal intensity	% signal intensity	DOM group	% signal intensity	% signal intensity
CHBr	0.1	0.0	CHON	2.4	1.5
CHCl	0.1	0.0	CHOS	1.6	0.2
CHF	0.1	0.0	CHOP	0.0	0.0
CHN	0.9	0.3	CHONS	0.4	0.6
CHS	0.0	0.0	CHONP	0.0	0.0
CHP	0.0	0.0	CH	26	41
CHO	31	43	Other	38	13

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11.5 Supplementary material chapter 7

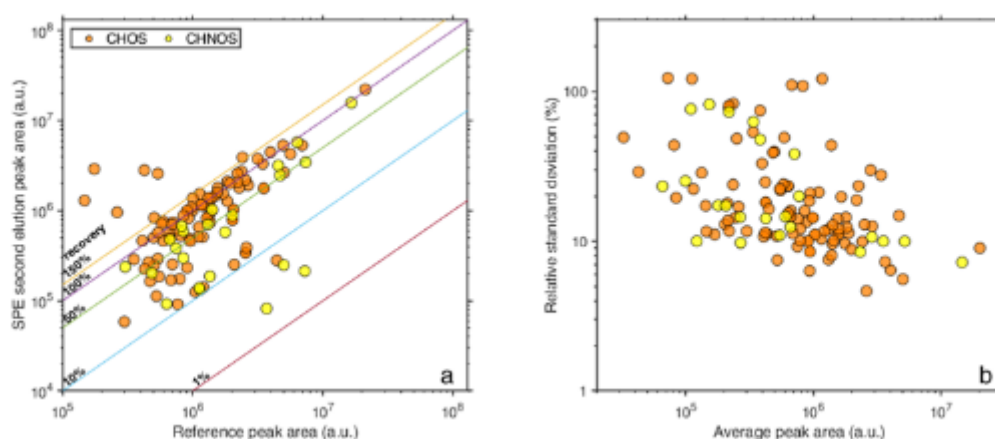


Figure S 11.5-1: Evaluation of the SPE isolation recovery (a) and reproducibility (b) for individual compounds using a PM2.5 filter extract from Handan (18.10.2018, daytime). We measure the all of the native extract, first SPE elution, second SPE elution, and flow through of Handan 1 (18.10.2018, daytime) in triplicated to evaluate the relative standard deviation of the SPE method.

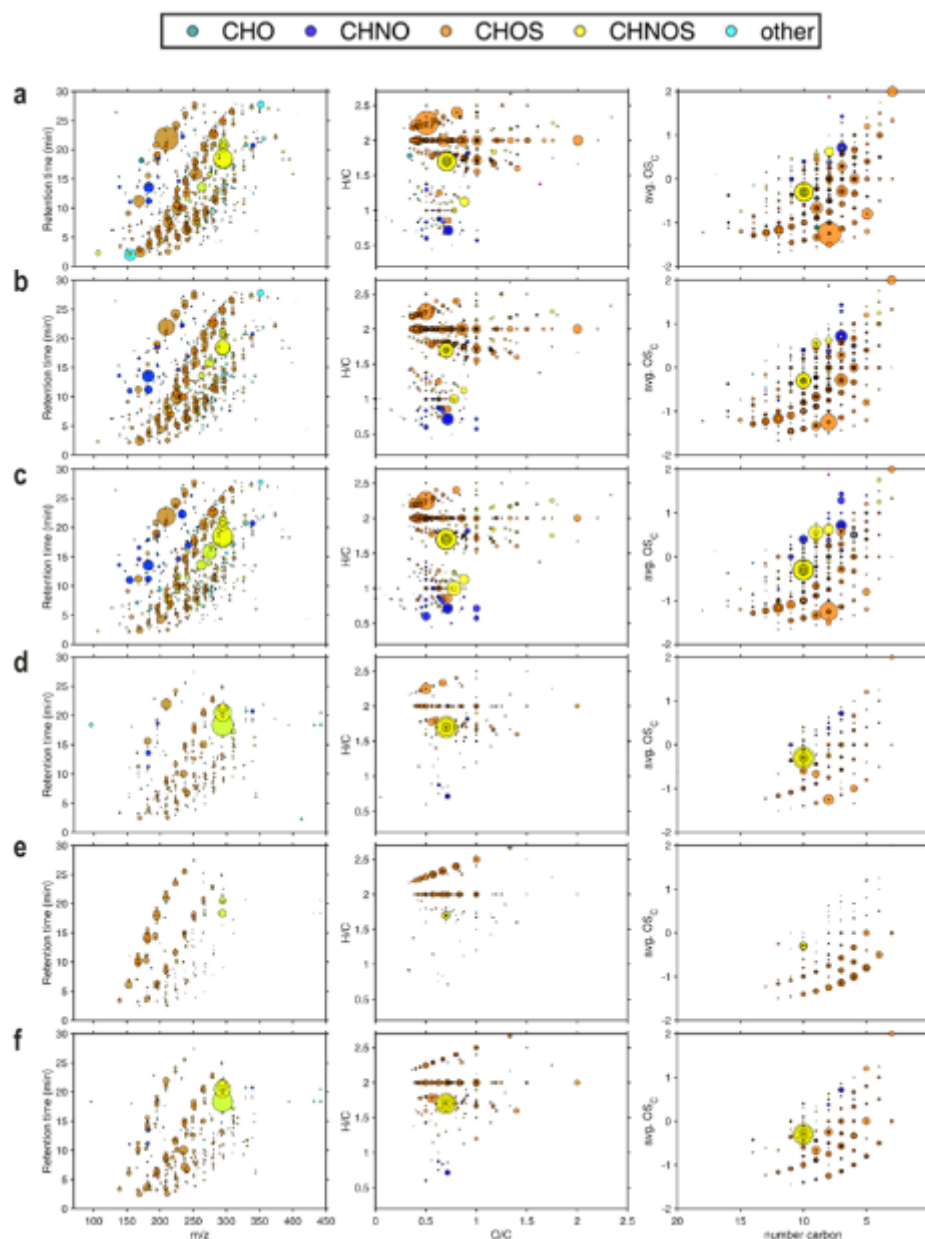


Figure S 11.5-2: Molecular fingerprints (m/z -RT plot, Van Krevelen diagram, and Kroll diagram) of the enriched OS fractions. (a) Handan 1: 18.10.2018, daytime; (b) Handan 2: 21.10.2018, daytime; (c) Handan 3: 21.10.2018, night-time; (d) TO 1: 11.12.2021, daytime; (e) TO 2: 14.01.2022, night-time; (f) TO 3: 28.02.2022, night-time

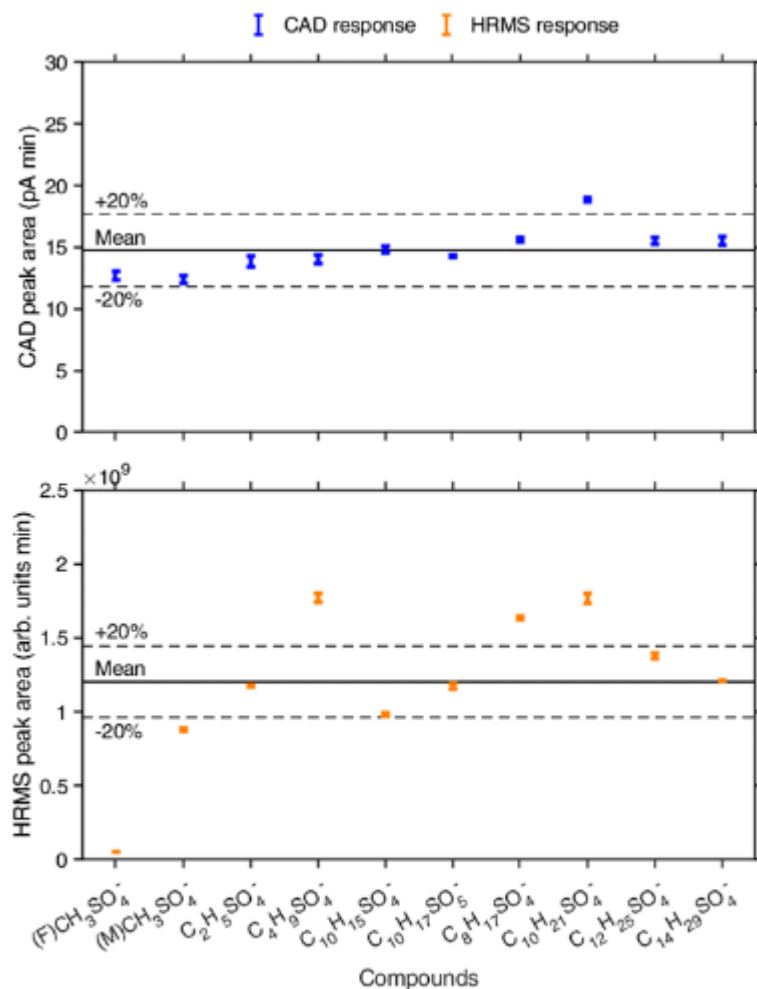


Figure S 11.5-3: Comparison of the CAD (blue, upper figure) and HRMS (orange, lower figure) response (mean $\pm$ SD) of ten OS standards at an isocratic gradient. The standards were prepared in one batch as an OS-mix. The mix contained: (1) Formaldehyde sodium bisulfite (CH₃SO₄Na), (2) Methyl sulfate sodium salt (CH₃SO₄Na), (3) Sodium ethyl sulfate (C₂H₅SO₄Na), (4) Butyl sulfate sodium salt (C₄H₁₀SO₄Na), (5) Camphor-10-sulfonic acid (C₁₀H₁₆SO₄), (6) 2-hydroxy- α -pinene OS (C₁₀H₁₈SO₅), (7) Sodium octyl sulfate (C₈H₁₇SO₄Na), (8) Sodium n-decyl sulfate (C₁₀H₂₁SO₄Na), (9) Sodium dodecyl sulfate (C₁₂H₂₅SO₄Na), and (10) Tetradecyl sulfate sodium salt (C₁₄H₂₉SO₄Na). Each OS standard had a concentration of 2 ng/ μ L. To test the stability of the instruments, we measured each standard concentration five times. The HPLC flowrate was set to 0.4 mL/min, with 83.5% being directed into the CAD and 16.5% being directed into the MS. The line (solid) is the average response of these compounds with a band (dash) of $\pm$ 20%.

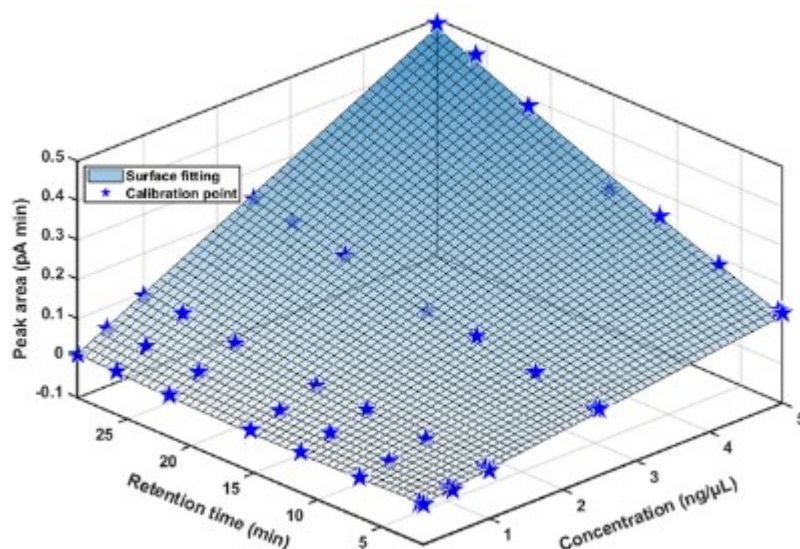


Figure S 11.5-4: Calibration surface fitted by OS standards. CAD measurement of eight different standards at five altered concentrations. The 40 data points were fitted by using a 2nd order polynomial function ($z = p00 + p10x + p01y + p11xy + p02y^2$ ($z = \text{peak area}$, $y = RT \text{ (min)}$, $x = \text{concentration (ng/}\mu\text{L)}$, $p00 = 0.005127$, $p10 = 0.01947$, $p01 = -0.001816$, $p11 = 0.002637$, $p02 = 0.000059$)) to get the calibration surface. Standards from low to high RT: Methyl sulfate sodium salt (RT: 1.70), Sodium ethyl sulfate (RT: 2.04), Butyl sulfate (RT: 6.73), Camphor-10-sulfonic acid (RT: 11.38), 2-hydroxy- α -pinene OS (RT: 15.33), Sodium octyl sulfate (RT: 21.73), Sodium n-decyl sulfate (RT: 25.87), Sodium dodecyl sulfate (RT: 28.93).

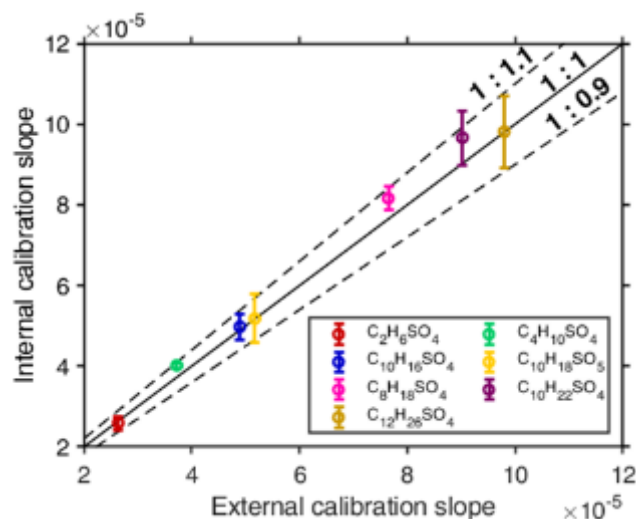


Figure S 11.5-5: Comparison of the internal and external calibration curve. The error bar indicates the standard deviation of the six samples.

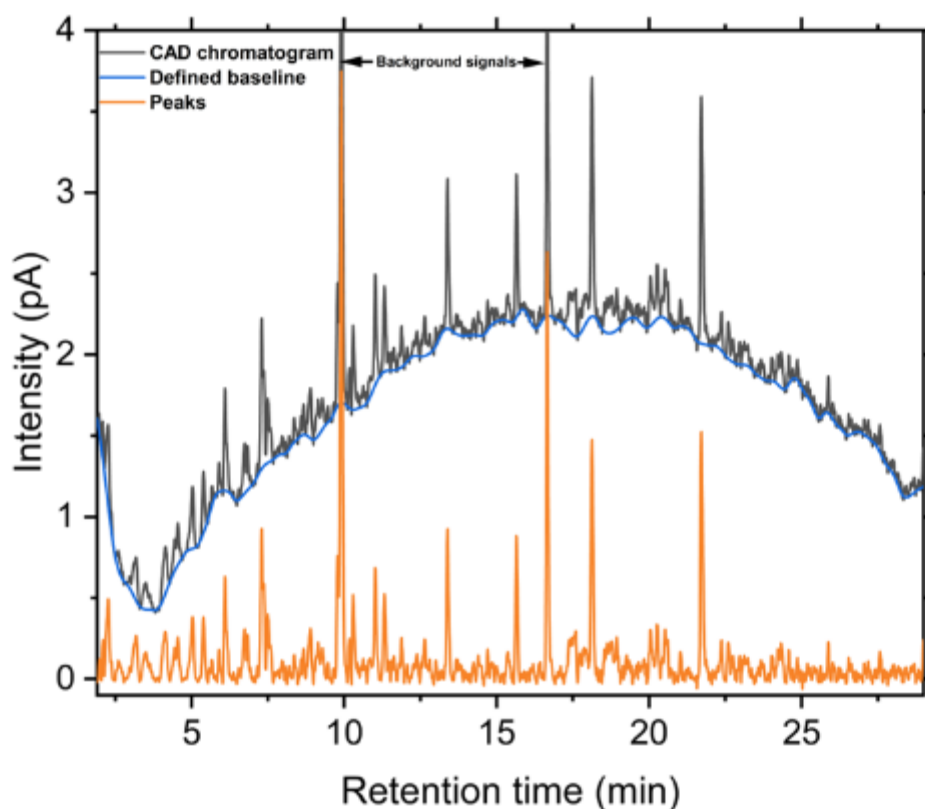


Figure S 11.5-6: Baseline fitting in the CAD chromatogram (Sample: Handan 18.10.2018, daytime). The blank-subtracted CAD chromatogram (grey) is fitted by a running baseline (blue). Subtraction of the baseline from the chromatogram results in a chromatogram solely representing the chromatographically-resolved peaks (orange).

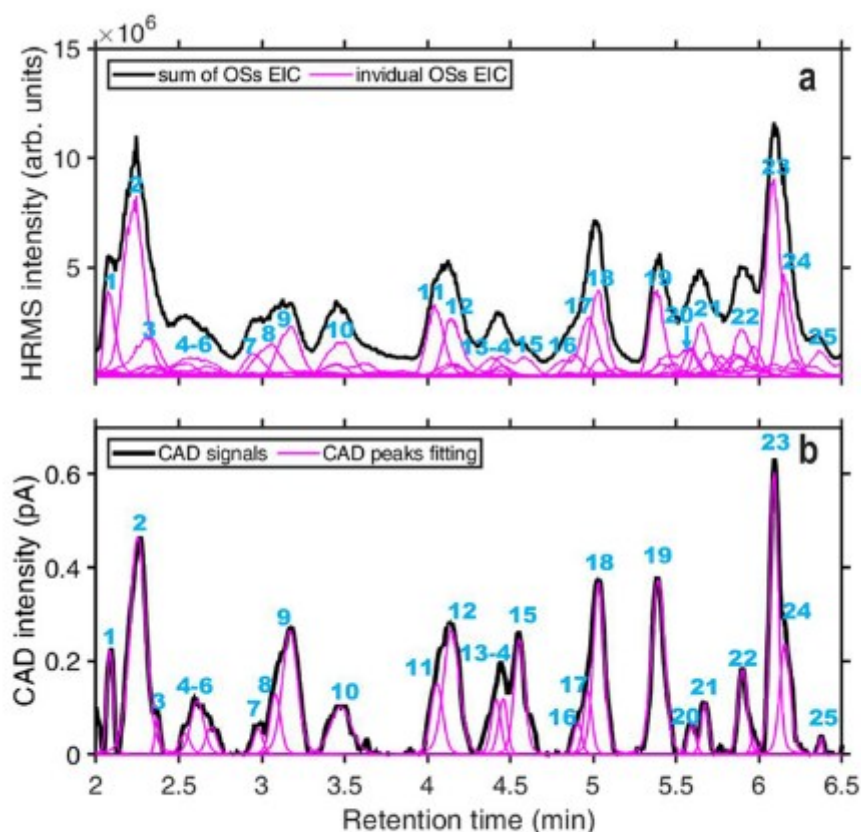


Figure S 11.5-7: CAD peak fitting by using the EIC of OSs as a reference (sample: Handan 18.10.2018, daytime). We used Fityk to fit the peaks and within RT range between 2-6.5 min as an example. (a) The indices are the notes for the reference peaks in HRMS. (b) The indices are the separated peak fittings of various compounds.

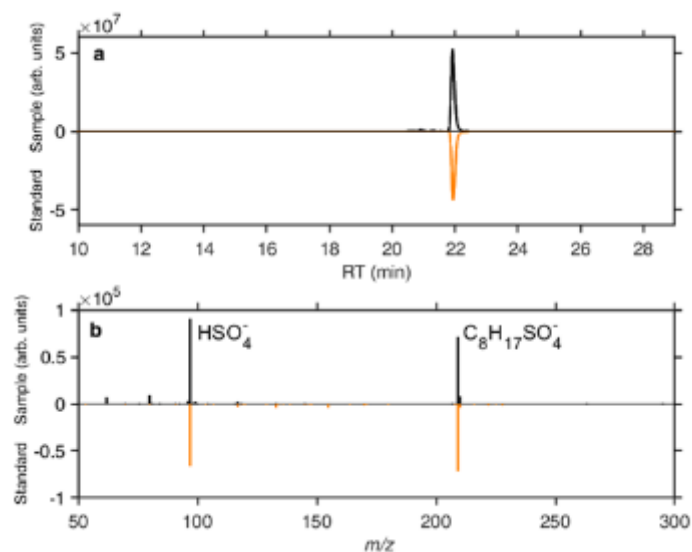


Figure S 11.5-8: Comparison of the (a) retention time (RT) and (b) MS/MS fragmentation patterns of octyl sulfate ($C_8H_{18}SO_4$) measured in an ambient sample (Handan, 18.10.2018 daytime, upward spectra, black) and their standards (downward spectra, orange).

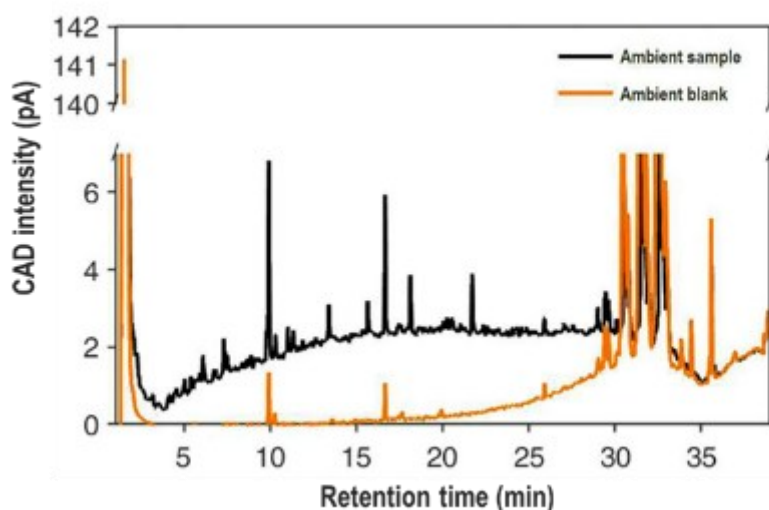


Figure S 11.5-9: Comparison of the UHPLC-CAD chromatograms (complete chromatograms) of the enriched OS fraction (second SPE elution) of the ambient filter sample (black line), and the enriched OS fraction (second SPE elution) of the according ambient filter blank (orange line).

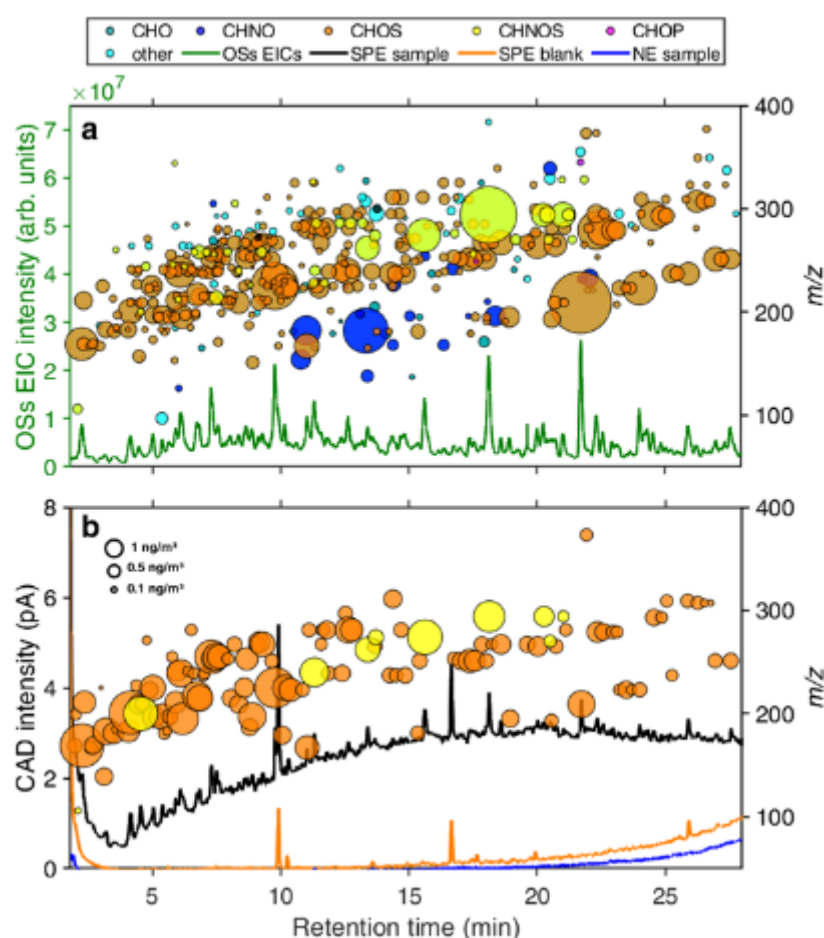


Figure S 11.5-10: Comparison of the chromatograms and fingerprints of the enriched OS fraction, measured by UHPLC-HRMS (a) and UHPLC-CAD (b), of a Handan filter (Handan 2, 21.10.2018 daytime). The x-axis, displaying the retention time (min), is zoomed in to 2.5-28 min of a total

method duration of 40 min. There was no integration possible for OS CAD peaks outside of this time window. (a) UHPLC-HRMS data of the enriched OS fraction: RT- m/z plot (fingerprints, right y-axis) and the sum of the extracted ion chromatograms (EIC, green line, left y-axis) of all the OS fingerprints appearing in the RT- m/z plot. The circle size represents the OS intensity. (b) Comparison of the UHPLC-CAD chromatograms of the enriched OS fraction (second SPE elution) of the ambient filter sample (SPE sample, black line), the enriched OS fraction of the according ambient filter blank (SPE blank, orange line), and the native extraction (regular liquid extraction technique) of the same ambient filter sample (NE sample, blue line) with the molecular fingerprints of the quantifiable OSs of the SPE sample. The circle size represents the OS concentration, determined from the three-dimensional calibration (Figure S 11.5-4).

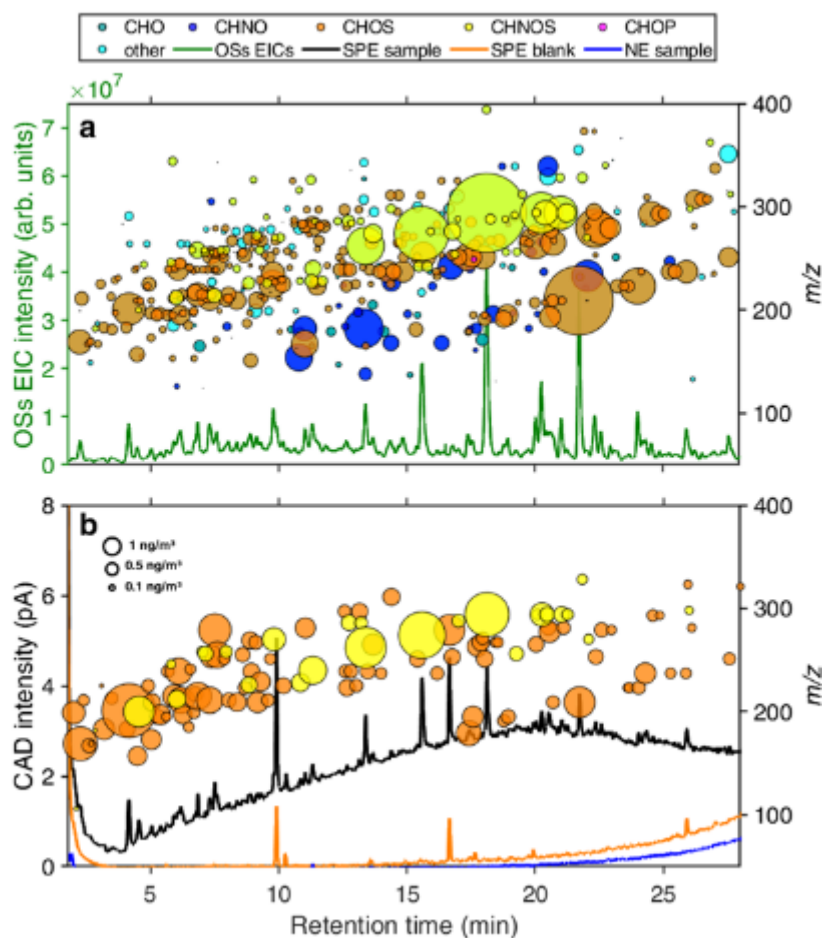


Figure S 11.5-11: Comparison of the chromatograms and fingerprints of the enriched OS fraction, measured by UHPLC-HRMS (a) and UHPLC-CAD (b), of a Handan filter (Handan 3, 21.10.2018 night-time). The x-axis, displaying the retention time (min), is zoomed in to 2.5-28 min of a total method duration of 40 min. There was no integration possible for OS CAD peaks outside of this time window. (a) UHPLC-HRMS data of the enriched OS fraction: RT- m/z plot (fingerprints, right y-axis) and the sum of the extracted ion chromatograms (EIC, green line, left y-axis) of all the OS fingerprints appearing in the RT- m/z plot. The circle size represents the OS intensity. (b) Comparison of the UHPLC-CAD chromatograms of the enriched OS fraction (second SPE elution) of the ambient filter sample (SPE sample, black line), the enriched OS fraction of the according ambient filter blank (SPE blank, orange line), and the native extraction (regular liquid extraction technique) of the same ambient filter sample (NE sample, blue line) with the molecular fingerprints of the quantifiable OSs of the SPE sample. The circle size represents the OS concentration, determined from the three-dimensional calibration (Figure S 11.5-4).

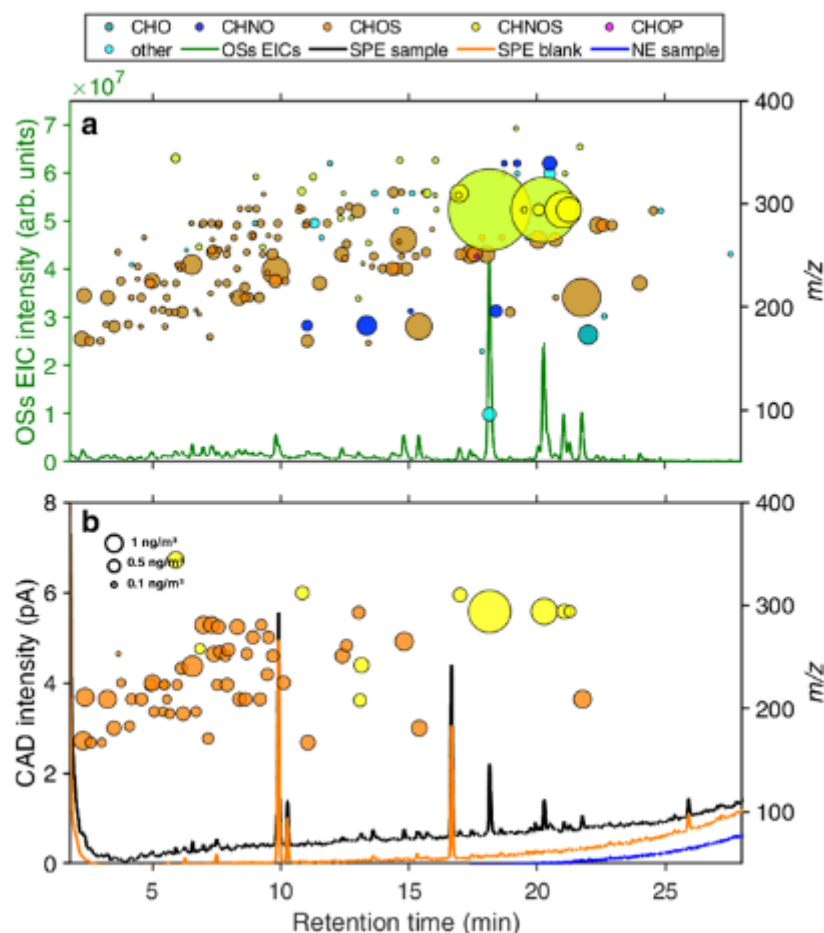


Figure S 11.5-12: Comparison of the chromatograms and fingerprints of the enriched OS fraction, measured by UHPLC-HRMS (a) and UHPLC-CAD (b), of a TO filter (TO 1, 11.12.2021 daytime). The x-axis, displaying the retention time (min), is zoomed in to 2.5-28 min of a total method duration of 40 min. There was no integration possible for OS CAD peaks outside of this time window. The complete CAD chromatogram is shown in Fig. S8. (a) UHPLC-HRMS data of the enriched OS fraction: RT- m/z plot (fingerprints, right y-axis) and the sum of the extracted ion chromatograms (EIC, green line, left y-axis) of all the OS fingerprints appearing in the RT- m/z plot. The circle size represents the OS intensity. (b) Comparison of the UHPLC-CAD chromatograms of the enriched OS fraction (second SPE elution) of the ambient filter sample (SPE sample, black line), the enriched OS fraction of the according ambient filter blank (SPE blank, orange line), and the native extraction (regular liquid extraction technique) of the same ambient filter sample (NE sample, blue line) with the molecular fingerprints of the quantifiable OSs of the SPE sample. The circle size represents the OS concentration, determined from the three-dimensional calibration (Figure S 11.5-4).

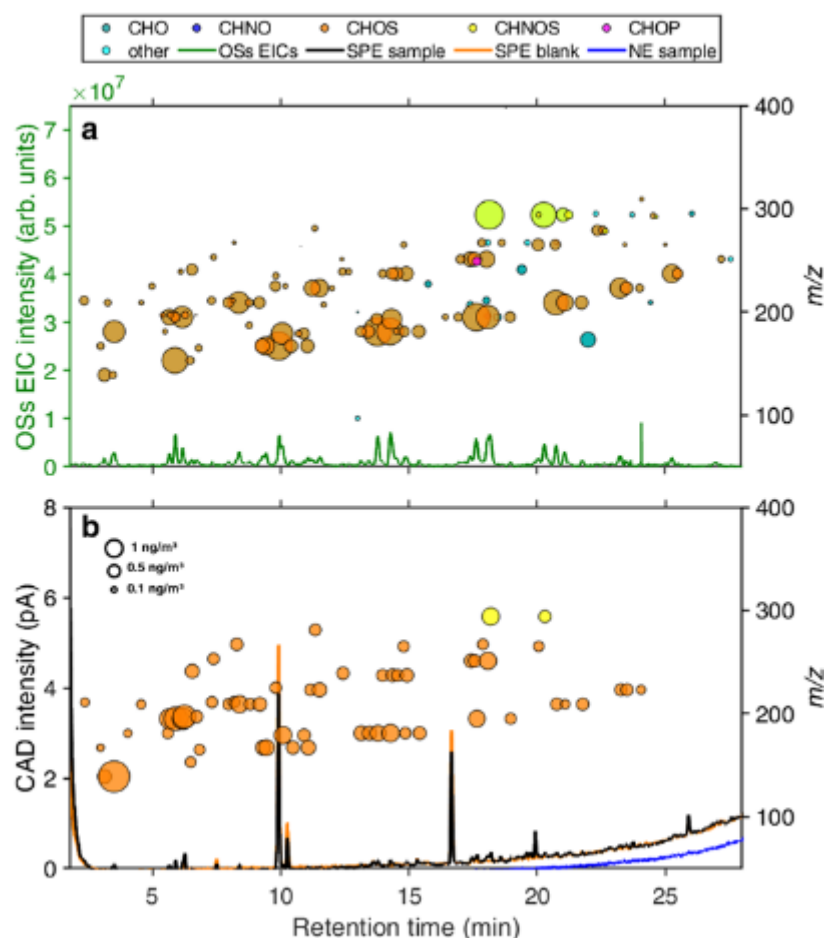


Figure S 11.5-13: Comparison of the chromatograms and fingerprints of the enriched OS fraction, measured by UHPLC-HRMS (a) and UHPLC-CAD (b), of a TO filter (TO 2, 24.1.2022 night-time). The x-axis, displaying the retention time (min), is zoomed in to 2.5-28 min of a total method duration of 40 min. There was no integration possible for OS CAD peaks outside of this time window. (a) UHPLC-HRMS data of the enriched OS fraction: RT- m/z plot (fingerprints, right y-axis) and the sum of the extracted ion chromatograms (EIC, green line, left y-axis) of all the OS fingerprints appearing in the RT- m/z plot. The circle size represents the OS intensity. (b) Comparison of the UHPLC-CAD chromatograms of the enriched OS fraction (second SPE elution) of the ambient filter sample (SPE sample, black line), the enriched OS fraction of the according ambient filter blank (SPE blank, orange line), and the native extraction (regular liquid extraction technique) of the same ambient filter sample (NE sample, blue line) with the molecular fingerprints of the quantifiable OSs of the SPE sample. The circle size represents the OS concentration, determined from the three-dimensional calibration (Figure S 11.5-4).

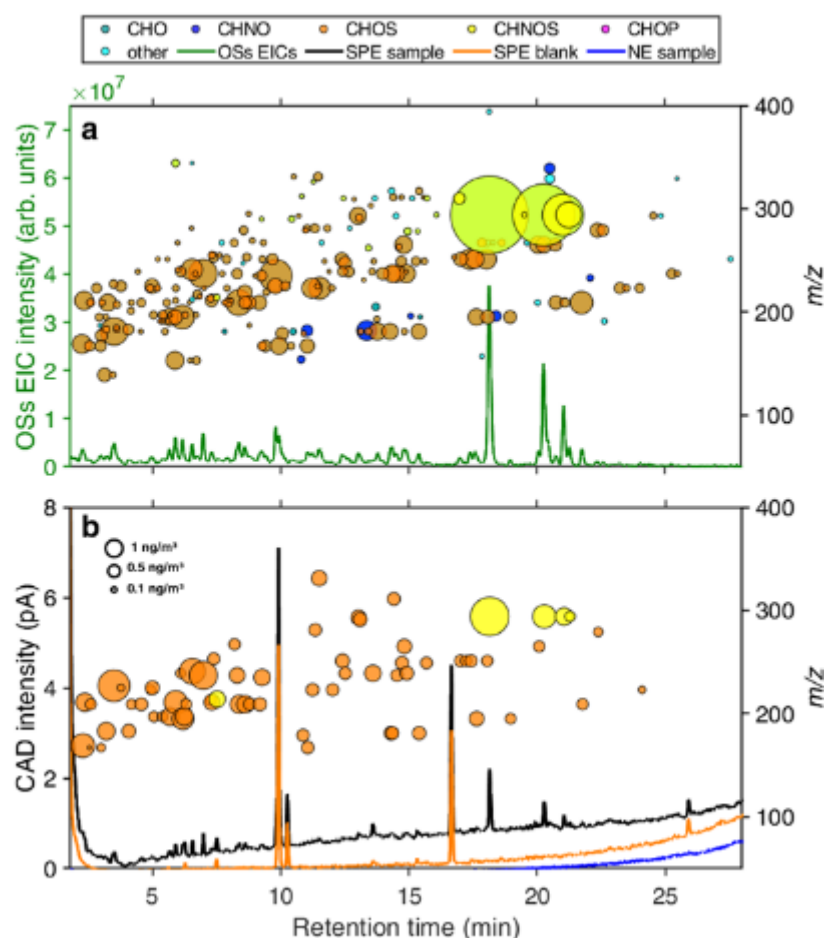


Figure S 11.5-14: Comparison of the chromatograms and fingerprints of the enriched OS fraction, measured by UHPLC-HRMS (a) and UHPLC-CAD (b), of a TO filter (TO 3, 28.02.2022 night-time). The x-axis, displaying the retention time (min), is zoomed in to 2.5-28 min of a total method duration of 40 min. There was no integration possible for OS CAD peaks outside of this time window. (a) UHPLC-HRMS data of the enriched OS fraction: RT- m/z plot (fingerprints, right y-axis) and the sum of the extracted ion chromatograms (EIC, green line, left y-axis) of all the OS fingerprints appearing in the RT- m/z plot. The circle size represents the OS intensity. (b) Comparison of the UHPLC-CAD chromatograms of the enriched OS fraction (second SPE elution) of the ambient filter sample (SPE sample, black line), the enriched OS fraction of the according ambient filter blank (SPE blank, orange line), and the native extraction (regular liquid extraction technique) of the same ambient filter sample (NE sample, blue line) with the molecular fingerprints of the quantifiable OSs of the SPE sample. The circle size represents the OS concentration, determined from the three-dimensional calibration (Figure S 11.5-4).

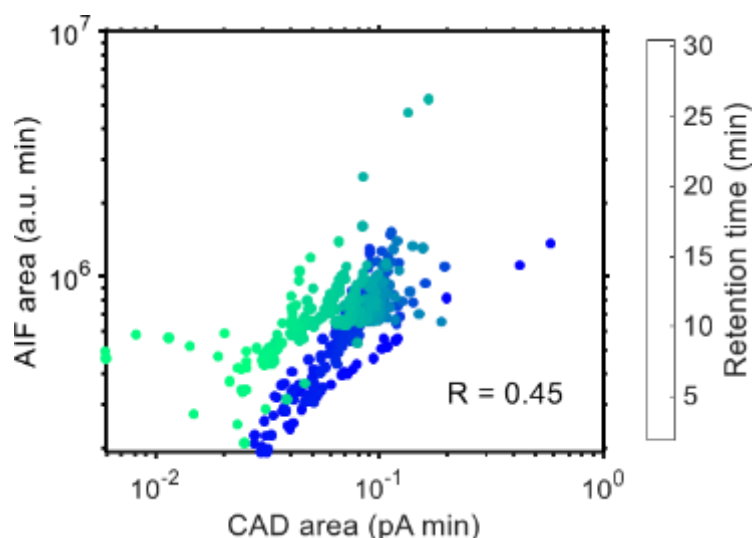


Figure S 11.5-15: Correlation of blank-subtracted UHPLC-CAD and UHPLC-HRMS chromatograms (OS ions HSO_4^- , HSO_3^- , SO_4^{2-} , and SO_3^{2-} in AIF mode) of an exemplary Handan filter (18.10.2018 daytime). We averaged the data points of each chromatogram in 0.05-minute intervals and use the signal intensity of AIF (a.u.) and CAD (pA) multiplied by the time step (0.05, min), respectively, to get the area of each retention time for both chromatograms. The color bar represents the chromatographic retention time (min).

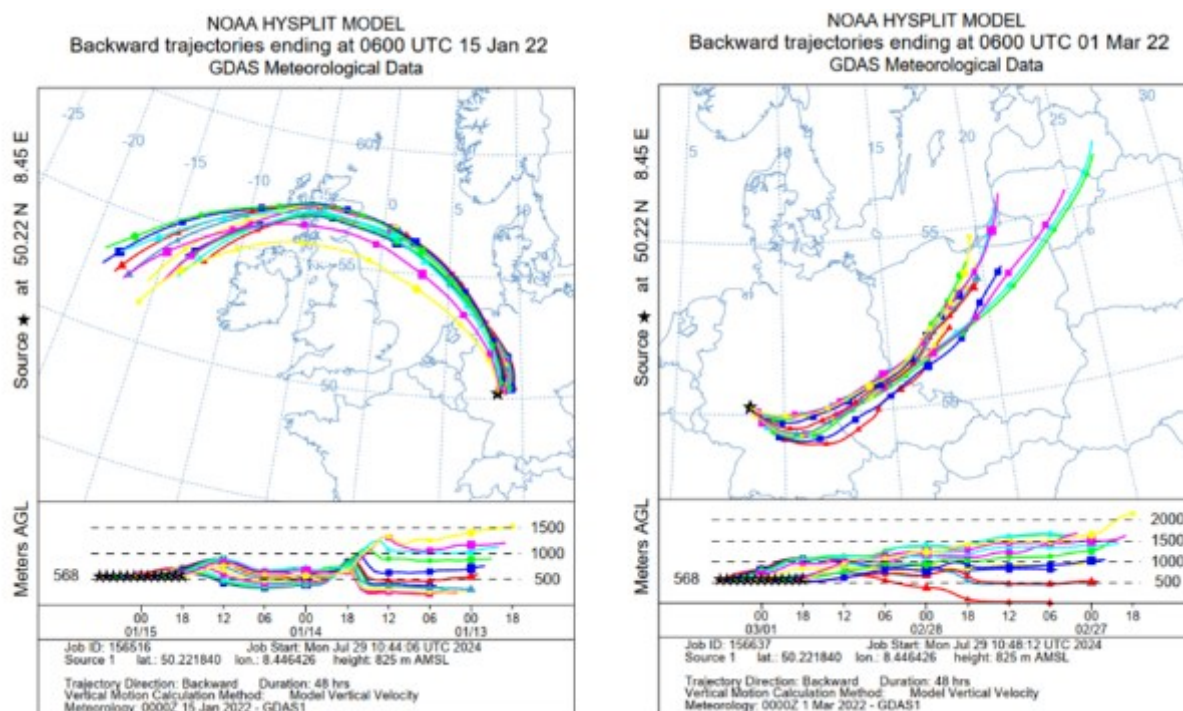


Figure S 11.5-16: Backward trajectories for samples TO-2 (a) and TO-3 (b). Backward trajectories for Taunus Observatory (825 m.a.s.l.) starting every hour for the 12-hour filter sampling duration. Duration of backward trajectories is 48 hours and was calculated based on the online web version of the NOAA Hysplit Model 1.

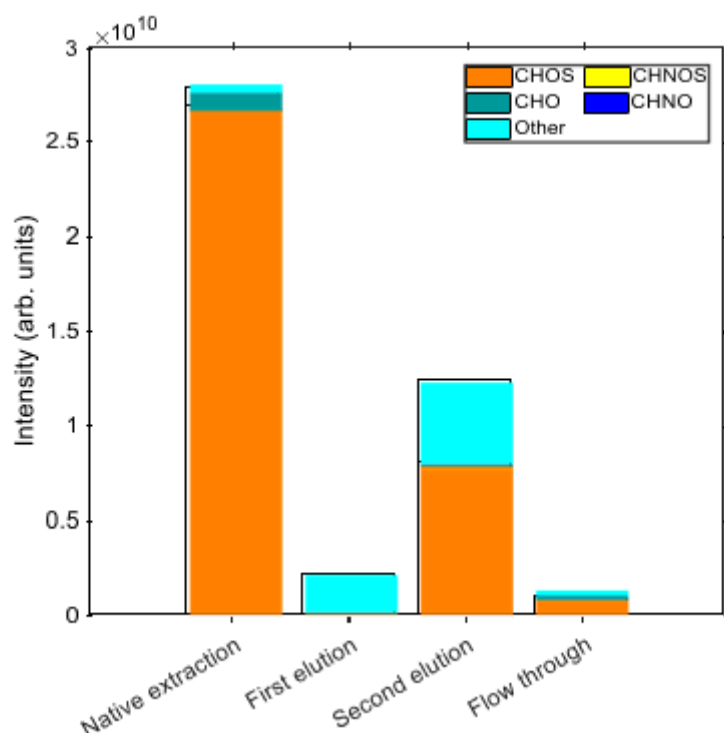


Figure S 11.5-17: Summed peak areas of different compound classes in the isoprene-derived OS sample across the native extraction, first elution, second elution, and flow-through, analyzed using the HILIC column.

We conducted a PAM chamber experiment to generate isoprene derived OSs. Using a PAM-OFR, isoprene was oxidized by O_3 (2 ppm) and photooxidation (OH was generated by UV light ($\lambda = 254$ nm) inside the OFR). Additionally, we inject SO_2 (55 ppb) at relative humidity ~60%. The SOA exiting the OFR passed through two 50 cm denuders filled with charcoal to remove reactive gas-phase compounds. SOA particles were collected on glass fiber filters at a flow rate of 3 L min^{-1} over 120 minutes. We extracted the filters and applied the SPE method described in the paper, using a HILIC column for the separation of isoprene OSs.

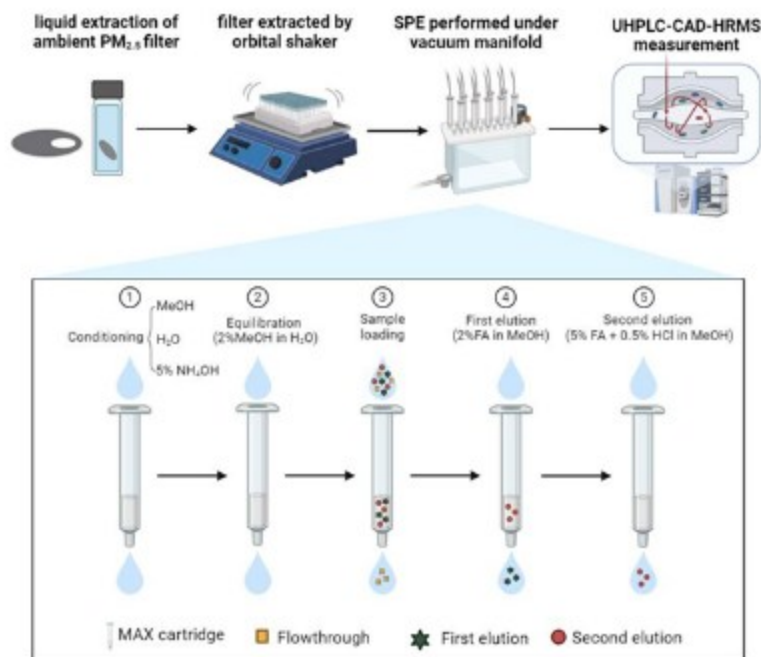


Figure S 11.5-18: Workflow of the filter preparation, SPE separation, and UHPLC-CAD-HRMS measurement. Created in BioRender. Ma, J. (2025) <https://BioRender.com/r78h920>.

Table S 11.5-1: Quantification of all OSs in the Handan 1 ambient filter sample (18.10.2018, daytime) sorted by ascending retention time. The chemical formula, retention time (RT), mass-to-charge ratio (m/z), and OS concentration (ng/m^3) are given for each OS.

RT (min)	Chemical formula	m/z	Conc. ng/m^3
1.92	C3 H6 O5 S	152.9861	0.01
1.97	C5 H8 O6 S	194.9968	0.59
2.01	C4 H8 O7 S	198.9917	0.01
2.09	C H N O3 S	105.9603	1.07
2.24	C3 H6 O6 S	168.9811	3.55
2.32	C5 H8 O7 S	210.9916	3.05
2.37	C5 H8 O7 S	210.9916	0.20
2.54	C4 H8 O5 S	167.0019	0.30
2.61	C4 H8 O5 S	167.0019	1.18
2.70	C4 H10 O5 S	169.0176	0.45
2.96	C4 H8 O5 S	167.0019	0.21
3.00	C6 H10 O7 S	225.0074	0.19
3.08	C3 H8 O4 S	139.0070	1.08

3.17	C4 H8 O6 S	182.9968	3.19
3.48	C5 H10 O5 S	181.0177	1.69
4.06	C4 H8 O6 S	182.9967	1.43
4.14	C7 H6 O5 S	200.9863	3.15
4.43	C6 H10 O6 S	209.0124	2.18
4.55	C6 H10 O6 S	209.0124	1.98
4.91	C7 H12 O6 S	223.0281	0.57
4.97	C6 H12 O8 S	225.0073	0.97
5.03	C5 H10 O6 S	197.0125	2.87
5.39	C5 H10 O6 S	197.0125	3.30
5.59	C5 H12 O5 S	183.0330	0.57
5.67	C6 H12 O5 S	195.0331	0.77
5.90	C6 H12 O6 S	211.0281	1.32
5.97	C6 H10 O8 S	241.0025	0.40
6.09	C7 H12 O7 S	239.0231	3.42
6.16	C6 H12 O5 S	195.0333	1.83
6.37	C8 H14 O9 S	285.0283	0.39
6.67	C5 H10 O6 S	197.0125	0.45
6.74	C8 H10 O5 S	217.0174	2.46
6.83	C8 H10 O5 S	217.0174	1.38
7.30	C7 H12 O8 S	255.0180	5.43
7.37	C8 H14 O7 S	253.0389	2.32
7.50	C10 H16 O7 S	279.0543	2.09
7.59	C7 H12 O8 S	255.0182	1.23
7.97	C8 H14 O7 S	253.0389	1.32
8.08	C6 H12 O6 S	211.0280	0.56
8.19	C9 H16 O7 S	267.0543	0.56
8.37	C7 H14 O5 S	209.0488	1.08
8.43	C9 H7 N O5 S	239.9972	0.56
8.58	C7 H14 O6 S	225.0437	0.68

8.67	C8 H14 O7 S	253.0387	1.07
8.83	C8 H14 O7 S	253.0387	0.97
8.89	C8 H16 O6 S	239.0596	2.04
9.08	C9 H16 O7 S	267.0544	0.87
9.15	C7 H14 O5 S	209.0488	1.50
9.25	C9 H18 O7 S	269.0700	0.96
9.30	C9 H16 O7 S	267.0544	0.99
9.47	C8 H14 O7 S	253.0387	0.75
9.66	C9 H16 O6 S	251.0595	0.83
9.79	C7 H14 O6 S	225.0438	4.28
10.17	C7 H14 O6 S	225.0438	1.39
10.56	C11 H18 O9 S	325.0600	0.83
10.63	C9 H16 O8 S	283.0493	0.91
10.83	C9 H10 O6 S	245.0123	0.86
11.02	C5 H12 O4 S	167.0383	3.12
11.11	C10 H18 O8 S	297.0648	0.59
11.33	C6 H11 N O7 S	240.0184	3.28
11.44	C7 H14 O6 S	225.0438	0.67
11.49	C8 H16 O5 S	223.0645	0.66
11.57	C9 H16 O7 S	267.0543	0.68
11.64	C10 H18 O7 S	281.0700	0.88
11.80	C10 H18 O7 S	281.0700	0.70
11.89	C8 H16 O6 S	239.0596	1.57
12.01	C9 H18 O6 S	253.0751	0.51
12.06	C8 H17 N O8 S	286.0602	0.67
12.27	C8 H16 O5 S	223.0645	0.67
12.32	C7 H13 N O9 S	286.0239	0.54
12.39	C8 H16 O6 S	239.0596	1.16
12.53	C10 H18 O8 S	297.0648	0.61
12.59	C8 H18 O5 S	225.0802	0.60

12.64	C8 H16 O6 S	239.0595	1.04
12.81	C8 H16 O6 S	239.0596	0.60
13.01	C11 H18 O7 S	293.0702	0.81
13.17	C10 H18 O8 S	297.0650	0.63
13.39	C8 H9 N O7 S	262.0026	4.07
13.46	C6 H14 O3 S	165.0590	0.69
13.62	C8 H16 O6 S	239.0596	0.48
13.83	C6 H14 O4 S	181.0541	0.64
14.24	C6 H14 O4 S	181.0540	0.84
14.39	C11 H20 O8 S	311.0806	0.77
14.45	C11 H20 O7 S	295.0855	0.57
14.49	C6 H14 O4 S	181.0541	0.63
14.71	C11 H20 O8 S	311.0806	0.85
14.79	C10 H18 O6 S	265.0751	0.53
14.84	C9 H18 O5 S	237.0803	0.60
14.88	C9 H16 O6 S	251.0595	0.53
15.27	C10 H20 O6 S	249.0801	0.42
15.36	C6 H14 O4 S	181.0541	1.13
15.42	C9 H16 O6 S	251.0594	0.67
15.65	C9 H18 O6 S	253.0751	3.66
16.19	C10 H20 O7 S	283.0857	0.71
16.39	C9 H18 O6 S	253.0752	0.60
16.43	C9 H18 O6 S	253.0751	0.51
17.38	C10 H20 O5 S	251.0959	1.01
18.13	C10 H17 N O7 S	294.0656	5.54
18.29	C10 H11 N O7 S	288.0185	0.37
18.63	C10 H20 O6 S	267.0909	0.98
18.76	C8 H16 O3 S	191.0748	0.89
18.94	C7 H16 O4 S	195.0694	0.82

19.29	C8 H16 O4 S	207.0696	1.34
19.83	C10 H18 O6 S	265.0754	0.62
20.06	C11 H22 O5 S	265.1116	1.40
20.27	C10 H17 N O7 S	294.0656	1.48
20.43	C10 H17 N O7 S	294.0656	0.59
20.53	C14 H24 O5 S	303.1276	1.17
20.60	C11 H22 O6 S	281.1066	0.74
20.72	C11 H22 O5 S	265.1117	0.46
21.02	C10 H17 N O7 S	294.0656	0.69
21.24	C10 H17 N O7 S	294.0656	0.31
21.72	C8 H18 O4 S	209.0854	5.46
22.37	C12 H24 O5 S	279.1273	0.88
22.60	C12 H24 O5 S	279.1273	0.63
22.96	C12 H24 O5 S	279.1273	0.51
23.12	C12 H24 O5 S	279.1273	0.46
23.24	C13 H24 O7 S	323.1171	0.39
24.04	C9 H20 O4 S	223.1011	0.58
24.30	C13 H26 O5 S	293.1431	1.66
24.58	C13 H26 O5 S	293.1431	0.40
24.87	C13 H26 O5 S	293.1431	0.39
25.87	C13 H26 O5 S	293.1431	0.43
25.94	C10 H22 O4 S	237.1167	0.10
26.55	C14 H28 O5 S	307.1587	0.26
27.58	C11 H24 O4 S	251.1323	0.37

Table S 11.5-2: Quantification of all OSs in the Handan 2 ambient filter sample (21.10.2018, daytime) sorted by ascending retention time. The chemical formula, retention time (RT), mass-to-charge ratio (m/z), and OS concentration (ng/m^3) are given for each OS.

RT (min)	Chemical formula	<i>m/z</i>	Conc. ng/m ³
1.97	C3 H6 O5 S	168.8910	0.73
2.00	C4 H8 O7 S	198.9917	0.42
2.09	C H N O3 S	105.9603	0.14
2.25	C3 H6 O6 S	168.8910	6.42
2.34	C5 H8 O7 S	210.9916	1.74
2.59	C4 H8 O5 S	167.0019	0.55
2.67	C4 H10 O5 S	169.0176	1.01
2.99	C6 H10 O7 S	225.0074	0.06
3.11	C3 H8 O4 S	139.0070	1.04
3.19	C4 H8 O6 S	182.9968	2.43
3.48	C5 H10 O5 S	181.0177	1.50
3.60	C4 H10 O6 S	185.0125	0.34
4.06	C4 H8 O6 S	182.9967	1.65
4.15	C7 H6 O5 S	200.9863	6.29
4.37	C6 H12 O7 S	227.0231	0.47
4.45	C6 H10 O6 S	209.0124	1.28
4.54	C3 H7 N O7 S	199.9869	3.96
4.61	C6 H10 O6 S	209.0124	0.73
4.77	C7 H12 O9 S	271.0127	0.27
4.89	C7 H12 O6 S	223.0281	0.94
5.01	C6 H12 O8 S	225.0073	2.18
5.05	C5 H10 O6 S	197.0125	1.71
5.27	C5 H8 O6 S	194.9968	0.44
5.39	C5 H10 O6 S	197.0124	2.26
5.46	C5 H10 O5 S	181.0177	0.51
5.57	C5 H12 O5 S	183.0332	0.29
5.65	C6 H12 O5 S	195.0331	0.44
5.69	C6 H14 O5 S	197.0489	0.84
5.76	C7 H12 O8 S	255.0182	0.42

5.90	C6 H12 O6 S	211.0281	1.59
5.96	C6 H10 O8 S	241.0025	1.40
6.09	C7 H12 O7 S	239.0231	2.53
6.17	C6 H12 O5 S	195.0333	3.39
6.38	C7 H14 O7 S	241.0386	0.36
6.51	C9 H14 O8 S	281.0335	0.46
6.62	C7 H12 O7 S	239.0230	0.46
6.74	C8 H10 O5 S	217.0174	2.94
6.84	C8 H8 O5 S	215.0019	2.31
6.98	C8 H14 O6 S	237.0437	0.44
7.02	C7 H12 O7 S	239.0231	0.45
7.30	C7 H12 O8 S	255.0181	3.81
7.37	C8 H14 O7 S	253.0389	1.89
7.50	C8 H16 O7 S	255.0544	2.52
7.59	C7 H12 O8 S	255.0181	1.90
7.94	C8 H14 O7 S	253.0389	0.50
8.05	C8 H8 O5 S	215.0018	1.03
8.19	C9 H16 O7 S	267.0543	0.79
8.36	C7 H14 O5 S	209.0488	1.13
8.58	C7 H14 O6 S	225.0437	1.33
8.68	C8 H14 O7 S	253.0387	1.73
8.79	C7 H8 O4 S	187.0070	0.99
8.89	C6 H14 O5 S	197.0489	2.63
9.08	C9 H16 O7 S	267.0544	0.97
9.16	C9 H18 O7 S	269.0700	1.51
9.30	C9 H16 O7 S	267.0544	2.07
9.65	C9 H16 O6 S	251.0595	0.66
9.78	C7 H14 O6 S	225.0438	5.56
10.06	C7 H12 O6 S	179.0384	1.11
10.17	C7 H14 O6 S	225.0438	2.17

10.38	C8 H16 O5 S	223.0645	1.84
10.85	C8 H16 O5 S	223.0645	0.63
11.03	C5 H12 O4 S	167.0383	1.93
11.10	C10 H18 O7 S	281.0700	0.66
11.31	C6 H11 N O7 S	240.0184	2.86
11.58	C9 H16 O7 S	267.0544	0.51
11.65	C10 H18 O7 S	281.0700	0.63
11.80	C10 H18 O7 S	281.0700	1.07
11.86	C8 H16 O6 S	239.0596	0.68
12.40	C8 H16 O6 S	239.0596	0.93
12.53	C10 H18 O8 S	297.0648	0.70
12.63	C10 H18 O7 S	281.0700	2.32
12.77	C10 H18 O7 S	281.0700	1.75
13.39	C8 H9 N O7 S	262.0026	2.10
13.67	C12 H10 O5 S	265.0177	0.73
13.71	C9 H9 N O7 S	274.0029	0.79
14.25	C9 H18 O5 S	237.0802	0.78
14.37	C11 H20 O8 S	311.0806	1.13
14.50	C9 H18 O5 S	237.0802	0.65
14.69	C10 H18 O7 S	281.0700	0.74
14.86	C9 H18 O5 S	237.0802	0.85
15.34	C6 H14 O4 S	181.0541	0.70
15.42	C9 H16 O6 S	251.0594	0.81
15.62	C9 H9 N O7 S	274.0028	4.13
16.76	C9 H18 O6 S	253.0751	0.64
17.04	C10 H20 O5 S	251.0959	1.08
17.38	C10 H20 O5 S	251.0957	1.87
17.57	C10 H20 O5 S	251.0958	1.51
17.84	C10 H20 O6 S	267.0908	0.82
18.02	C10 H20 O5 S	251.0959	0.74

18.13	C10 H17 N O7 S	294.0652	3.31
18.23	C10 H20 O6 S	267.0908	0.45
18.59	C10 H20 O6 S	267.0906	1.32
18.95	C7 H16 O4 S	195.0694	1.05
19.61	C10 H20 O6 S	267.0909	0.89
20.03	C11 H22 O5 S	265.1116	1.32
20.27	C10 H17 N O7 S	294.0652	1.37
20.50	C8 H17 N O7 S	270.0656	0.54
20.56	C8 H18 O3 S	193.0905	0.61
20.74	C11 H22 O5 S	265.1117	0.70
21.02	C10 H17 N O7 S	294.0656	0.44
21.12	C11 H22 O6 S	281.1066	0.54
21.73	C8 H18 O4 S	209.0853	2.50
21.93	C16 H22 O8 S	373.0965	0.54
22.35	C12 H24 O5 S	279.1273	1.46
22.58	C12 H24 O5 S	279.1273	0.95
22.95	C12 H24 O5 S	279.1273	0.61
23.11	C12 H24 O5 S	279.1273	0.50
23.21	C9 H20 O4 S	223.1011	0.47
23.48	C9 H20 O4 S	223.1011	1.02
23.68	C9 H20 O4 S	223.1011	0.36
24.00	C9 H20 O4 S	223.1011	0.70
24.55	C13 H26 O5 S	293.1431	0.94
24.85	C13 H26 O5 S	293.1431	0.47
25.06	C13 H26 O6 S	309.1380	0.52
25.26	C10 H22 O4 S	237.1167	0.48
25.87	C13 H26 O6 S	309.1380	0.65
26.27	C14 H28 O5 S	307.1587	0.60
26.53	C14 H28 O5 S	307.1587	0.22

26.77	C14 H28 O5 S	307.1587	0.14
26.95	C11 H24 O4 S	251.1323	0.70
27.56	C11 H24 O4 S	251.1323	0.82
27.70			0.13
27.75			0.12
28.43	C12 H26 O3 S	249.1531	0.75
28.66	C15 H32 O5 S	323.1900	0.05
28.99		168.8910	0.72

Table S 11.5-3: Quantification of all OSs in the Handan 3 ambient filter sample (21.10.2018, night-time) sorted by ascending retention time. The chemical formula, retention time (RT), mass-to-charge ratio (m/z), and OS concentration (ng/m^3) are given for each OS.

RT (min)	Chemical formula	m/z	Conc. ng/m^3
2.00	C4 H8 O7 S	198.9917	1.74
2.09	C H N O3 S	105.9603	0.07
2.26	C3 H6 O6 S	168.9811	3.91
2.38	C5 H8 O7 S	210.9916	0.45
2.60	C4 H8 O5 S	167.0019	0.68
2.68	C4 H10 O5 S	169.0176	0.12
2.84	C3 H5 N O6 S	181.9765	0.05
3.09	C6 H10 O7 S	225.0074	0.06
3.19	C4 H8 O6 S	182.9968	1.53
3.48	C5 H10 O7 S	213.0074	0.54
4.08	C4 H8 O6 S	182.9967	9.87
4.16	C7 H6 O5 S	200.9863	0.85
4.49	C6 H6 O3 S	156.9963	3.26
4.55	C3 H7 N O7 S	199.9869	1.21
4.91	C6 H10 O7 S	225.0073	0.57
5.03	C6 H6 O4 S	172.9913	1.37
5.05	C6 H10 O6 S	209.0125	1.02
5.28	C5 H8 O6 S	194.9968	0.77
5.39	C5 H10 O6 S	197.0124	1.36

5.62	C6 H12 O5 S	195.0331	0.32
5.68	C7 H12 O7 S	239.0232	0.55
5.80	C8 H9 N O6 S	246.0077	0.30
5.92	C8 H8 O5 S	215.0021	1.80
6.03	C4 H7 N O7 S	211.9871	1.11
6.10	C7 H12 O7 S	239.0231	2.40
6.19	C6 H12 O6 S	211.0281	2.31
6.26	C6 H14 O5 S	197.0489	1.19
6.49	C7 H6 O4 S	184.9914	0.38
6.55	C7 H14 O7 S	241.0388	0.40
6.69	C8 H8 O4 S	199.0070	0.48
6.74	C8 H10 O5 S	217.0174	0.76
6.85	C8 H8 O5 S	215.0019	2.56
7.02	C6 H13 N O8 S	258.0287	0.41
7.15	C6 H11 N O8 S	256.0133	0.79
7.30	C6 H12 O6 S	211.0282	2.37
7.38	C8 H14 O7 S	253.0389	1.64
7.51	C10 H16 O7 S	279.0543	3.60
7.60	C7 H12 O8 S	255.0179	2.36
7.88	C9 H16 O6 S	251.0594	0.45
7.95	C6 H13 N O8 S	258.0288	0.54
8.06	C6 H12 O6 S	211.0280	0.74
8.38	C7 H14 O5 S	209.0488	1.14
8.59	C8 H16 O7 S	255.0543	0.74
8.68	C8 H16 O5 S	223.0647	0.63
8.80	C5 H10 Cl N O8 S	277.9742	0.55
8.84	C5 H9 N O7 S	226.0027	0.92
8.88	C8 H14 O8 S	269.0336	0.99
8.93	C8 H16 O6 S	239.0596	0.92
9.10	C10 H16 O9 S	267.0544	0.67

9.17	C7 H14 O5 S	209.0488	1.48
9.29	C9 H10 O5 S	229.0175	1.31
9.58	C7 H16 O5 S	211.0645	0.58
9.67	C9 H16 O6 S	251.0595	0.43
9.81	C7 H13 N O8 S	270.0287	1.86
10.18	C7 H14 O6 S	225.0438	0.86
10.85	C5 H11 N O7 S	228.0184	1.14
11.04	C10 H18 O7 S	281.0700	1.40
11.33	C6 H11 N O7 S	240.0184	2.70
12.56	C10 H18 O8 S	297.0649	0.57
12.59	C8 H16 O6 S	239.0595	0.55
12.66	C8 H16 O5 S	223.0645	0.93
12.74	C8 H17 N O8 S	286.0602	0.84
12.82	C8 H16 O6 S	239.0596	0.63
13.03	C9 H18 O7 S	225.0802	0.58
13.15	C10 H18 O8 S	297.0650	0.93
13.21	C7 H13 N O9 S	286.0240	0.55
13.39	C8 H9 N O7 S	262.0026	5.71
13.47	C8 H16 O6 S	239.0596	0.81
13.68	C12 H10 O5 S	265.0177	1.55
13.99	C9 H18 O5 S	237.0802	0.46
14.40	C11 H20 O8 S	311.0806	1.00
15.41	C9 H16 O6 S	251.0594	0.89
15.59	C9 H9 N O7 S	274.0028	7.43
16.18	C9 H18 O5 S	237.0802	0.62
16.66	C13 H12 O5 S	279.0333	3.21
16.77	C9 H18 O6 S	253.0751	0.89
17.01	C10 H11 N O7 S	288.0183	0.59
17.42	C7 H16 O3 S	179.0747	2.14
17.58	C7 H16 O4 S	195.0696	1.52

17.75	C11 H20 O5 S	263.0957	1.38
17.88	C10 H20 O6 S	267.0908	1.02
17.95	C7 H12 O9 S	271.0127	0.96
18.03	C10 H20 O5 S	251.0959	0.56
18.12	C10 H17 N O7 S	294.0652	6.62
18.45	C10 H20 O6 S	267.0908	0.40
18.55	C10 H20 O6 S	267.0908	0.39
18.78	C8 H16 O3 S	191.0748	0.72
18.95	C7 H16 O4 S	195.0697	0.55
19.27	C7 H15 N O7 S	256.0497	0.70
20.04	C11 H22 O5 S	265.1116	0.83
20.10	C10 H17 N O7 S	294.0656	0.42
20.27	C10 H17 N O7 S	294.0656	1.91
20.46	C10 H17 N O7 S	294.0656	0.74
20.52	C11 H22 O6 S	281.1066	0.75
20.56	C12 H22 O5 S	277.1117	1.49
20.70	C8 H18 O4 S	209.0854	0.58
21.03	C10 H17 N O7 S	294.0656	0.89
21.11	C11 H22 O6 S	281.1066	0.60
21.27	C10 H17 N O7 S	294.0656	0.46
21.73	C8 H18 O4 S	209.0853	3.25
21.84	C10 H19 N O9 S	328.0711	0.37
22.09	C8 H17 N O7 S	270.0654	0.36
22.37	C10 H22 O5 S	253.1116	0.77
22.59	C12 H24 O5 S	279.1273	0.71
22.97	C12 H24 O5 S	279.1273	0.33

23.59	C9 H20 O4 S	223.1011	0.60
23.67	C9 H20 O4 S	223.1010	0.26
24.04	C9 H20 O4 S	223.1010	0.37
24.30	C10 H22 O4 S	237.1167	1.52
24.59	C13 H26 O5 S	293.1431	0.47
24.86	C13 H26 O5 S	293.1431	0.26
25.28	C10 H22 O4 S	237.1167	0.39
25.88	C10 H22 O4 S	237.1167	0.40
25.96	C14 H28 O6 S	323.1536	0.26
26.01	C10 H21 N O7 S	298.0967	0.24
26.06			0.26
26.11	C12 H26 O5 S	281.1430	0.14
27.30			1.45
27.58	C11 H24 O4 S	251.1324	0.51
28.01	C15 H30 O5 S	321.1743	0.34
28.22	C14 H30 O4 S	293.1794	0.19

Table S 11.5-4: Quantification of all OSs in the Taunus Observatory (TO) 1 ambient filter sample (11.12.2021, daytime) sorted by ascending retention time. The chemical formula, retention time (RT), mass-to-charge ratio (m/z), and OS concentration (ng/m^3) are given for each OS.

RT (min)	Chemical formula	m/z	Conc. ng/m^3
2.28	C3 H6 O6 S	168.9813	1.13
2.36	C5 H8 O7 S	210.9918	1.10
2.59	C4 H8 O5 S	167.0019	0.40
3.02	C4 H8 O5 S	167.0020	0.29
3.24	C6 H10 O6 S	209.0124	1.10
3.49	C5 H10 O5 S	181.0175	0.69
3.67	C7 H10 O8 S	253.0023	0.08
3.77	C6 H10 O7 S	225.0074	0.27
4.10	C4 H8 O6 S	182.9968	0.37

4.18	C6 H10 O6 S	209.0125	0.43
4.56	C6 H10 O6 S	209.0123	0.54
4.93	C7 H12 O6 S	223.0281	0.89
4.99	C6 H10 O7 S	225.0073	0.58
5.06	C5 H10 O6 S	197.0124	0.37
5.41	C5 H10 O6 S	197.0123	0.32
5.43	C7 H12 O6 S	223.0280	0.36
5.46	C7 H12 O6 S	223.0280	0.27
5.56	C6 H10 O6 S	209.0124	0.28
5.67	C6 H12 O5 S	195.0331	0.35
5.90	C10 H19 N O10 S	344.0657	0.91
5.96	C7 H14 O7 S	223.0280	0.36
6.12	C7 H12 O7 S	239.0228	0.49
6.19	C6 H12 O5 S	195.0332	0.66
6.56	C7 H14 O7 S	241.0387	1.46
6.69	C5 H10 O6 S	197.0122	0.36
6.85	C6 H13 N O8 S	258.0288	0.38
6.98	C9 H14 O8 S	281.0334	1.02
7.17	C7 H8 O3 S	171.0122	0.43
7.31	C9 H14 O8 S	281.0335	0.91
7.39	C8 H14 O7 S	253.0386	0.82
7.52	C7 H12 O6 S	223.0282	0.42
7.57	C10 H16 O7 S	279.0542	0.65
7.62	C7 H12 O8 S	255.0180	0.51
7.85	C9 H16 O6 S	251.0594	0.40
7.91	C8 H12 O8 S	223.0282	0.61
7.96	C7 H14 O8 S	257.0335	0.58
8.30	C10 H16 O7 S	279.0543	0.77
8.40	C7 H14 O5 S	209.0488	0.66
8.61	C7 H14 O5 S	209.0488	0.60

8.68	C8 H14 O7 S	253.0386	0.45
8.91	C8 H14 O8 S	269.0336	0.58
9.19	C7 H14 O5 S	209.0487	0.57
9.24	C9 H14 O8 S	281.0336	0.44
9.47	C9 H14 O5 S	233.0488	0.52
9.52	C9 H18 O7 S	269.0702	0.52
9.69	C9 H16 O6 S	251.0593	0.53
10.11	C7 H14 O6 S	225.0438	0.63
10.84	C9 H15 N O9 S	312.0393	0.61
11.06	C5 H12 O4 S	167.0382	0.74
12.40	C9 H16 O6 S	251.0594	0.73
12.56	C10 H14 O6 S	261.0437	0.50
13.04	C11 H18 O7 S	293.0701	0.54
13.09	C7 H15 N O4 S	208.0648	0.58
13.15	C7 H13 N O9 S	242.0340	0.78
14.82	C10 H18 O6 S	265.0752	1.13
15.41	C6 H14 O4 S	181.0539	0.86
17.00	C10 H17 N O8 S	310.0601	0.68
18.15	C10 H17 N O7 S	294.0653	6.07
20.28	C10 H17 N O7 S	294.0654	2.35
21.05	C10 H17 N O7 S	294.0654	0.72
21.28	C10 H17 N O7 S	294.0654	0.47
21.77	C8 H18 O4 S	209.0852	1.10

Table S 11.5-5: Quantification of all OSs in the Taunus Observatory (TO) 2 ambient filter sample (14.01.2022, night-time) sorted by ascending retention time. The chemical formula, retention time (RT), mass-to-charge ratio (m/z), and OS concentration (ng/m³) are given for each OS.

RT (min)	Chemical formula	m/z	Conc. ng/m ³
2.28			0.11
2.36	C5 H8 O7 S	210.9918	0.29
2.59			0.12
2.97	C4 H8 O5 S	167.0020	0.20
3.12	C3 H8 O4 S	139.0070	0.67
3.50	C3 H8 O4 S	139.0070	3.31
4.04	C5 H10 O5 S	181.0175	0.23
4.55	C6 H10 O6 S	209.0123	0.30
5.67	C6 H12 O5 S	195.0331	1.41
5.59	C5 H10 O5 S	181.0176	0.42
5.90	C6 H12 O5 S	195.0332	1.89
6.19	C6 H12 O5 S	195.0332	1.56
6.24	C6 H14 O5 S	197.0488	1.82
6.49	C4 H10 O4 S	153.0225	0.40
6.55	C7 H14 O7 S	241.0387	0.67
6.72	C5 H10 O6 S	197.0122	0.51
6.83	C5 H10 O4 S	165.0226	0.39
7.32	C6 H12 O6 S	211.0281	0.44
7.38	C8 H14 O7 S	253.0386	0.46
7.97	C7 H14 O5 S	209.0487	0.47
8.18	C7 H16 O5 S	211.0643	0.45
8.28	C9 H16 O7 S	267.0543	0.54
8.39	C7 H14 O5 S	209.0488	1.01
8.81	C7 H14 O5 S	209.0489	0.48
9.18	C7 H14 O5 S	209.0487	0.66
9.31	C5 H12 O4 S	167.0383	0.78
9.44	C5 H12 O4 S	167.0383	0.86

9.81	C7 H14 O6 S	225.0438	0.46
10.09	C6 H12 O4 S	179.0384	1.03
10.48	C5 H12 O4 S	167.0382	0.60
10.91	C6 H12 O4 S	179.0384	0.55
11.07	C5 H12 O4 S	167.0382	0.73
11.16	C8 H16 O5 S	223.0644	0.47
11.24			0.51
11.35	C10 H18 O7 S	281.0700	0.47
11.51	C8 H16 O5 S	223.0645	0.70
12.43	C8 H16 O6 S	239.0595	0.53
13.14	C6 H14 O4 S	181.0540	0.74
13.46	C6 H14 O4 S	181.0540	0.69
13.80	C6 H14 O4 S	181.0540	0.86
13.97	C9 H18 O5 S	237.0801	0.49
14.28	C6 H14 O4 S	181.0540	1.06
14.37	C9 H18 O5 S	237.0799	0.60
14.56	C9 H18 O5 S	237.0801	0.51
14.79	C10 H18 O6 S	265.0752	0.43
14.86	C6 H14 O4 S	181.0540	0.46
14.92	C9 H18 O5 S	237.0801	0.62
15.42	C6 H14 O4 S	181.0539	0.58
17.42	C10 H20 O5 S	251.0959	0.65
17.65	C7 H16 O4 S	195.0696	0.95
17.57	C10 H20 O5 S	251.0958	0.55
17.89	C10 H20 O6 S	267.0907	0.40
18.08	C10 H20 O5 S	251.0959	1.01
18.19	C10 H17 N O7 S	294.0653	1.04
18.97	C7 H16 O4 S	195.0696	0.42
19.94	C45 H72 O5 S	723.5033	1.78
20.06	C11 H22 O5 S	265.1115	0.36

20.30	C10 H17 N O7 S	294.0654	0.51
20.77	C8 H18 O4 S	209.0852	0.52
21.10	C8 H18 O4 S	209.0852	0.30
21.78	C8 H18 O4 S	209.0852	0.52
23.27	C9 H20 O4 S	223.1009	0.51
23.50	C9 H20 O4 S	223.1010	0.51
24.06	C9 H20 O4 S	223.1010	0.29

Table S 11.5-6: Quantification of all OSs in the Taunus Observatory (TO) 3 ambient filter sample (28.02.2022, night-time) sorted by ascending retention time. The chemical formula, retention time (RT), mass-to-charge ratio (m/z), and OS concentration (ng/m^3) are given for each OS.

RT (min)	Chemical formula	m/z	Conc. ng/m^3
2.28	C3 H6 O6 S	168.9813	1.94
2.36	C5 H8 O7 S	210.9918	1.15
2.54	C4 H8 O5 S	167.0019	0.06
2.59	C6 H10 O6 S	209.0124	0.42
2.99	C4 H8 O5 S	167.0020	0.26
3.19	C4 H8 O6 S	182.9967	1.06
3.49	C6 H12 O7 S	227.0230	3.42
3.77	C6 H10 O7 S	225.0074	0.20
4.07	C4 H8 O6 S	182.9968	0.65
4.18	C6 H10 O6 S	209.0125	0.36
4.56	C6 H10 O6 S	209.0123	0.58
4.93	C7 H12 O6 S	223.0281	0.34
4.99	C6 H10 O7 S	225.0073	0.66
5.06	C5 H10 O6 S	197.0124	0.39
5.39	C5 H10 O6 S	197.0123	0.38
5.68	C6 H14 O5 S	197.0488	1.08
5.90	C6 H12 O6 S	211.0282	1.83
6.10	C7 H12 O7 S	239.0228	0.34
6.18	C6 H12 O5 S	195.0332	1.59

6.24	C6 H14 O5 S	197.0488	1.09
6.31	C7 H14 O5 S	209.0488	0.40
6.55	C7 H14 O7 S	241.0387	2.26
6.98	C8 H14 O6 S	237.0437	2.67
7.27	C8 H6 O5 S	212.9864	0.44
7.31	C6 H12 O6 S	211.0281	0.85
7.38	C8 H14 O7 S	253.0386	0.50
7.52	C4 H9 N O7 S	214.0026	0.94
8.20	C9 H16 O7 S	267.0543	0.45
8.30	C8 H14 O6 S	237.0436	0.83
8.39	C7 H14 O5 S	209.0488	1.16
8.61	C7 H14 O5 S	209.0488	1.04
8.79	C7 H16 O6 S	209.0488	0.53
9.18	C7 H14 O5 S	209.0487	0.63
9.27	C9 H16 O5 S	235.0647	0.94
10.87	C6 H12 O4 S	179.0384	0.53
11.05	C5 H12 O4 S	167.0382	0.53
11.24	C8 H16 O5 S	223.0644	0.57
11.35	C10 H18 O7 S	281.0700	0.55
11.50	C14 H20 O7 S	331.0855	0.82
12.03	C8 H16 O5 S	223.0645	0.54
12.41	C9 H16 O6 S	251.0594	0.68
12.51	C8 H16 O6 S	239.0595	0.53
13.03	C11 H18 O7 S	293.0701	0.78
13.09	C12 H20 O6 S	291.0908	0.67
13.59	C8 H16 O6 S	239.0595	0.94
14.30	C6 H14 O4 S	181.0540	0.64
14.35	C6 H14 O4 S	181.0540	0.57
14.41	C11 H20 O8 S	311.0808	0.57
14.53	C9 H18 O5 S	237.0801	0.52

14.73	C10 H18 O5 S	249.0801	0.58
14.82	C10 H18 O6 S	265.0752	0.74
14.92	C8 H16 O6 S	239.0593	0.64
15.40	C6 H14 O4 S	181.0539	0.61
15.68	C10 H18 O5 S	249.0801	0.49
17.02	C10 H20 O5 S	251.0958	0.51
17.23	C10 H20 O5 S	251.0959	0.44
17.42	C10 H20 O5 S	251.0958	0.52
17.64	C7 H16 O4 S	195.0696	0.73
18.06	C10 H20 O5 S	251.0959	0.44
18.15	C10 H17 N O7 S	294.0653	5.06
18.97	C7 H16 O4 S	195.0696	0.39
20.08	C11 H22 O5 S	265.1115	0.43
20.28	C10 H17 N O7 S	294.0654	1.86
21.05	C10 H17 N O7 S	294.0654	1.07
21.29	C10 H17 N O7 S	294.0654	0.38
21.78	C8 H18 O4 S	209.0852	0.44
22.38	C12 H24 O5 S	279.1272	0.32
24.10	C9 H20 O4 S	223.1010	0.20

Table S 11.5-7: Summary of the OS fraction in OM across different locations, quantified by various techniques.

Direct quantification				
location	Particle size	OS fraction in OM (%)	Instruments	Reference
Beijing, China	PM _{2.5}	0.31	HPLC/MS	Wang et al., 2018 ²
Shanghai, China	PM _{2.5}	0.62	UPLC/ToF-MS	Wang et al., 2021 ³
Beijing (Winter), China	PM _{2.5}	0.7	UHPLC/Orbitrap-MS	Ma et al., 2022 ⁴
Xi'an (Winter), China	PM _{2.5}	1.4	UHPLC/ToF-MS	Glasius et al., 2022 ⁵

4 sites, Asia	PM _{2.5}	1.4	UPLC/ ToF-MS	Stone et al., 2012 ⁶
Beijing, China	PM ₁	2	FIGAERO ToF-CIMS	Le Breton et al., 2018 ⁷
19 sites, USA	PM _{2.5}	3.22	UPLC/ToF-MS	Chen et al., 2021 ⁸
Bohai and Yellow Sea, China	PM _{2.5}	3.47	UHPLC/Orbitrap-MS	Wang et al., 2023 ⁹
Beijing (Summer), China	PM _{2.5}	4	UHPLC/Orbitrap-MS	Ma et al., 2022 ⁴
Xi'an (Summer), China	PM _{2.5}	7	UHPLC/ToF-MS	Glasius et al., 2022 ⁵
Indirect quantification				
Fairbanks, USA	PM _{2.5}	1.29	XRF, IC	Shakya et al., 2013 ¹⁰
Hongkong, China	PM ₁	5 (Minimum estimation)	HR-ToF-AMS	Huang et al., 2015 ¹¹
334 sites, USA	PM _{2.5}	7.5	XRF, IC	Shakya et al., 2015 ¹²
12 sites, USA	PM _{2.5}	8.12	XRF, IC	Tolocka et al., 2012 ¹³
Riverside, USA	PM _{1.5}	12	AMS, IC	Farmer et al., 2010 ¹⁴
19 sites, USA	PM _{2.5}	14.51	ICP–OES, IC	Chen et al., 2021 ⁸
Beijing, China	PM _{2.5}	25.05	XRF, IC	He et al., 2001 ¹⁵
K-pusztá, Hungary	PM _{2.5}	29	XRF, IC	Lukács et al., 2009 ¹⁶
K-pusztá, Hungary	PM _{2.5}	30	XRF, IC	Surratt et al., 2008 ¹⁷

Table S 11.5-8: Compound Discoverer workflow for the UHPLC HRMS sequence.

Processing node 42: Input Files

Input Data:

- File Name(s) (Hidden):

Processing node 2: Select Spectra

1. Spectrum Properties Filter:

- Lower RT Limit: 1
- Upper RT Limit: 18.5
- First Scan: 0
- Last Scan: 0
- Ignore Specified Scans: (not specified)
- Lowest Charge State: 0
- Highest Charge State: 0
- Min. Precursor Mass: 50 Da
- Max. Precursor Mass: 5000 Da
- Total Intensity Threshold: 0
- Minimum Peak Count: 1

2. Scan Event Filters:

- Mass Analyzer: Is FTMS
- MS Order: Any
- Activation Type: Is HCD
- Min. Collision Energy: 0
- Max. Collision Energy: 1000
- Scan Type: Any
- Polarity Mode: Is -
- MS1 Mass Range: (not specified)

- FAIMS CV: (not specified)

3. Peak Filters:

- S/N Threshold (FT-only): 5

4. Replacements for Unrecognized Properties:

- Unrecognized Charge Replacements: 1
- Unrecognized Mass Analyzer Replacements: ITMS
- Unrecognized MS Order Replacements: MS2
- Unrecognized Activation Type Replacements: HCD
- Unrecognized Polarity Replacements: -
- Unrecognized MS Resolution@200 Replacements: 60000
- Unrecognized MSn Resolution@200 Replacements: 30000

5. General Settings:

- Precursor Selection: Use MS1 Precursor
- Use Isotope Pattern in Precursor Reevaluation: True
- Provide Profile Spectra: Automatic
- Store Chromatograms: False

Processing node 23: Align Retention Times (ChromAlign)

1. General Settings:

- Reference File: 20220805_H_HCl1_neg01

Processing node 24: Detect Compounds

1. General Settings:

- Mass Tolerance [ppm]: 4 ppm

- Min. Peak Intensity: 10000
- Min. # Scans per Peak: 5
- Use Most Intense Isotope Only: False

2. Trace Detection:

- Max. Number of Gaps to Correct: 2
- Min. Number of Adjacent Non-Zeros: 2

3. Peak Detection:

- Chromatographic S/N Threshold: 1.5
- Remove Baseline: False
- Gap Ratio Threshold: 0.35
- Max. Peak Width [min]: 0.2
- Min. Relative Valley Depth: 0.1

4. Isotope Pattern Detection:

- Group Isotopes for: Br; Cl
- Use Peak Quality for Isotope Grouping: True
- Filter out Features with Bad Peaks Only: True
- Zig-Zag Index Threshold: 0.2
- Jaggedness Threshold: 0.4
- Modality Threshold: 0.9
- Remove Potentially False Positive Isotopes: True

5. Compound Detection:

- Ions: [2M-H]-1; [M-H]-1; [M-H-H₂O]-1
- Base Ions: [M-H]-1
- Remove Singlets: True

6. AcquireX Settings:

- Detect Persistent Background Ions: False

Processing node 4: Group Compounds

1. General Settings:

- Mass Tolerance: 2 ppm
- RT Tolerance [min]: 0.1
- Align Peaks: False
- Preferred Ions: [M-H]⁻1
- Area Integration: Most Common Ion

2. Peak Rating Contributions:

- Area Contribution: 3
- CV Contribution: 1
- FWHM to Base Contribution: 5
- Jaggedness Contribution: 5
- Modality Contribution: 5
- Zig-Zag Index Contribution: 5

3. Peak Rating Filter:

- Peak Rating Threshold: 3
- Number of Files: 1

Processing node 41: Fill Gaps

1. General Settings:

- Mass Tolerance: 2 ppm
- S/N Threshold: 1.5
- Use Real Peak Detection: True
- Apply Restrictive Gap Filling: True

Processing node 18: Mark Background Compounds

1. General Settings:

- Max. Sample/Blank: 5
- Max. Blank/Sample: 0
- Hide Background: True

Processing node 11: Assign Compound Annotations

1. General Settings:

- Mass Tolerance: 1 ppm

2. Data Sources:

- Data Source #1: Predicted Compositions
- Data Source #2: mzCloud Search
- Data Source #3: ChemSpider Search
- Data Source #4: (not specified)
- Data Source #5: (not specified)
- Data Source #6: (not specified)
- Data Source #7: (not specified)

3. Scoring Rules:

- Use mzLogic: True
- Use Spectral Distance: True
- SFit Threshold: 20
- SFit Range: 20

4. Reprocessing:

- Clear Names: False

Processing node 38: Search mzCloud

1. General Settings:

- Compound Classes: All
- Precursor Mass Tolerance: 10 ppm
- FT Fragment Mass Tolerance: 10 ppm
- IT Fragment Mass Tolerance: 0.4 Da
- Library: Autoprocessed; Reference
- Post Processing: Recalibrated
- Max. # Results: 10
- Annotate Matching Fragments: False
- Search MSn Tree: False

2. DDA Search:

- Identity Search: HighChem HighRes
- Match Activation Type: True
- Match Activation Energy: Match with Tolerance
- Activation Energy Tolerance: 20
- Apply Intensity Threshold: True
- Similarity Search: None
- Match Factor Threshold: 60

3. DIA Search:

- Use DIA Scans for Search: False
- Max. Isolation Width [Da]: 500
- Match Activation Type: False
- Match Activation Energy: Any
- Activation Energy Tolerance: 100

- Apply Intensity Threshold: False
- Match Factor Threshold: 20

Processing node 5: Predict Compositions

1. Prediction Settings:

- Mass Tolerance: 2 ppm
- Min. Element Counts: C H
- Max. Element Counts: C90 H190 Br3 Cl4 N4 O20 P S3
- Min. RDBE: 0
- Max. RDBE: 40
- Min. H/C: 0.1
- Max. H/C: 3.5
- Max. # Candidates: 10
- Max. # Internal Candidates: 200

2. Pattern Matching:

- Intensity Tolerance [%]: 30
- Intensity Threshold [%]: 0.1
- S/N Threshold: 5
- Min. Spectral Fit [%]: 30
- Min. Pattern Cov. [%]: 90
- Use Dynamic Recalibration: True

3. Fragments Matching:

- Use Fragments Matching: True
 - Mass Tolerance: 1 ppm
 - S/N Threshold: 5
-

Processing node 34: Merge Features

1. Peak Consolidation:

- Mass Tolerance: 2 ppm
- RT Tolerance [min]: 0.05

Table S 11.5-9: CD-workflow for the UHPLC-CAD-HRMS sequence.

Processing node 42: Input Files

Input Data:

- File Name(s) (Hidden):
-

Processing node 2: Select Spectra

1. Spectrum Properties Filter:

- Lower RT Limit: 1
- Upper RT Limit: 38.5
- First Scan: 0
- Last Scan: 0
- Ignore Specified Scans: (not specified)
- Lowest Charge State: 0
- Highest Charge State: 0
- Min. Precursor Mass: 50 Da
- Max. Precursor Mass: 5000 Da
- Total Intensity Threshold: 0
- Minimum Peak Count: 1

2. Scan Event Filters:

- Mass Analyzer: Is FTMS

- MS Order: Any
- Activation Type: Is HCD
- Min. Collision Energy: 0
- Max. Collision Energy: 1000
- Scan Type: Any
- Polarity Mode: Is -
- MS1 Mass Range: (not specified)
- FAIMS CV: (not specified)

3. Peak Filters:

- S/N Threshold (FT-only): 5

4. Replacements for Unrecognized Properties:

- Unrecognized Charge Replacements: 1
- Unrecognized Mass Analyzer Replacements: ITMS
- Unrecognized MS Order Replacements: MS2
- Unrecognized Activation Type Replacements: HCD
- Unrecognized Polarity Replacements: -
- Unrecognized MS Resolution@200 Replacements: 60000
- Unrecognized MSn Resolution@200 Replacements: 30000

5. General Settings:

- Precursor Selection: Use MS1 Precursor
- Use Isotope Pattern in Precursor Reevaluation: True
- Provide Profile Spectra: Automatic
- Store Chromatograms: False

Processing node 23: Align Retention Times (ChromAlign)

1. General Settings:

- Reference File: 20231120_40RT_ambient_SPE_Handan_20181018D_CAD25_neg00

Processing node 24: Detect Compounds

1. General Settings:

- Mass Tolerance [ppm]: 4 ppm
- Min. Peak Intensity: 10000
- Min. # Scans per Peak: 5
- Use Most Intense Isotope Only: False

2. Trace Detection:

- Max. Number of Gaps to Correct: 2
- Min. Number of Adjacent Non-Zeros: 2

3. Peak Detection:

- Chromatographic S/N Threshold: 1.5
- Remove Baseline: False
- Gap Ratio Threshold: 0.35
- Max. Peak Width [min]: 0.2
- Min. Relative Valley Depth: 0.1

4. Isotope Pattern Detection:

- Group Isotopes for: Br; Cl
- Use Peak Quality for Isotope Grouping: True
- Filter out Features with Bad Peaks Only: True
- Zig-Zag Index Threshold: 0.2
- Jaggedness Threshold: 0.4
- Modality Threshold: 0.9
- Remove Potentially False Positive Isotopes: True

5. Compound Detection:

- Ions: [2M-H]-1; [M-CO2-H]-1; [M-H]-1; [M-H-H2O]-1
- Base Ions: [M-H]-1
- Remove Singlets: True

6. AcquireX Settings:

- Detect Persistent Background Ions: False

Processing node 4: Group Compounds

1. General Settings:

- Mass Tolerance: 2 ppm
- RT Tolerance [min]: 0.1
- Align Peaks: False
- Preferred Ions: [M-H]-1
- Area Integration: Most Common Ion

2. Peak Rating Contributions:

- Area Contribution: 3
- CV Contribution: 1
- FWHM to Base Contribution: 5
- Jaggedness Contribution: 5
- Modality Contribution: 5
- Zig-Zag Index Contribution: 5

3. Peak Rating Filter:

- Peak Rating Threshold: 3
 - Number of Files: 1
-

Processing node 41: Fill Gaps

1. General Settings:

- Mass Tolerance: 2 ppm
 - S/N Threshold: 1.5
 - Use Real Peak Detection: True
 - Apply Restrictive Gap Filling: True
-

Processing node 18: Mark Background Compounds

1. General Settings:

- Max. Sample/Blank: 5
 - Max. Blank/Sample: 0
 - Hide Background: True
-

Processing node 11: Assign Compound Annotations

1. General Settings:

- Mass Tolerance: 1 ppm

2. Data Sources:

- Data Source #1: Predicted Compositions
- Data Source #2: mzCloud Search
- Data Source #3: ChemSpider Search
- Data Source #4: (not specified)
- Data Source #5: (not specified)
- Data Source #6: (not specified)
- Data Source #7: (not specified)

3. Scoring Rules:

- Use mzLogic: True
- Use Spectral Distance: True
- SFit Threshold: 20
- SFit Range: 20

4. Reprocessing:

- Clear Names: False

Processing node 36: Search ChemSpider

1. Search Settings:

- Database(s):
 - EAWAG Biocatalysis/Biodegradation Database
 - Nature Chemistry
 - Sigma-Aldrich
- Search Mode: By Formula or Mass
- Mass Tolerance: 2 ppm
- Max. # of results per compound: 100
- Max. # of Predicted Compositions to be searched per Compound: 3
- Result Order (for Max. # of results per compound): Order By Reference Count (DESC)

2. Predicted Composition Annotation:

- Check All Predicted Compositions: False

Processing node 38: Search mzCloud

1. General Settings:

- Compound Classes: All

- Precursor Mass Tolerance: 10 ppm
- FT Fragment Mass Tolerance: 10 ppm
- IT Fragment Mass Tolerance: 0.4 Da
- Library: Autoprocessed; Reference
- Post Processing: Recalibrated
- Max. # Results: 10
- Annotate Matching Fragments: False
- Search MSn Tree: False

2. DDA Search:

- Identity Search: HighChem HighRes
- Match Activation Type: True
- Match Activation Energy: Match with Tolerance
- Activation Energy Tolerance: 20
- Apply Intensity Threshold: True
- Similarity Search: None
- Match Factor Threshold: 60

3. DIA Search:

- Use DIA Scans for Search: False
- Max. Isolation Width [Da]: 500
- Match Activation Type: False
- Match Activation Energy: Any
- Activation Energy Tolerance: 100
- Apply Intensity Threshold: False
- Match Factor Threshold: 20

Processing node 5: Predict Compositions

1. Prediction Settings:

- Mass Tolerance: 2 ppm
- Min. Element Counts: C H
- Max. Element Counts: C90 H190 Br3 Cl4 N4 O20 P S3
- Min. RDBE: 0
- Max. RDBE: 40
- Min. H/C: 0.1
- Max. H/C: 4.5
- Max. # Candidates: 10
- Max. # Internal Candidates: 200

2. Pattern Matching:

- Intensity Tolerance [%]: 30
- Intensity Threshold [%]: 0.1
- S/N Threshold: 5
- Min. Spectral Fit [%]: 30
- Min. Pattern Cov. [%]: 90
- Use Dynamic Recalibration: True

3. Fragments Matching:

- Use Fragments Matching: True
- Mass Tolerance: 1 ppm
- S/N Threshold: 5

Processing node 34: Merge Features

1. Peak Consolidation:

- Mass Tolerance: 2 ppm
- RT Tolerance [min]: 0.05

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12 Personal list of publications

12.1 Journal articles

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12.2 Scientific conferences

Oral presentations

Hildmann, S.; Meller, B.; Engert, J.; Hoffmann, T. Aerosol chemistry, ATTO Workshop, Manaus, Brazil, 16-18.9.2025

Hildmann, S.; Brill, S.; Kremper, L.; Pöhlker, C.; Hoffmann, T. Assessing size-resolved molecular characteristics of primary and secondary organic aerosols in the Amazon rainforest by high-resolution Orbitrap mass spectrometry, EAC, Lecce, Italy, 31.8-5.9.2025

Hildmann, S.; Kremper, L.; Pöhlker, C.; Sà, M.; Solci, M.C.; Hoffmann, T. Size resolver molecular characterization of organic aerosols in the Amazon rainforest by high-resolution Orbitrap mass spectrometry, EAC, Tampere, Finland, 25-30.8.2024

Hildmann, S.; Siebecker, J.; Klink, D.; Karbach, N.; Hoffmann, T. Accessing the chemical information from so far uncharacterised BVOC emissions at hard-to-reach locations by drone sampling and chiral GC-HR-Orbitrap-MS analysis, Doktorandenseminar of the AK Separation Science (GDCh), Hohenroda, Germany, 7-9.1.2024

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Hildmann, S.; Kremper, L.; Pöhlker, C.; Sà, M.; Solci, M.C.; Hoffmann, T. Detailed molecular characterization of size-resolved organic aerosols in the Amazon rainforest by high-resolution Orbitrap mass spectrometry, ANAKON, Leipzig, Germany, 10-15.3.2025

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