

OPTIMIZATION AND APPLICATION OF NOVEL METHODS TO SEPARATE, COLLECT AND
ANALYSE ULTRAFINE PARTICLES IN AIR

Kumulative Dissertation

Zur Erlangung des akademischen Grades einer Doktorin der
Naturwissenschaften (Dr. rer. nat.) in der Bayreuther
Graduiertenschule für Mathematik und Naturwissenschaften (BayNAT)
der Universität Bayreuth

vorgelegt von

Elisabeth Eckenberger
aus München

Bayreuth, 2026

Die vorliegende Arbeit wurde in der Zeit von (03/2021) bis (02/2026) in Bayreuth am Lehrstuhl Atmosphärische Chemie unter Betreuung von Frau Professorin Dr. Anke Nölscher angefertigt.

Vollständiger Abdruck der von der Bayreuther Graduiertenschule für Mathematik und Naturwissenschaften (BayNAT) der Universität Bayreuth genehmigten Dissertation zur Erlangung des akademischen Grades einer Doktorin der Naturwissenschaften (Dr. rer. nat.).

Form der Dissertation:	Kumulative Dissertation
Dissertation eingereicht am:	21.02.2026
Zulassung durch das Leitungsgremium:	25.03.2026
Wissenschaftliches Kolloquium:	14.07.2026

Amtierender Direktor: Prof. Dr. Jürgen Senker

Prüfungsausschuss:

Prof. Dr. Anke Nölscher (Gutachterin)

Prof. Dr. Eva Lehdorff (Gutachterin)

Prof. Dr. Martin Obst (Vorsitz)

Prof. Dr. Andreas Held

Die vorliegende Arbeit ist als Kumulative Dissertation in englischer Sprache verfasst.

Teile der Arbeit sind bereits in den folgenden Publikationen erschienen:

Performance evaluation of four cascade impactors for airborne ultrafine-particle (UFP) collection: the influence of particle type, concentration, mass, and chemical nature

Eckenberger, E., Mittereder, A., Gawlitta, N., Schnelle-Kreis, J., Sklorz, M., Brüggemann, D., Zimmermann, R., & Nölscher, A. C. (2025)

Aerosol Research, 3, 45–64

<https://doi.org/10.5194/ar-3-45-2025>

Sodium Thiosulfate-Coated Ceramic Denuders for Ozone Removal in Ultrafine Particle Sampling

Eckenberger, E., Mittereder, A., Gawlitta, N., Sklorz, M., Brüggemann, D., Zimmermann, R., & Nölscher, A. C. (2026)

Atmospheric Measurement Techniques, 19(12), 4035–4047

<https://doi.org/10.5194/amt-19-4035-2026>

About the Variability of Tire and Road Wear Marker Components in Air: From Emissions to Atmospheric Deposition

Eckenberger, E., Younes, M., Mayer, T., Loeber, M., Bondorf, L., Schripp, T., Kernchen, S., Laforsch, C., & Nölscher, A. C. (2026)

Environ. Sci. Technol. 60(2), 2023–2036

<https://doi.org/10.1021/acs.est.5c12735>

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Abstract

Airborne ultrafine particles (UFP, ≤ 100 nm) are a highly dynamic fraction of particulate matter in the atmosphere. Their high number concentrations, small size, large surface area, and chemical heterogeneity render UFP relevant for both climate and toxicology. At the same time, these properties make it challenging to reliably sample and chemically analyse UFP, while evaporation, adsorption, and oxidation during sampling can further introduce substantial artefacts. As a result, understanding molecular fingerprints, sources, atmospheric transformations, and impacts of UFP is hindered, despite increasing evidence of their importance for air quality, human and environmental health, and climate.

In this thesis, four interrelated studies are presented that together aim to address one overarching problem: how measurement methodology, atmospheric pathways, and source-specific composition determine the observed molecular fingerprint of UFP.

Firstly, a systematic comparison of four cascade impactors was conducted, demonstrating that design-specific characteristics can significantly bias the measured chemical composition of UFP. These results emphasize the need for greater awareness of artefacts arising from different UFP-sampling approaches. Secondly, an O₃ denuder was developed and validated that selectively removes O₃ upstream of the collection substrate, thereby reducing in-situ oxidation of UFP-bound compounds such as polycyclic aromatic hydrocarbons (PAH) and tyre additives. Thirdly, with such artefacts better constrained, a combined impactor–denuder setup together with Two-Dimensional Gas Chromatography coupled to Time-of-Flight Mass Spectrometry (GC×GC–TOFMS) was applied to resolve the molecular fingerprint of ambient UFP. The resulting dataset revealed distinct seasonal and episodic patterns, was validated against an established High-Performance Liquid Chromatography coupled to a Fluorescence Detector (HPLC–FLD) method, and demonstrated how source- and transport-related processes are reflected in UFP chemistry. Fourthly, the previous methodologies were applied to the emerging field of non-exhaust traffic emissions: tyre-related particle markers were tracked from tyre materials through abrasion emissions to atmospheric UFP and deposition samples. The observed progressive oxidation of antiozonant markers exemplifies both their diagnostic potential and the limitations for quantitative source apportionment.

Together, this thesis establishes a workflow from artefact-aware UFP-sampling and chemical analysis to source- and process-oriented interpretation. It is concluded that chemical UFP characterisation requires (i) quantifying, mitigating, and accounting for sampling-induced artefacts and (ii) non-target molecular analysis of fingerprints or the analysis of targeted chemical marker compounds. This integrated approach reduces sampling- and oxidation-related artefacts, enables chemical non-target fingerprint analysis, and targeted organic marker quantification, thereby improving the methodological basis for source- and process-oriented interpretation of chemical UFP composition.

Zusammenfassung

Ultrafeine Partikel (UFP, ≤ 100 nm) in der Luft sind ein hochdynamischer Anteil der Partikel in der Atmosphäre. Aufgrund ihrer hohen Anzahl, geringen Größe, großen Oberfläche und chemischen Heterogenität sind UFP sowohl für das Klima als auch für die Toxikologie von Bedeutung. Gleichzeitig erschweren diese Eigenschaften eine zuverlässige Probenahme und chemische Analyse von UFP, während Verdunstung, Adsorption und Oxidation während der Probennahme weitere erhebliche Artefakte verursachen können. Infolgedessen wird das Verständnis der molekularen Fingerabdrücke, Quellen, atmosphärischen Umwandlungen und Auswirkungen von UFP trotz der zunehmenden Bedeutung dieser Partikel für die Luftqualität, die Gesundheit von Mensch und Umwelt sowie das Klima erschwert.

In dieser Arbeit werden vier miteinander verbundene Studien vorgestellt, die gemeinsam darauf abzielen, ein übergeordnetes Problem zu bearbeiten: Wie bestimmen Messmethodik, atmosphärische Wege und quellenbezogene Zusammensetzung den beobachteten molekularen Fingerabdruck von UFP?

Zunächst wurde ein systematischer Vergleich von vier Kaskadenimpaktoren durchgeführt, der zeigte, dass konstruktionsspezifische Eigenschaften die gemessene chemische Zusammensetzung von UFP erheblich beeinflussen können. Diese Ergebnisse verdeutlichen die Notwendigkeit eines stärkeren Bewusstseins für Artefakte, die durch unterschiedliche UFP-Probenahmeverfahren entstehen. Im nächsten Schritt wurde ein O₃-Denuder entwickelt und validiert, der O₃ selektiv vor dem Sammelsubstrat entfernt und dadurch die in-situ-Oxidation von UFP-gebundenen Verbindungen wie polyzyklischen aromatischen Kohlenwasserstoffen (PAK) und Reifenzusatzstoffen reduziert. Anschließend kam eine kombinierte Impaktor-Denuder-Anordnung in Verbindung mit zweidimensionale Gaschromatographie gekoppelt mit Flugzeit-Massenspektrometrie (GC×GC-TOFMS) zum Einsatz, um den molekularen Fingerabdruck von UFP in der Umgebung zu entschlüsseln. Der resultierende Datensatz zeigte ausgeprägte saisonale und episodische Muster, die mit einer etablierten Hochleistungsflüssigkeitschromatographie gekoppelt mit einem Fluoreszenzdetektor (HPLC-FLD) Methode validiert wurden. Dies demonstriert, wie sich quellen- und transportbezogene Prozesse in der UFP-Chemie widerspiegeln. Abschließend wurden die bisherigen Methoden auf den Bereich der Nicht-Abgas-Verkehrsemissionen übertragen: Reifenbezogene Partikelmarker wurden von Reifenmaterialien über Abriebemissionen sowie atmosphärische UFP- und Ablagerungsproben verfolgt. Die beobachtete fortschreitende Oxidation von Antiozonantmarkern verdeutlicht sowohl ihr diagnostisches Potenzial als auch die Grenzen der quantitativen Quellenzuordnung.

Insgesamt etabliert diese Arbeit einen Arbeitsablauf, der von der artefaktbewussten UFP-Probenahme und chemischen Analyse bis zur quell- und prozessorientierten Interpretation reicht. Die Ergebnisse zeigen, dass die chemische Charakterisierung von UFP sowohl die Quantifizierung, Minderung und Berücksichtigung durch Probenahme verursachter Artefakte als auch die nicht-zielgerichtete molekulare

Analyse von Fingerabdrücken oder die Analyse zielgerichteter chemischer Marker erfordert. Der integrierte Ansatz reduziert probenahme- und oxidationsbedingte Artefakte, ermöglicht eine chemische Nicht-Ziel-Fingerabdruckanalyse sowie eine zielgerichtete Quantifizierung organischer Marker und verbessert damit die methodische Grundlage für eine quellen- und prozessorientierte Interpretation der chemischen Zusammensetzung von UFP.

List of abbreviations

μ FTIR	Micro-Fourier transform infrared spectroscopy
6PPD	N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine
6PPD-Q	6PPD-quinone
AMS	Aerosol mass spectrometer
ATOFMS	Aerosol time-of-flight mass spectrometer
BaP	Benzo[a]pyrene
BeP	Benzo[e]pyrene
C_c	Cunningham slip correction factor
CCN	Cloud condensation nuclei
CEN	European Committee for Standardization (Comité Européen de Normalisation)
CPC	Condensation particle counter
d_a	Aerodynamic diameter
DAD	Diode-array detection
DMA	Differential mobility analyser
DMS500	Fast mobility spectrometer model DMS500
d_{p50}	50% cut-off aerodynamic diameter
DPG	1,3-Diphenylguanidine
DPPD	N,N'-diphenyl-p-phenylenediamine
DTD	Direct thermal desorption
EC	Elemental carbon
EDX	Energy-dispersive X-ray spectroscopy
EEA	European Environment Agency

ELPI	Electrical low-pressure impactor
EN	European Norm / European Standard
ESI	Electrospray ionisation
EU	European Union
FID	Flame ionisation detector
FLD	Fluorescence detection
GC	Gas chromatography
GC×GC	Comprehensive two-dimensional gas chromatography
HPLC	High-performance liquid chromatography
IC	Ion chromatography
INP	ice-nucleating particles
IPPD	N-isopropyl-N'-phenyl-p-phenylenediamine
LOD	Limit of Detection
MARGA	Monitor for Aerosols and Gases in Ambient Air
MOUDI	Micro-orifice uniform deposit impactor
MPSS	Mobility particle size spectrometer
MS	Mass spectrometry
NIST	National Institute of Standards and Technology
NO ₂	Nitrogen dioxide
O ₃	Ozone
OC	Organic carbon
OH	Hydroxyl radical
PAH	Polycyclic aromatic hydrocarbon
PALMS	Particle Analysis by Laser Mass Spectrometry
PENS	Personal nanoparticle sampler

PILS	Particle-into-liquid sampler
PM10	Particulate matter with aerodynamic diameter $\leq 10\ \mu\text{m}$
PM2.5	Particulate matter with aerodynamic diameter $\leq 2.5\ \mu\text{m}$
PNC	Particle number concentration
PNSD	Particle number size distribution
PTFE	Polytetrafluoroethylene
Py	Pyrolysis
QA/QC	Quality assurance / Quality control
QFF	Quartz fibre filter
RSMS-II	Rapid Single-Particle Mass Spectrometer II
SEM	Scanning electron microscopy
SIM	Selected ion monitoring
SMPS	Scanning mobility particle sizer
SOA	Secondary organic aerosol
SPAMS	Single particle aerosol mass spectrometer
SP-AMS	Soot particle aerosol mass spectrometer
SPME	Solid-phase microextraction
SRM	Standard Reference Material
Stk	Stokes number
TD	Thermal desorption
TEM	Transmission electron microscopy
TOC	Total organic carbon
TOFMS	Time-of-flight mass spectrometry
TRWP	Tyre and road wear particles
TSOD	Sodium thiosulfate-coated ozone denuder

TWP	Tyre wear particles
UFP	Ultrafine particles
VOC	Volatile organic compound
WHO	World Health Organization
WSOC	Water-soluble organic carbon

1. Introduction to airborne ultrafine particles

Airborne ultrafine particles (UFP, ≤ 100 nm) are increasingly recognized as a distinct and policy-relevant fraction of airborne particulate matter (PM). While they contribute negligibly to total PM mass, UFP dominate in terms of particle number concentration (PNC) and surface area. These properties, together with their dynamic atmospheric behaviour, define a unique toxicological and environmental profile for UFP.

Their unique properties facilitate deposition throughout the respiratory tract and translocation across biological barriers, and they also promote the transport of adsorbed toxic compounds. Consequently, UFP have increasingly come into focus in toxicological studies, climate-relevant aerosol processes, and source apportionment (Kumar et al., 2021; Kwon et al., 2020; Oberdörster et al., 2005). However, the characteristics of UFP also pose analytical challenges: the very low mass strongly limits routine chemical characterisation. Due to the high surface-to-volume ratio, UFP are prone to gas–particle partitioning processes. Evaporation from, or adsorption to, sampling substrates can induce substantial sampling artefacts (Kristensen et al., 2016; Kuwabara et al., 2016; Subramanian et al., 2004; Surdu et al., 2021; Ungeheuer et al., 2021). Consequently, developing robust, artefact-minimising methods for the collection and chemical analysis of UFP is necessary for the reliable identification of UFP sources, atmospheric processing, and health-relevant properties (Lei et al., 2024; Moreno-Ríos et al., 2022).

This research need has recently been formalised by European regulatory action. In 2024, for the first time, UFP became a regulated parameter to protect air quality in the European Union (EU). The revised Ambient Air Quality Directive (2024/2881) defines UFP as particles with a diameter of ≤ 100 nanometres (nm). It is stipulated that UFP are measured as particle number concentrations (PNC; cm^{-3}) above a lower cut-off diameter of 10 nm, in accordance with European Standard EN 16976 (Bustin et al., 2019; European Parliament and Council of the European Union, 2024). This deviates from the regulatory treatment of PM with aerodynamic diameters ≤ 10 μm (PM₁₀) and ≤ 2.5 μm (PM_{2.5}), which are regulated in terms of the total particle mass concentration ($\mu\text{g m}^{-3}$) (European Parliament and Council of the European Union, 2024). The official recognition of UFP as a distinct fraction of particulate matter marks a shift in air quality governance. Previously, UFP were not adequately covered by the already implemented PM₁₀ and PM_{2.5} standards. In contrast to the PNC approach for UFP, PM₁₀ and PM_{2.5} are analysed mass-based, which does not take the unique physicochemical properties of UFP into account. Consequently, this regulatory approach highlights the need to comprehensively understand the specific physical and chemical properties of UFP and to develop new approaches for their measurement and assessment (Kumar et al., 2014; Kwon et al., 2020; Oberdörster et al., 2005; Ohlwein et al., 2019). While the PNC metric already addresses key public health and environmental concerns, it does not provide information about the chemical composition of UFP. However, linking PNC with their chemical composition is essential for source apportionment, conducting targeted toxicological and

epidemiological studies, and understanding atmospheric processing. This need for complementary, mass-based chemical analysis also exposes a methodological gap in accurately characterising the chemical composition of UFP. Established sampling and chemical analysis methods that are suitable and routinely used for PM₁₀ and PM_{2.5} are, in most cases, not applicable to UFP, where collection and chemical characterisation are severely constrained by the low particle size and mass (Lei et al., 2024; Moreno-Ríos et al., 2022). In addition, the dynamic behaviour of UFP including gas–particle partitioning and the semi-volatile nature of many UFP-bound organics makes separation and collection methods prone to sampling artefacts due to adsorption, evaporation, and in-sampler chemical transformation (Kristensen et al., 2016; Kuwabara et al., 2016; Subramanian et al., 2004). Consequently, there is a need for methods that can (i) collect sufficient UFP mass, (ii) provide precise size segregation in the <100 nm range, and (iii) minimise sampling artefacts to preserve the chemical composition. Addressing these challenges through the development and validation of a novel and existing methodologies for the collection and chemical analysis of UFP is the central objective of this dissertation.

Physical properties of UFP

UFP represent the smallest size range of the atmospheric aerosol size spectrum, and differ from fine (PM_{2.5}) and coarse (PM₁₀) particles in their behaviour, sources, and potential health impacts (Donaldson et al., 2001; Kumar et al., 2014; Kwon et al., 2020; Oberdoerster, 2000; Schraufnagel, 2020). Although they contribute negligibly to the total particle mass, UFP dominate the PNC in most environments (Figure 1) (Donaldson et al., 2001; Hussein et al., 2004; Shi et al., 1999). Their small size promotes high Brownian diffusivity, which leads to short atmospheric lifetimes due to coagulation with larger particles or deposition, including onto the human respiratory tract (Hinds & Zhu, 2022; Seinfeld et al., 1998). This size-metric mismatch explains why mass-based indicators underrepresent their relevance for exposure and processes (Kumar et al., 2014). The distinct physical behaviour of UFP is primarily governed by their small size. Furthermore, because the diameters of UFP are similar to the mean free path of air molecules (~60–70 nm), gas–particle interactions occur in the transition between continuum and molecular regimes. At this scale, air slip at the particle surface reduces drag and makes mass and heat transfer less efficient, as the air no longer behaves as a continuous medium. As a result, UFP have low inertia and closely follow airflow, making inertial impaction unlikely, while diffusion becomes more important. Their transport and condensational growth occur in the transition regime and therefore require non-continuum (slip-flow) corrections (Cunningham, 1910; Hinds & Zhu, 2022; Kulkarni et al., 2011; Seinfeld et al., 1998).

Another distinct physical characteristic of UFP is their high surface-area-to-mass ratio, which is several orders of magnitude greater than that of micrometre-sized particles. This enhances gas-particle

interactions, accelerates heterogeneous surface reactions, and increases toxicological potential through intensified interactions with biological tissues (Kwon et al., 2020; N. Li et al., 2003; Schmid & Stoeger, 2016). Over the highly curved surface of UFP, the Kelvin effect raises the equilibrium vapour pressure. Consequently, the condensation of semi-volatile species is inhibited and the growth through the uptake of low-volatility compounds is favoured (Kousaka et al., 1985; B. Y. H. Liu et al., 1984; Patoulias & Pandis, 2022). As condensation proceeds, UFP often transition from externally mixed to internally mixed (core-shell) morphologies, such as organic or sulfate coatings on soot cores, which in turn influence their optical properties, hygroscopicity, and chemical reactivity (Patoulias & Pandis, 2022; Pöschl, 2005a; Seinfeld & Pandis, 2016).

Figure 1 illustrates why mass-based air quality standards (PM_{2.5}, PM₁₀) fail to reflect the relevance of UFP: while their contribution to particle mass concentration ($dM/d\log dp$) is negligible, they dominate in both number concentration ($dN/d\log dp$) and surface area ($dA/d\log dp$) due to their distinct physical properties.

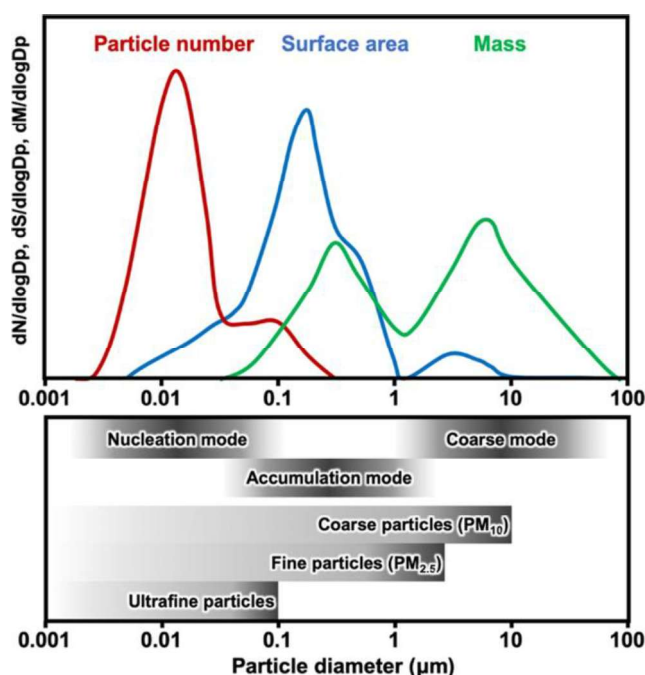


Figure 1. Schematic comparison of coarse, fine, and ultrafine particle contributions to total aerosol mass, number, and surface area for an equal mass of particles. Ultrafine particles contribute negligibly to the total mass but dominate in number concentration and surface area. Adapted from Kwon et al., 2020.

Chemical properties and sources of UFP

Chemically, UFP have a diverse composition, comprising both organic and inorganic fractions. Organic compounds can account for 20–90 % of the UFP mass, ranging from highly volatile hydrocarbons to low-volatility polycyclic aromatic hydrocarbons (PAH) and oxygenated organic species (Jimenez et al., 2009; Pöschl, 2005). Inorganic components often include sulfates, nitrates, ammonium, and sea salt, together contributing 10–50 % of UFP mass in many environments (Cass et al., 2000; Fang et al., 2006;

Xiu et al., 2004). Additionally, trace metals such as Fe, Cu, Zn, and Mn can be enriched in UFP, particularly in urban air, where they may constitute several percent of particle mass but can dominate in toxicological response through redox activity (Fernández-Camacho et al., 2012; Nico et al., 2009; Utsunomiya et al., 2004; Waheed et al., 2011). Black carbon (BC) and elemental carbon (EC) constitute a further fraction, which typically accounts for 5–30 % of the UFP mass in traffic-influenced environments (Riffault et al., 2015). This chemical heterogeneity is highly dynamic, as volatile and semi-volatile compounds in UFP can equilibrate rapidly with the surrounding gas phases, while their composition is sensitive to atmospheric conditions such as temperature, humidity, and oxidants (Brown, 2003; Pöschl, 2005). Accordingly, UFP can be emitted from a wide range of anthropogenic and biogenic processes, which are categorized as primary or secondary sources. Primary UFP are emitted directly into the atmosphere, for example from combustion processes, industrial activities, or mechanical abrasion (e.g. brake wear and tyre abrasion). In contrast, secondary UFP form in the atmosphere via new particle formation (NPF) from low-volatility vapours such as sulfuric acid with bases (NH_3 /amines) and highly oxygenated organic molecules through photochemical reactions followed by condensational growth (Brown, 2003; Donaldson et al., 2001; Kerminen et al., 2018; Y. Li et al., 2020; Lv et al., 2020; Moreno-Ríos et al., 2022; Posner & Pandis, 2015; Riffault et al., 2015; Z. B. Wang et al., 2011).

A common pathway is the oxidation of volatile organic compounds (VOC) to yield less volatile products, which subsequently condense onto existing particle surfaces or nucleate to form new particles, collectively referred to as secondary organic aerosol (SOA) (Chen et al., 2021; Donahue et al., 2006, 2013; Patoulias et al., 2015). Thus, the accurate chemical characterisation and source apportionment of UFP remain challenging, as their composition and mixing state evolve rapidly through condensation, coagulation, and heterogeneous chemistry, introducing large uncertainties in determining their chemical composition. Addressing these uncertainties requires size-resolved and chemically resolved measurements with high temporal resolution.

Impact on environmental and human health

Due to their small size, UFP can penetrate deeply into the respiratory tract and translocate across epithelial barriers into the bloodstream, from where they are transported to secondary organs such as the heart, liver, and brain (Oberdoerster, 2000; Oberdörster et al., 1990, 2005; Schraufnagel, 2020). Their large reactive surface and direct interaction with biological tissues induce oxidative stress, inflammation, and endothelial dysfunction, which have been linked to respiratory and cardiovascular diseases, neurodegenerative disorders, and adverse birth outcomes (Donaldson et al., 2001; Kwon et al., 2020; N. Li et al., 2003; Schmid & Stoeger, 2016). Besides human health, UFP also pose potential ecotoxicological risks: they can deposit onto terrestrial and aquatic surfaces, where they can interact

with microorganisms, biofilms, and aquatic organisms, potentially disrupting their enzymatic activity, nutrient cycling, and trophic transfer (Handy et al., 2008; Holzer et al., 2022).

In the atmosphere, UFP influence climate-relevant processes by acting as cloud condensation nuclei (CCN) or ice-nucleating particles (INP), thereby affecting cloud microphysics, albedo, and precipitation efficiency (Kerminen et al., 2018; Shrivastava et al., 2024; Sun et al., 2024). Moreover, the strong size dependence of their optical properties enables UFP to scatter and absorb solar radiation, modifying the atmospheric radiation budget (Fatima et al., 2011; Kazil et al., 2010; Makkonen et al., 2012; Sun et al., 2024; M. Wang & Penner, 2009). Consequently, UFP represent a critical pollutant linking air quality, human health, ecosystem integrity, and climate regulation.

Challenges for measurement and analysis

Their physicochemical properties not only determine the environmental fate of UFP but also complicate their accurate measurement, chemical characterisation, and source attribution. Comprehensive chemical characterisation is essential to assess both their causes and impacts. Yet, their diverse sources, rapid atmospheric transformation, and short lifetimes lead to pronounced temporal and spatial variability (Daher et al., 2013; Dall'Osto et al., 2011; Y. Wang et al., 2012). This variability makes particle size and chemical composition critical parameters for assessing UFP sources, atmospheric transformation processes, and potential adverse effects on health and the environment. At the same time, the properties that render UFP environmentally and toxicologically relevant also complicate their accurate sampling and analysis (Brown, 2003; Daher et al., 2013; Dall'Osto et al., 2011; Hinds & Zhu, 2022). Consequently, robust UFP measurements demand a combination of complementary methods, including continuous particle number monitoring, size-resolved counting, and offline or online chemical analysis, each with distinct capabilities and limitations. Importantly, these limitations are not merely technical details, as they can systematically bias their results and thereby affect source attribution as well as transformation and risk assessments of UFP.

2. Synopsis – an integrated framework for artefact-aware ultrafine particle characterisation

This synopsis links the four manuscripts of this cumulative thesis into a coherent workflow for the chemical characterisation of airborne UFP. The central hypothesis is that apparent UFP chemical composition is not solely determined by atmospheric processes, but can be substantially influenced by methodological decisions in size separation, sampling, and subsequent analysis. Accordingly, the overarching objective of this cumulative dissertation is to analyse the chemical composition of airborne UFP in a robust and comparable manner by identifying, quantifying, and minimising artefacts during UFP separation, collection, and chemical analysis.

The work is structured in four manuscripts; each manuscript addresses one methodological gap on the chain from UFP separation through sampling to the chemical analysis and the resulting interpretation (Figure 2).

First (Manuscript I), potential biases originating from size-segregated UFP separation, which can already affect the chemical composition of the targeted size fraction, are investigated. Design- and operation-related characteristics of cascade impactors are therefore evaluated in order to assess how and to what extent they may affect the size-resolved molecular compositions and which compound classes are expected to be most susceptible.

Second (Manuscript II), the focus shifts from biases mostly introduced by physical separation methodology to the preservation of the chemical composition during collection. Because reactive particle-bound organics can be transformed on sampling substrates by ambient oxidants, such as O₃, upstream O₃ removal is implemented as a targeted measure to minimise artefacts. The approach is designed to minimise O₃-driven in-situ reactions while maintaining the particle transmission, so that differences in marker composition can be attributed to atmospheric variability rather than artefacts that are introduced during sampling.

Third (Manuscript III), the artefact-aware sampling framework from manuscripts I and II is combined with subsequent molecular analysis that provides sufficient sensitivity and chemical resolution despite inherently low UFP mass. A non-target approach is applied to derive molecular fingerprints of ambient UFP beyond a set of targeted markers, while targeted quantification is used for quantitative validation.

Finally (Manuscript IV), the outcomes of the manuscripts I–III are transferred to an applied source-to-atmosphere context with a focus on UFP-relevant markers. Targeted chemical analysis is performed across multiple sample types, which range from reference material through emissions to ambient UFP and deposition, to evaluate how systematic compositional shifts arise along the emission pathway and how emission and atmospheric processes affect the chemical transformation of marker compounds.

Taken together, each manuscript reduces a distinct source of uncertainty in UFP chemical characterisation, spanning physical separation biases through to transformation-aware source and process interpretation.

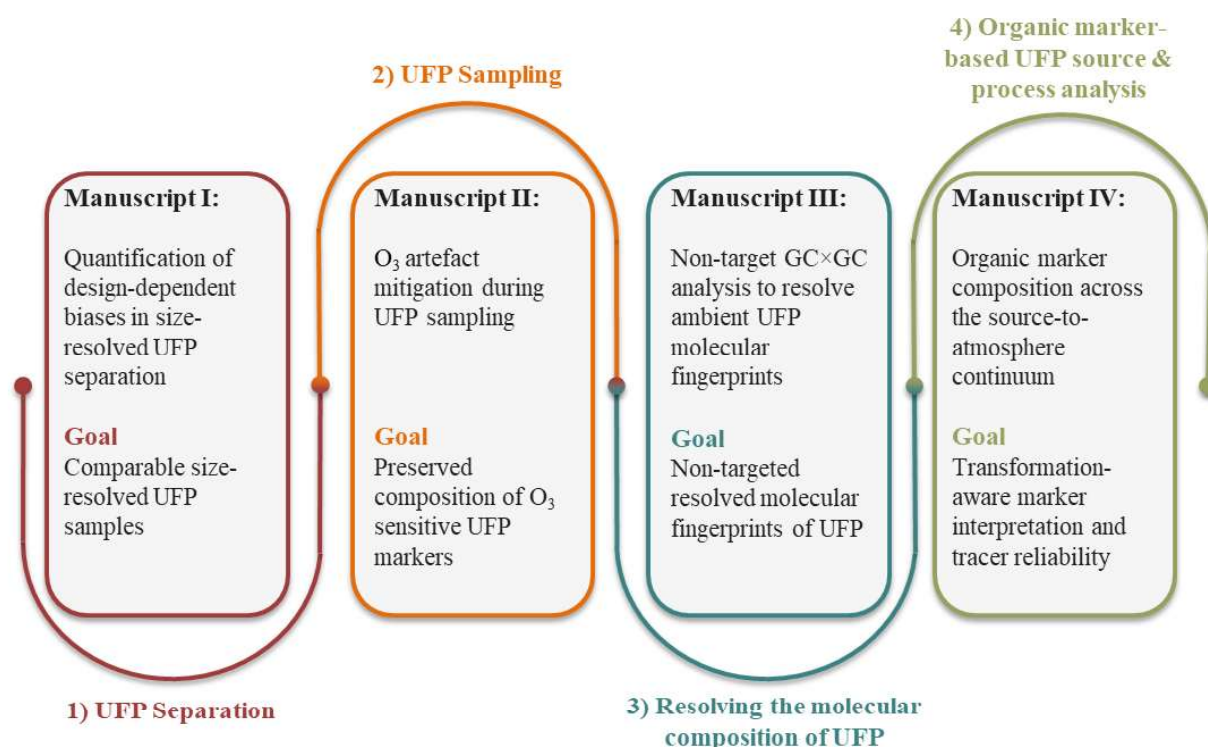


Figure 2. Synopsis linking the four manuscripts: (1) quantification of design-dependent biases in size-resolved UFP separation (Manuscript I), (2) mitigation of O₃-induced artefacts during UFP sampling (Manuscript II), (3) non-target GC×GC analysis to resolve ambient UFP molecular fingerprints (Manuscript III), and (4) organic marker-based source and process analysis across the source-to-atmosphere continuum (Manuscript IV). The goal of each step is indicated within the corresponding manuscript panel.

2.1 Artefact-aware size-segregated sampling of UFP

Methods to measure UFP require novel or modified methodologies that are distinct from those applied to larger PM, mainly due to their low mass and dynamic transport behaviour. Approaches generally fall into three categories: physical characterisation (size and number), online chemical characterisation, and offline chemical characterisation via prior collection. As detailed above, the regulatory focus on PNC necessitates sensitive instruments for counting, while the chemical characterisation requires analytical techniques that can overcome the challenge of low mass and sampling methods that minimise sampling artefacts.

Number-size characterisation

The quantification of the PNC is a fundamental metric in UFP characterisation, as UFP dominate number concentrations. PNC is typically measured with condensation particle counters (CPCs). CPCs first grow particles to optically detectable sizes via supersaturation with a working fluid such as butanol and subsequently count them (Brown, 2003; Giechaskiel & Melas, 2022; Hinds & Zhu, 2022; Aitken, 1889; McMurry, 2000). The upcoming European standard for UFP monitoring (CEN prEN 16976) defines CPC-based PNC measurements as the reference method (CEN, 2023). CPCs are highly sensitive and can detect particles as small as 7–10 nm, while ultrafine or “nano” CPCs have been developed for research applications and can reach lower cut-off diameters of approximately 2.5–3 nm. While CPCs provide total particle number concentrations, they provide no size-resolved information (Asbach et al., 2017; Giechaskiel & Melas, 2022; Kumar et al., 2016; Matson et al., 2004; Tuch et al., 2016; Singh & Kuang, 2024; Stolzenburg & McMurry, 1991).

For resolving the particle number size distribution (PNSD), scanning mobility particle sizers (SMPS), also referred to as mobility particle size spectrometers (MPSS), are deployed (Kumar et al., 2016; Wiedensohler et al., 2012). These instruments classify particles by their electrical mobility using a differential mobility analyser (DMA), followed by counting with a CPC. SMPS systems provide high-resolution PNSDs typically spanning 10 to 800 nm and are widely deployed in atmospheric research, supported by standardized operating protocols (CEN, 2020). However, SMPS instruments require scan times of several minutes and corrections for multiple charging and diffusion losses, particularly at the ultrafine end of the spectrum (Kulkarni et al., 2011; Kumar et al., 2016; Wiedensohler et al., 2012).

For applications requiring high temporal resolution, such as measuring traffic plumes or laboratory chamber studies, fast mobility spectrometers (e.g., the DMS500) can provide a full PNSD at up to 10 Hz using unipolar corona charging and multiple electrometer channels (Bergmann et al., 2007; Kumar et al., 2009; Symonds et al., 2007). While these instruments enable rapid PNSD characterisation for highly dynamic particles and are widely applied in vehicle exhaust studies, they typically exhibit higher detection limits and lower sizing resolution compared to SMPS (Kumar et al., 2009; Ristimäki et al., 2002).

While number–size instrumentation is increasingly standardized, chemically resolved information for UFP remains limited by low mass and sampling artefacts, motivating offline size-segregated collection.

Sampling of UFP

UFP originate from diverse sources and additionally can undergo rapid chemical transformations during their atmospheric lifetime. Thus, their composition is variable but also provides insight into their sources, reactivity, and health relevance. Online and semi-online techniques can therefore provide near-

real-time chemical data. Yet, most of these techniques have intrinsic limitations for particles with diameters below 100 nm. The aerosol mass spectrometer (AMS) quantifies species that evaporate rapidly at 600 °C under vacuum conditions with high temporal and size resolution (Canagaratna et al., 2007; DeCarlo et al., 2006). However, its inbuilt aerodynamic lens only transmits particles larger than ~50–70 nm. For smaller particles, the transmission efficiency rapidly drops, which results in an underrepresentation of the nucleation-mode (P. S. K. Liu et al., 2007). The soot-particle AMS (SP-AMS) extends this capability to refractory Black Carbon (BC) (Onasch et al., 2012), but still suffers from transmission losses for small particles. Single-particle mass spectrometers such as ATOFMS, PALMS, or RSMS-II provide online information on particle composition and mixing state (Gard et al., 1997; Mallina et al., 2000; Murphy & Thomson, 1997b, 1997a). Nevertheless, the combination of minimal light scattering and low ionisation efficiency for extremely small particles also results in a decline in detection efficiency below ~70–80 nm. By contrast, RSMS-II can in principle assess particles down to ~15 nm, but at the cost of very low detection efficiency and strong composition biases (Kane & Johnston, 2000; Middlebrook et al., 2003).

Semi-continuous systems such as the particle-into-liquid sampler (PILS) or the Monitor for Aerosols and Gases in Ambient Air (MARGA) enable near-real-time quantification of water-soluble ions (Orsini et al., 2003; Rumsey et al., 2014; Weber et al., 2001). In the PILS, the sample flow is mixed with water-saturated air to create supersaturation so that particles grow into droplets and are inertially impacted into a continuously flowing aqueous stream, which is then analysed by ion chromatography or total organic carbon; because the PILS has no intrinsic size resolution, it relies on an upstream classifier such as an impactor or mobility selector to target the UFP fraction (Orsini et al., 2003; Weber et al., 2001). The MARGA combines a wet diffusion denuder for soluble gases such as HNO₃, NH₃ and SO₂ with a steam-jet aerosol collector that dissolves particle-bound ions into separate liquid channels, followed by online anion and cation ion chromatography with hourly time resolution. Like the PILS, it measures size-integrated aerosol behind the inlet and therefore depends on pre-classification to isolate UFP (Rumsey et al., 2014). However, their detection limits, typically on the order of 0.05–0.1 µg m⁻³, are frequently above the range of mass concentrations of UFP (Sorooshian et al., 2006; Weber et al., 2001).

Size-segregated sampling by impaction

In practice, online and semi-online techniques provide valuable information for accumulation-mode particles but offer incomplete coverage of the physicochemical composition of UFP. Consequently, detailed chemical characterisation of UFP still relies on offline analysis following size-segregated sampling, most commonly achieved with impactors.

Impactors allow for separation of particles in air samples based on their aerodynamic diameter (d_a). The physical separation of particles within an impactor is based on the particle's inertia, which causes

relatively smaller particles to follow the airflow when it bends sharply, e.g. when forced through nozzles, orifices, or slits. For predicting particle impaction, the dimensionless Stokes number (Stk) can be used to describe the ratio of particle response time to the transit time of the airflow (Kulkarni et al., 2011):

$$Stk = \frac{\rho_p C_c d_p^2 U}{9\eta W} \quad (1)$$

Where ρ_p is the particle density, C_c represents the Cunningham slip correction factor, d_p is the particle diameter, U is the average air velocity at the nozzle exit, η is the viscosity of the air or gas, and W is the diameter of the round nozzles or slit width. Particles with a Stokes number significantly greater than 1 are likely to impact on the collection surfaces due to their inability to follow the rapidly changing direction of the air streams within the impactor. Conversely, particles with lower Stokes numbers remain airborne, following the air streamlines through the impactor (Kulkarni et al., 2011).

Upon separation, the particles can be collected on the impaction plates or downstream of the impactor, by placing filter substrates. Particles caught in the substrate can be extracted and undergo chemical analysis to determine their composition (Canepari et al., 2010; Daher et al., 2011).

To describe the separation and collection efficiency of an impactor, the cut-off diameter dp_{50} is used. This parameter is defined as the aerodynamic particle diameter at which 50 % of particles are collected on the impaction plate, while smaller particles are transmitted to subsequent stages. Thus, it characterises the effective size threshold of a given impactor stage. The dp_{50} value depends on the Stokes number and is, for a given impactor geometry and flow rate, proportional to the square root of the Stokes number (Kulkarni et al., 2011; Marple, 2004).

Cascade impactors

A stack of impaction and nozzle plate pairs, is a cascade impactor. Within the cascade impactor, the nozzles or slits become increasingly smaller, so that the air moves progressively faster through these orifices. As the aerosol flows through, particles with sufficiently high inertia (large Stokes number) cannot follow the streamlines and impact onto the impaction plates. Progressively smaller particles stay with the air flow to reach later stages. In this way, particles are size-segregated by aerodynamic diameter. The final stage and filter can collect the particle fraction that penetrates the upper stages (Figure 3).

The journey of cascade impactors began in 1860 when researchers aimed to collect and study airborne particles for the first time to understand their relationship with diseases (Marple, 2004). Later, from 1920 to 1945, impactors were refined for studying industrial aerosols in mine environments, shifting the focus to the quantification of particle concentrations. In 1945, the May cascade impactor provided insights into particle size distribution and concentration (May, 1945), which was spurred by military

studies on chemical dispersion. Post-1945, numerous impactor designs proliferated, with many being variations of the original May cascade impactor. Theoretical analyses and computational methods from 1970 onwards revolutionized the understanding of impactors' fluid and particle dynamics, enabling precise size classification. In the mid-20th century, further progress was made by pushing cut-off sizes to sub- μm ranges (Berner et al., 1979; Brink, 1958; Mitchell & Pilcher, 1959). One example is the Berner impactor, which allowed the collection of UFP achieving a cut size of $0.082\ \mu\text{m}$ at the lowest stage through an ingenious pressure drop mechanism. This concept evolved with the electrical low-pressure impactor (ELPI), which harnessed low pressure to achieve even smaller particle cut sizes and introduced electrometer-based charged particle detection with a potential for real-time data acquisition (Keskinen et al., 1992; Marjamäki et al., 2000). Another approach for ultrafine cut-off sizes uses small nozzles, such as implemented for the micro-orifice uniform deposit impactor (MOUDI) which is capable of capturing particles as small as $0.056\ \mu\text{m}$ (Marple et al., 1991). Finally, miniaturized impactors were developed to study personal exposure, such as the Personal Nanoparticle Sampler (PENS) (Tsai et al., 2012). This summary is not intended to be comprehensive, but to illustrate key milestones leading to UFP-capable impactor designs.

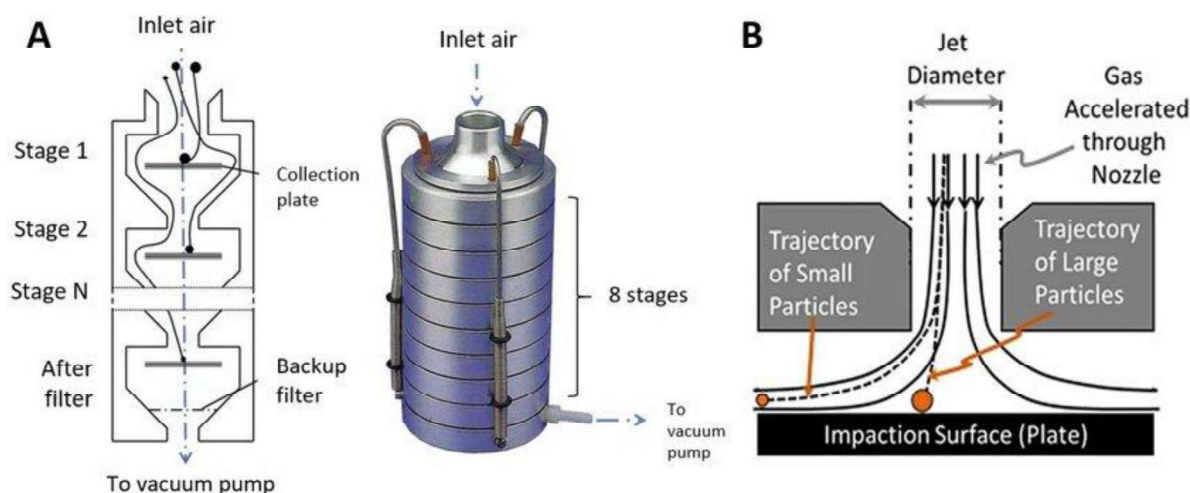


Figure 3. (A) Schematic cross section of a multi-stage cascade impactor with the aerosol inlet, sequential impaction stages with collection plates, and the downstream backup filter. (B) Principle of inertial impactation. The particle transporting jet accelerates through a nozzle, and the trajectory of particles depends on their inertia. Larger particles cannot follow the sharp bend of the streamline and impact on the impaction plate, whereas smaller particles follow the gas streamlines and pass to the next stage. Adapted from (Knap et al., 2023).

The low mass of UFP poses a challenge to their collection, and separation from the atmosphere using cascade impactors. Unlike PM_{2.5} and PM₁₀, this low mass renders gravimetry and mass-based chemical analysis difficult. In particular, the following factors affect UFP collection with cascade impactors:

The nominal 50 % cut-off diameter (dp_{50}), defined as an aerodynamic diameter, is sensitive to particle shape, effective density, and flow conditions, so that the effective collection efficiency of UFP ($dp_{50} \approx 100$ nm) can also shift into the lower accumulation mode. Because of the steep mass increase with particle size, even shifts in cut size can therefore bias the collected UFP mass and thus the chemical composition with larger particles (Huang, 2005; Kulkarni et al., 2011). In addition, aerosols in the impactor are subject to internal losses, with coarser particles lost by inertial deposition and finer particles by diffusional wall losses (C.-N. Liu et al., 2013; Newton et al., 1977). Following impaction, particle bounce and re-entrainment may fragment larger particles into apparent UFP. Additionally, semi-volatile particle-bound compounds can evaporate from deposited material under reduced pressure and continuous flow within the impactor, thereby altering both the apparent mass and composition of UFP (Dunbar et al., 2005; Dzubay et al., 1976; Cornette et al., 2023; Yao et al., 2022).

Consequently, the observed mass and chemical composition of impactor UFP samples is not solely the result of source contribution and atmospheric transport and transformation. It is also influenced by the choice of impactor. However, impactor-based size segregation of UFP remains a standard method for offline UFP chemical characterisation. **A central methodological gap is that impactor-induced biases are rarely quantified in a way that allows robust cross-study comparison of UFP mass and composition.**

Manuscript I addresses this gap by comprehensively evaluating four UFP-capable cascade impactors under controlled laboratory conditions with different generated aerosols, as well as in a side-by-side field deployment. The study quantifies pressure drop, cut-off behaviour, transmission losses, particle bounce and transmitted particle mass, and links these physical metrics to differences in UFP-resolved mass concentrations of six organic compounds analysed by HPLC-MS/FLD. Manuscript I describes systematic, design-dependent biases and provides a quantitative basis for interpreting and comparing UFP datasets obtained with different impactor types.

The comparison reveals that UFP-resolved mass and marker concentrations can differ substantially between impactors despite similar nominal cut-offs. This is mainly attributable to impactor-specific differences in cut-off behaviour, pressure drop, internal losses, and bounce, which are design-dependent. The concentrations of UFP-bound semi-volatile organic compounds are most affected by these differences, consistent with evaporative losses at higher pressure drops and altered collection/re-entrainment behaviour. Overall, the manuscript delivers bias metrics that aim to improve cross-study comparability and to raise awareness of the importance of impactor selection and operation for UFP chemistry. In summary, impactor-based size segregation remains indispensable for offline UFP chemistry, but the recovered UFP composition can be systematically shaped by impactor-dependent physical artefacts. After analysing and minimising impactor related artefacts, oxidant-driven in-situ reactions during the UFP sampling process, remain a source of uncertainty, motivating upstream ozone removal strategies (Section 2.2 / Manuscript II).

2.2 In-situ oxidation artefacts and ozone removal in UFP sampling

Ongoing in-situ reactions during collection can change the chemical composition even when size-resolved UFP sampling with cascade impactors is optimised to minimise artefacts. Specifically, during sampling time, particle-bound compounds that have already been deposited on the sampling substrate may react with atmospheric oxidant ozone (O_3). Consequently, this in-situ oxidation can cause an underestimation of the parent compounds and an overestimation of their oxidation products (Berberler & Karakaş, 2024; Dhawan & Biswas, 2019; K. Liu et al., 2014; Menichini, 2009; S. Zhang et al., 2015). These oxidation processes are particularly relevant for molecular compounds that readily react with O_3 , such as PAH (Berberler & Karakaş, 2024; Chu et al., 2010; K. Liu et al., 2014) or certain rubber additives like N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) (Rossomme et al., 2023). In order to ensure that subsequent chemical analyses of UFP accurately reflect the ambient composition at the time of sampling, it is crucial to reduce biases caused by O_3 .

To mitigate on-filter oxidation, O_3 denuders remove O_3 upstream of the collection substrate. Different denuder materials, however, rely on distinct scrubbing mechanisms, each with specific advantages and disadvantages. Potassium iodide (KI) coatings remove O_3 via stoichiometric redox reactions but can release reactive iodine species that may cause secondary artefacts (Albinet et al., 2010; Williams & Grosjean, 1990). Manganese dioxide (MnO_2) removes O_3 through catalytic decomposition into O_2 . However, the effectiveness and selectivity of this denuder material strongly depends on operational conditions such as humidity, which can reduce efficiency and promote side reactions (Y. Liu et al., 2006). Activated-carbon-based denuders, including carbonaceous monoliths, remove O_3 by adsorption but are non-selective and may scavenge other gaseous or semi-volatile species (Mikuška et al., 2012; Williams & Grosjean, 1990). In contrast, sodium thiosulfate ($Na_2S_2O_3$) coatings offer a selective stoichiometric reaction with O_3 , via conversion to inert sulfate thus avoiding the generation of reactive by-products (Ernle et al., 2023).

These denuder materials can be used in various geometries for different applications. For example, annular denuders offer a high surface area to volume ratio and can handle comparatively high flow rates (Sekiguchi et al., 2009), whereas honeycomb/monolith denuders combine a large surface area with low pressure drop (Kohlmeier et al., 2018; Poon et al., 1994; Sioutas et al., 1994). Cartridge-style impregnated denuders are easy to replace but can add flow resistance and particle losses, and are therefore more common for gas-phase sampling than for UFP chemistry (Mikuška et al., 2012).

Despite their ability to scrub O_3 from the sampling air, the performance of the denuder also depends on environmental conditions and operational parameters. O_3 concentrations, sampling flow rates, or relative humidity can affect the scrubbing efficiency and/or the lifetime of the coating (e.g., Albinet et al., 2010; Duong et al., 2019; Ho et al., 2013; Parmar & Grosjean, 1990). Regular maintenance or replacement is therefore required to ensure consistent O_3 removal (Albinet et al., 2010; Garcia-Fouqué et al., 1999).

Selecting a suitable denuder material and sampling configuration requires balancing the O₃ removal efficiency, its chemical selectivity, flow adjustment, and the risk of introducing additional unintended interferences (e.g., Garcia-Fouqué et al., 1999; Sekiguchi et al., 2009).

To obtain representative UFP chemical measurements, the selection of an ozone denuder upstream of the collection substrate is critical (Tsapakis & Stephanou, 2003). Because UFP combine a disproportionately large surface area and small particle mass, they are particularly susceptible to surface oxidation reactions (Hinds & Zhu, 2022; Kwon et al., 2020; Pöschl, 2005; Schmid & Stoeger, 2016). Even minor oxidative reactions can result in relatively large concentration biases, affecting both source apportionment (Hopke et al., 2022) and toxicological assessment (Oberdörster et al., 2005; Z. Tian et al., 2021). A major limitation of current O₃ scrubbers is that gains in removal efficiency are often achieved at the expense of selectivity, increasing the likelihood of sampling artefacts, for example, through the distortion of the gas-particle partitioning and/or particle losses. Because offline chemical characterisation of UFP is inherently mass-limited, even small O₃-induced chemical reactions during UFP collection can disproportionately distort the recovered molecular composition. **This leaves a methodological gap: a selective ozone-removal method that is UFP-compatible, field-deployable over the sampling durations required to accumulate sufficient UFP mass for offline analysis, and demonstrably does not affect particle number–size distributions and gas–particle partitioning.**

Manuscript II addresses this gap by presenting a sodium-thiosulfate–coated ceramic ozone denuder (TSOD) for UFP sampling. This denuder is evaluated for its O₃ -removal efficiency, particle losses and selectivity under controlled laboratory conditions. Furthermore, the denuder is used in a dual-channel approach in a field experiment to quantify in-situ O₃-induced artefacts in various UFP-bound organic compounds. This demonstrates efficient O₃ scrubbing without measurably affecting particle number or semi-volatile partitioning. It is demonstrated that the sodium-thiosulfate–coated denuder removes ozone efficiently while introducing negligible particle losses across the UFP size range under relevant operating conditions. In dual-channel field deployment, the denuded line yields higher concentrations of ozone-sensitive parent compounds and lower levels of corresponding oxidation products, directly quantifying the magnitude of in-situ O₃ artefacts during UFP sampling. This establishes a field-ready mitigation strategy that preserves reactive organic signals without introducing measurable distortions of particle number or partitioning. The dual-channel setup also delivers a practical approach to quantify ozone-driven reactions of UFP-bound organic compounds under realistic sampling conditions.

Notably, precise chemical characterisation of UFP is still inherently difficult, even when sampling- and ozone-induced artefacts are reduced. Primary reasons are the low mass and chemical heterogeneity of UFP. Thus, there is a need for sophisticated, comprehensive analytical techniques that can resolve UFPs' molecular composition.

2.3 Molecular analysis of UFP

The chemical characterisation of UFP requires analytical approaches that can, on the one hand, resolve their molecular composition and, on the other hand, cope with their extremely low particle mass. Subsequent offline analysis following size-segregated sampling therefore remains indispensable for obtaining compositional UFP data. In this approach, UFP are first collected on suitable substrates, the choice of which depends on the targeted analytes, the subsequent analytical method, and the need to minimise artefacts such as adsorption, volatilisation, or chemical reactions with the substrate. Commonly used filter substrates include pre-baked QFF, PTFE membranes, aluminium foils, and polycarbonate filters (Lin et al., 2007; Perrino et al., 2013; Ungeheuer et al., 2021).

Once UFP are deposited on a chosen substrate, several approaches provide direct information on their composition and morphology. Thermal–optical analysis yields information on bulk elemental and organic carbon (EC/OC) fractions (K. H. Kim et al., 2011; Kudo et al., 2012), while scanning and transmission electron microscopy (SEM/TEM) combined with energy-dispersive X-ray spectroscopy (EDX) deliver morphological and elemental information at the single-particle level (Lü et al., 2012; Mäkelä et al., 2002; Tumolva et al., 2010; Y. Wang et al., 2019). Most mass-based chemical analyses, including elemental, ionic, and organic analysis, require particle-bound compounds to be transferred from the sampling substrate into a suitable liquid or gaseous phase. The corresponding extraction strategies are therefore a critical step and are discussed in the following section.

Extraction

Beyond direct characterisation, particle-bound analytes often need to be transferred from the sampling substrate into a form which is suitable for the distinct chemical analysis. For targeted organic analytes in UFP, solvent-based extraction methods are commonly used. Depending on the volatility and the polarity of the compounds of interest, solvents which differ in polarity are often used in sequential polarity-increasing schemes, to extract both non-polar tracers (e.g., PAH, hopanes) and more polar species (e.g., oxygenated aromatics, nitrophenols) (e.g. (Chow & Watson, 2007; Ungeheuer et al., 2021; Vaze et al., 2024; Zhai et al., 2016). For water-soluble compounds, aqueous extractions are applied followed by ion chromatography (IC) for inorganic ions such as sulfate, nitrate, and ammonium, or total organic carbon (TOC) analysis for water-soluble organic carbon (WSOC) (e.g., Chow & Watson, 2007; Lin et al., 2007; C. Ning et al., 2024)

Thermal desorption (TD) techniques provide a solvent-free alternative. TD volatilises organic compounds from the substrate under controlled heating into an inert carrier gas. This enables the direct introduction of the analyte compounds to gas chromatographic analysers. While TD preserves thermally stable semi-volatile compounds (Held et al., 2009; X. Li et al., 2021; Schnelle-Kreis et al., 2005; Voisin

et al., 2003), Pyrolysis (Py) uses higher temperatures to thermally decompose non-volatile matrices into identifiable fragments (Fushimi et al., 2007; Reichel et al., 2020; Streibel et al., 2006). In contrast, headspace analysis targets volatile and semi-volatile compounds which are emitted from the sample into an enclosed vial. Analytes can be enriched, for example by solid-phase microextraction (SPME) fibres and subsequently analysed directly (Khanal & Shooter, 2004; Naing & Lee, 2020; Savareear et al., 2017).

Chemical analysis

Following the extraction of the UFP samples, there is a broad range of chromatographic and spectrometric techniques to resolve the mass-based molecular composition. Thereby, one of the largest challenges remains the low mass of UFP, which often approaches or falls below the Limit of Detection (LOD) of the instruments.

High-performance liquid chromatography (HPLC) coupled with ultraviolet (UV)/visible diode-array detection (DAD) or fluorescence detection (FLD) is a well-established technique to sensitively and selectively quantify particle-bound PAH (Bacaloni et al., 2004; Eiguren-Fernandez et al., 2013; Liaud et al., 2015). Coupling HPLC to tandem mass spectrometry (HPLC–MS/MS), frequently using electrospray ionisation (ESI), extends the analysis to polar and high molecular weight organic compounds. UFP studies utilizing HPLC–MS/MS quantify, among others, PAH, nitroaromatic compounds, anhydrosugars, and jet-oil markers (Feltracco et al., 2018; Schneider et al., 2022; Ungeheuer et al., 2021; Yassine et al., 2020).

Gas chromatography (GC), typically coupled to FID (Flame Ionisation Detector) or MS, is often applied to analyse volatile to semi-volatile, non-polar compounds (Fushimi et al., 2007; Hays et al., 2003; Rissanen et al., 2006; M. Wang et al., 2019). UFP studies have applied GC-MS to quantify n-alkanes (C18–C33), hopanes and steranes (lubricating-oil tracers), and 2–6-ring PAH (Fushimi et al., 2007, 2019; Lai et al., 2013; Phuleria et al., 2007; Riddle et al., 2007). However, conventional one-dimensional (1D) GC often suffers from co-elution when it is applied to complex UFP samples which often contain several structurally related hydrocarbons from mixed sources (Hamilton, 2010; Hamilton et al., 2004; Worton et al., 2012). Comprehensive two-dimensional (2D) gas chromatography (GC×GC) addresses this limitation. Thereby, two orthogonal separation mechanisms are combined, typically volatility in the first dimension and polarity in the second (Figure 4). Thus, an increase in the peak capacity is achieved, at the same time co-elution is reduced. In this manner, the resolution of up to thousands of individual compounds is enabled (Alam et al., 2024; Worton et al., 2012). Early applications of direct TD-GC×GC-TOFMS resolved over 10 000 organic components from ~10 µg of PM_{2.5} in a single run (Hamilton et al., 2004). Following studies have highlighted the use of this technique for both source apportionment and non-target analysis (Alam et al., 2024; Booyens et al., 2015; Kallio et al., 2006). The resulting

chromatographic patterns reveal molecular fingerprints that are indicative of specific emission sources and atmospheric ageing processes (Ruiz-Jiménez et al., 2011).

Within this methodological framework, Manuscript III deploys TD-GC×GC-TOFMS analysis to derive interpretable ambient molecular fingerprints of UFP. Applying the

modified and novel UFP sampling method and oxidant-mitigation strategy established in Manuscripts I and II, Manuscript III demonstrates that GC×GC fingerprint patterns in ambient UFP change across seasons and during pollution episodes. These shifts are overlapping with evolving source mixtures and atmospheric processing, rather than being attributable to analytical variability. To ensure compatibility with established analytical standard methods, Manuscript III compares TD-GC×GC-TOFMS-based PAH quantification against HPLC-FLD. The agreement confirms that the method reproduces targeted results, while the GC×GC provides additional compound-class resolution and pattern-based molecular fingerprints.

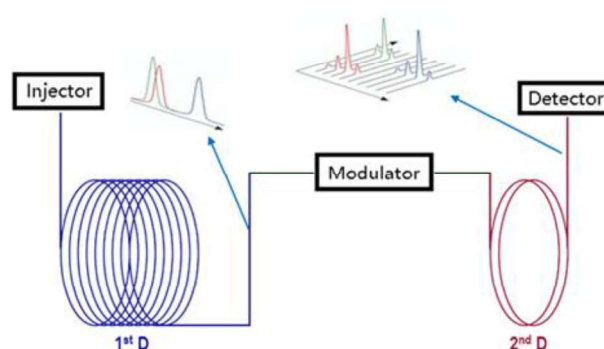


Figure 4. Schematic representation of comprehensive two-dimensional gas chromatography coupled to a detector, illustrating orthogonal separation in two capillary columns followed by detection. Adapted from (P. Zhang et al., 2023).

Targeted chemical analysis

Non-target chemical analysis is valuable for separating complex mixtures in UFP samples and detecting pattern shifts. However, these patterns become actionable only when they can be linked to quantifiable concentrations of compounds that connect the aerosol composition to emission sources and processing pathways (Cass, 1998; Schauer et al., 1999). Accordingly, marker-based analytical methods were developed to link the chemical composition to source- and process-specific information. In the early 1990s the concept of organic marker compounds was first established from GC-based analysis of emissions and ambient PM (Hildemann et al., 1991; Rogge et al., 1993; Schauer et al., 1999). In 1998, Cass set up a framework for this concept, emphasizing that markers are most useful when they are (i) sufficiently source-specific, (ii) emitted in reasonably stable and reproducible concentrations within a source class, (iii) detectable at ambient concentrations, and (iv) either inert in the atmosphere or at least their transformation pathways are understood well enough for reasonable interpretation (Cass, 1998; Simoneit, 2002).

For UFP, chemical analysis is limited by their low mass, as well as by measurement artefacts and interference. Thus, the concept of marker compounds, which provide quantifiable indicators, is especially compelling. providing a high information-per-mass approach (Cass, 1998; Simoneit, 2002;

Ungeheuer et al., 2021). Prominent examples of organic marker compounds which are applied in aerosol research include several marker groups that link the composition of UFP to sources and atmospheric pathways. For example, PAH are commonly analysed as indicators for combustion processes. In size-segregated near-road studies, their observed concentration and composition vary systematically with traffic and roadway setting (X. Li et al., 2021; S. Tian et al., 2024). A complementary, more source-constrained traffic marker is represented by hopanes and steranes, which originate from petroleum-derived lubricating oil and are observable in vehicle-exhaust-related particulate matter. These markers have been detected in airborne fine and ultrafine samples in roadside and tunnel environments (F. Li, 2018; Z. Ning et al., 2007; Shirmohammadi et al., 2016; Xue et al., 2022). n-Alkanes, and more specifically their carbon-number patterns, can reflect mixed fossil and wax-like additives, although they are typically interpreted within a broader marker set rather than as unique marker compounds (Nikolova et al., 2018; Z. Ning et al., 2007). Beyond fossil- and combustion-related markers, levoglucosan is widely used to trace and quantify the influence of biomass burning, as it is produced during cellulose pyrolysis and is commonly observed in wood-smoke-impacted atmospheric particles (Bhattacharai et al., 2019; Corsini et al., 2017; Müller et al., 2012; Simoneit et al., 1999). Finally, to trace atmospheric transformation pathways from fresh biogenic emissions to atmospherically processed aerosol, organic acids (including dicarboxylic acids and related oxygenated products) serve as organic markers for secondary aerosol formation and ageing, with size-dependent behaviour in submicron aerosols (Deshmukh et al., 2016; Kawamura & Bikkina, 2016; G. Wang et al., 2012). Well-established organic marker compounds (e.g., PAH, hopanes/steranes) were introduced due to the dominance of exhaust-related emissions of traffic signatures. Since tailpipe emissions have been reduced, non-exhaust traffic emissions (brake/tyre wear, road abrasion, resuspension) have become increasingly important (Fussell et al., 2022; Wei & Kumar, 2025). Historically, non-exhaust contributions were tracked mainly with metals (e.g., Cu/Fe/Sb for brake wear, Zn for tyre-related material), but these tracers can be confounded by mixed sources (especially resuspended road dust) and they provide limited access to the organic fraction and its transformation chemistry (Baensch-Baltruschat et al., 2020; Gietl et al., 2010; Klöckner et al., 2019; Thorpe & Harrison, 2008).

This has motivated a complementary targeted approach that searches for tyre-/rubber-associated organic markers, initially exemplified by traffic-influenced detections of benzothiazoles, and more recently expanded toward additive-derived compound classes such as substituted p-phenylenediamines (PPDs), guanidines (e.g., 1,3-diphenylguanidine (DPG)), and related transformation products (Avagyan et al., 2014; W. Wang et al., 2022).

2.4 Tyre and road wear particles and their organic markers

Recently, non-exhaust traffic emissions have gained attention as an increasingly important source of atmospheric UFP (Amato et al., 2014; Fussell et al., 2022; Guo et al., 2021). Their relevance is further appreciated by emerging regulatory action: the forthcoming Euro 7 standards will set legal limits for non-exhaust particulate emissions. Euro 7 will enter application in 2026 with limits for brake wear, followed by tyre abrasion limits starting in July 2028 (Giechaskiel, Grigoratos, Dilara, et al., 2024). Initially, these limits will regulate the emissions based on mass. This contrasts with recent studies which showed that tyre and road wear particles (TRWP) also contribute to the ultrafine fraction. Within this range, the high PNC, small size, and chemical composition of ultrafine TRWP raise concerns for human and environmental impacts (Baensch-Baltruschat et al., 2020; Grigoratos & Martini, 2014; Kole et al., 2017; Wagner et al., 2018).

Emission process

TRWP are primarily generated through mechanical abrasion of the tyre tread on the road surface, but thermal and oxidative degradation of tyre compounds during driving also contribute (De Oliveira et al., 2024; Gieré & Dietze, 2022; Kreider et al., 2010; Truong et al., 2025). Field and modelling studies estimate that the majority of TRWP by mass is deposited within a few meters from the road or transferred into adjacent soils and sediments (De Oliveira et al., 2024; Klöckner et al., 2020; Kunze et al., 2022; Mian et al., 2022; H. Wang et al., 2023). As a result, road runoff has been identified as a major transport pathway for TRWP into aquatic systems. This way, they are also carried into stormwaters and receiving rivers (Goehler et al., 2022; K. Li et al., 2023; McCarty et al., 2023; Tamis et al., 2021; Wik et al., 2008).

Nevertheless, a fraction of TRWP remains airborne and contributes to the atmospheric particle burden. Most airborne TRWP mass is found in the coarse and fine size fractions. However, by number, laboratory and on-road studies have consistently reported that > 90 % of emitted tyre-related particles are smaller than 100 nm (Bondorf et al., 2025; Dahl et al., 2006; Haugen et al., 2024; Kreider et al., 2010; Löber et al., 2024; Mathissen et al., 2011). These UFP often result from high-energy processes at the tyre-road interface (Chang et al., 2020; Foitzik et al., 2018; G. Kim & Lee, 2018; Mathissen et al., 2011). Reported emission rates for tyre-derived UFP are on the order of 10^{10} – 10^{12} particles km^{-1} vehicle $^{-1}$, although they only account for ~1–5 % of the total TRWP mass (Dahl et al., 2006; Giechaskiel, Grigoratos, Mathissen, et al., 2024; Khardi, 2024; Mathissen et al., 2011).

Chemical composition

Chemically, TRWP are heterogeneous mixtures of tyre- and road-derived material. The formulation of tyre rubber generally consists of 40–60 % natural and/or synthetic elastomers and 20–25 % reinforcing fillers such as carbon black or silica. Additionally, variable amounts of softeners, vulcanisation agents, and other additives are incorporated during production, while heat and friction during driving further alter the chemical composition of tyre surfaces and emitted particles (Müller et al., 2025; Wagner et al., 2018; Wik & Dave, 2009). The bulk elemental TRWP composition is dominated by carbon, hydrogen, sulfur, and zinc. Unfortunately, the ubiquitous occurrence of elements like zinc in the environment hinders their source-specific use as markers. Therefore, research has increasingly focused on organic trace markers for tyres. Among them para-phenylenediamine (PPD) antioxidants, vulcanisation accelerators (e.g., DPG), and benzothiazoles have gained attention (Klöckner et al., 2019, 2021; Kreider et al., 2010). In particular, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) is widely used in tyre formulations and has emerged as a key tracer. When PPD antioxidants react with O₃, they are oxidised to form quinones. Consequently, the oxidation product 6PPD-quinone (6PPDq) has emerged as both a marker of atmospheric transformation and a compound with ecotoxicological relevance (Jiang et al., 2024; Johannessen et al., 2022; Z. Tian et al., 2021; Y. Zhang et al., 2024). At the same time, abrasion processes and atmospheric transformations alter the tyre-related marker composition, which in turn also alters source profiles and complicates the direct attribution of TRWP.

Environmental occurrence

Various field studies show that tyre-related marker profiles vary strongly with environmental conditions, as reported by laboratory abrasion studies as well as field samples. The studies find order-of-magnitude shifts in parent-PPD:quinone ratios, depending on tyre composition, driving conditions, and oxidant levels (Kreider et al., 2010; Mattonai et al., 2022; Rauert et al., 2022; Y. Zhang et al., 2024). This heterogeneity complicates the quantitative use of markers for direct source apportionment. Reported concentrations of TRWP demonstrate their widespread environmental presence across multiple matrices. They were quantified in northern Atlantic marine air (Goßmann et al., 2023) and identified as a dominant nanoplastic fraction in high-Alpine glacier snow (Jurkschat et al., 2025), suggesting the potential for long-range atmospheric transport.

Taken together, current studies (i) show high tyre- and road-wear derived emissions by number, in the UFP range, (ii) report concentrations of tyre-related organic marker compounds in PM_{2.5} from pg to ng m⁻³ levels in urban air, and (iii) demonstrate regional to long-range atmospheric transport potential of TRWP.

Organic tyre-additive markers are therefore increasingly used to analyse and quantify non-exhaust emissions, but their robust application as tracers for source apportionment remains challenging. Abrasion processes and atmospheric ageing can influence both the absolute concentrations and the patterns of chemical markers. Not only are transformation products themselves environmentally relevant, they also undermine simple source-to-concentration back-calculations based on marker composition. **A key knowledge gap concerns how the composition of organic tyre-wear marker compounds evolves coherently across the full source-to-atmosphere continuum.**

Manuscript IV addresses this gap by establishing a unified HPLC–MS workflow for six widely used organic tyre wear markers and applying it on pristine tyre materials, testbed and on-road abrasion emissions, ultrafine particles, and monthly resolved total deposition samples. This enables the observation of directional shifts in organic marker compositions and how abrasion conditions and atmospheric processing jointly influence the composition and thus the interpretability of organic tyre wear markers in environmental samples. The data show coherent, directional changes in tyre-related marker profiles, consistent with progressive transformation along the source-to-atmosphere continuum. Parent PPD concentrations decrease while quinone fractions increase, showing that both wear conditions and ambient processing shape the marker signature and therefore tracer interpretability. The unified HPLC–MS approach enables consistent quantification across matrices and highlights that parent/product pairs are powerful for tracing, while compositional evolution complicates simple mass apportionment based on single markers.

3. Objectives of this thesis

This thesis aims to analyse the chemical composition of airborne UFP and to elucidate how measurement methodology, atmospheric processing, and source-specific emissions collectively influence the observed molecular fingerprints. Four specific objectives are pursued, each corresponding to a manuscript.

Objective I: Characterise and minimise the design-specific biases of cascade impactors when sampling UFP for chemical-composition analysis.

UFP impactors vary in cut-off size, internal geometry, substrate materials, and flow conditions, factors that influence the collection efficiency of UFP, diffusion and wall losses, and particle bounce. The extent to which these design differences affect the chemical composition of the collected UFP remains uncertain.

It is expected that design-specific characteristics of different impactors introduce systematic biases in size-resolved UFP chemistry that are compound-class-dependent, with the strongest effects expected for semi-volatile organics.

Accordingly, the first objective of this thesis is to determine whether UFP samples collected using different impactors display significant, systematic differences in size-resolved molecular composition (Manuscript I). This objective involves analysing physical impactor characteristics, as well as ambient side-by-side sampling of UFP, and performing subsequent chemical analysis to evaluate which compound classes (e.g., semiVOC, PAH) are affected and how.

Objective II: Remove ozone from the sampling air to suppress ozone-induced artefacts in UFP marker compounds.

O₃ present in the sampling stream can react with particle-bound organics during the collection of UFP. Thereby, marker concentrations can be artificially affected or unwanted artefact products can be generated.

It is anticipated that upstream O₃ removal would preserve measured concentrations of particle-bound marker components that are sensitive to O₃ exposure (e.g., PAH and PPD antiozonants), while decreasing the concentration of oxidation products, without disturbing UFP number-size distributions and particle transmission.

Therefore, the second objective of this thesis is the development and evaluation of an upstream ozone-removal technique for UFP sampling (Manuscript II). A TSOD is designed and tested under controlled laboratory and ambient conditions to quantify ozone scrubbing efficiency and to verify that particle number and size distribution of UFP remain unaffected. A dual-channel sampling setup (with and

without the denuder) is applied to assess whether concentrations of organic markers (PAH, antioxidant additives, organic acids) differ systematically between the two streams.

Objective III: Analyse variability in UFP chemical composition by non-target GC×GC analysis.

Sources and atmospheric processing of UFP differ across seasons and even days, which likely results in distinct molecular patterns of their chemical composition. However, resolving this chemical complexity requires comprehensive molecular analysis techniques.

The guiding question is whether seasonal changes in sources and atmospheric processing are translated into shifts in molecular UFP fingerprints that are not captured by targeted marker analysis but can be resolved using non-target GC×GC analysis.

Therefore, the third objective of this thesis is to characterise the molecular composition of ambient UFP using GC×GC-TOFMS and to link observed variability to sources and atmospheric conditions (Manuscript III). UFP samples are collected during contrasting seasons with the previously characterised impactor–denuder setup and analysed to identify chemical groups and compounds that vary significantly. Thereby, the added value of non-target GC×GC is demonstrated, while the method performance is validated against conventional analytical techniques to ensure quantitative.

Objective IV: Study the variability of TRWP-specific organic marker compounds and their chemical transformation from source to atmosphere.

TRWP release organic additives such as antiozonants, antioxidants, and vulcanisation agents, which serve as attractive molecular markers because of their abundance and source specificity. However, these compounds undergo chemical transformation during abrasion and atmospheric ageing, which complicates both source apportionment and risk assessment. Additionally, the high toxicity of certain transformation products raises ecotoxicological concerns.

The central hypothesis is that TRWP marker profiles evolve systematically along the source-to-atmosphere pathway, with progressive oxidation of PPD antiozonants to quinones, thereby altering the reliability of individual compounds as quantitative tracers.

Accordingly, the fourth objective of this thesis is to identify and quantify key TRWP marker compounds and their transformation products along the entire emission pathway, including pristine tyre material, controlled and on-road abrasion emissions, ambient ultrafine particles, and atmospheric deposition samples (Manuscript IV). A unified targeted HPLC–MS method is employed to detect six widely discussed markers and to evaluate how their relative abundances evolve. This approach also assesses the extent to which abrasion and atmospheric processing affect the reliability of individual compounds as quantitative tracers for TRWP.

3.1 Publications and own contributions

Performance evaluation of four cascade impactors for airborne ultrafine-particle (UFP) collection: the influence of particle type, concentration, mass, and chemical nature

Eckenberger, E., Mittereder, A., Gawlitta, N., Schnelle-Kreis, J., Sklorz, M., Brüggemann, D., Zimmermann, R., & Nölscher, A. C. (2025)

Aerosol Research, 3, 45–64. DOI: 10.5194/ar-3-45-2025

Own contribution:

Measurements, data analysis, and writing (original draft, review, and editing).

Author contributions:

AM, DB: DMS500 measurements, data analysis, and writing (review, and editing);

NG, JSK, MS, RZ, ACN: funding acquisition, conceptualisation, supervision, and writing (review and editing).

Sodium Thiosulfate-Coated Ceramic Denuders for Ozone Removal in Ultrafine Particle Sampling

Eckenberger, E., Mittereder, A., Gawlitta, N., Sklorz, M., Brüggemann, D., Zimmermann, R., & Nölscher, A. C. (2026)

Atmospheric Measurement Techniques, 19(12), 4035–4047. DOI: 10.5194/amt-19-4035-2026

Own contribution:

denuder design and preparation, laboratory and field deployment, measurements, chemical analyses, data processing and interpretation, and writing (original draft, review, and editing).

Author contributions:

AM, DB: DMS500 measurements, data analysis.

NG: filter collection and writing (review and editing).

MS, RZ, ACN: funding acquisition, conceptualization, supervision, and writing (review and editing).

About the Variability of Tire and Road Wear Marker Components in Air: From Emissions to Atmospheric Deposition

Eckenberger, E., Younes, M., Mayer, T., Loeber, M., Bondorf, L., Schripp, T., Kernchen, S., Laforsch, C., & Nölscher, A. C. (2026)

Environ. Sci. Technol. 60(2), 2023–2036. DOI: 10.1021/acs.est.5c12735

Own contribution:

Sampling, Measurements, data analysis, and writing (original draft, review, and editing).

Author contributions:

MY, SK: Deposition samples, extractions, and writing (review, and editing).

TM: Extractions and first proof of concept.

ML, LB, TS: Sampling of testbed and on-road driving emissions

CL, ACN: funding acquisition, conceptualisation, supervision, and writing (review and editing).

Sampling and Chemical Characterization of Ambient Ultrafine Particles using Direct Thermal Desorption GC×GC-MS: A Case Study in Augsburg, Germany

Gawlitta, N., **Eckenberger, E.**, Sklorz, M., Schnelle-Kreis, J., Cyrys, J., Nölscher, A. C., Zimmermann, R.

Submitted Manuscript; submitted to Environmental Science: Atmospheres (2026)

Own contribution:

Development and deployment of the automated UFP sampling device, HPLC-FLD measurements, writing (draft, review and editing)

Author contributions:

NG: automated UFP sampling, GC×GC-MS analysis, data analysis and curation, conceptualization, writing – original draft, writing (review and editing)

MS: Conceptualization, writing (review and editing)

JSK: Supervision, conceptualization, data curation, writing (review and editing)

JC: Data (MPSS, CPC, Aethalometer) analysis, writing (review and editing)

ACN: Resources, Funding Acquisition, Conceptualization, data curation, writing – original draft, writing (review and editing)

RZ: Resources, Funding Acquisition, Project administration, Conceptualization, writing (review and editing)

3.2 Summary of the published article – Objective I

Published article I: Performance evaluation of four cascade impactors for airborne ultrafine-particle (UFP) collection: the influence of particle type, concentration, mass, and chemical nature

Accurate chemical characterisation of UFP is challenged by their low mass and by sampling artefacts that are highly dependent on instrument design. Cascade impactors separate particles by aerodynamic diameter, but differences in cut-off size, stage geometry, flow configuration, and substrate treatment can affect particle collection efficiency, diffusion and wall losses, as well as bounce or re-entrainment. This study conducted a systematic, side-by-side evaluation of four UFP-capable cascade impactors (the 120R MOUDI-II, ultraMOUDI, ELPI, and PENS) under controlled laboratory conditions and in parallel field sampling to determine how such design differences introduce biases in measured chemical UFP fingerprints.

Laboratory experiments employed various aerosol types, including sodium chloride, α -pinene SOA, and diesel soot, to assess stage cut-off characteristics, transmission efficiencies, and susceptibility to particle losses and bounce. The instruments exhibited notable differences in physical performance. Cut-off diameters varied depending on particle type, and maximum transmission at 30 nm ranged from ~69 % (ELPI) to ~84 % (PENS). Higher pressure drops were correlated with greater potential for evaporation of semi-volatile compounds, while design features such as the number of stages and the use of coated substrates influenced the extent of particle bounce.

Three parallel 24-hour sampling campaigns were conducted in an urban environment. Six marker compounds, representing different sources and volatilities, were quantified: two PAH (benzo[a]pyrene, benzo[b]fluoranthene), two SOA-derived organic acids (pinic acid and terpenylic acid), the biomass-burning tracer levoglucosan, and the tyre-derived antioxidant 6PPD. Low-volatility PAH exhibited relatively consistent concentrations across all impactors. In contrast, semi-volatile species showed systematic trends, with concentrations generally decreasing from PENS to ultraMOUDI to 120R MOUDI-II to ELPI. This pattern aligns with greater evaporative losses at higher pressure drops and differences in bounce behaviour. The maximum observed disagreement between instruments for a given compound reached ~60 %.

Overall, the study demonstrated that even impactors with similar nominal cut-off sizes can produce substantially different size-resolved chemical profiles as a result of design-dependent artefacts. These findings highlight the necessity for methodological harmonisation in UFP sampling, particularly for semi-volatile compounds, and offers quantitative guidance for interpreting and comparing data obtained with different impactor designs.

3.3 Summary of the published article – Objective II

Published article II: Sodium Thiosulfate-Coated Ceramic Denuders for Ozone Removal in Ultrafine Particle Sampling: Performance from Laboratory to Field.

O₃ is a strong atmospheric oxidant that can artefactually degrade particle-bound organic components during sampling, particularly in the ultrafine fraction due to its high specific surface area. Such degradation biases the measured concentrations of organic markers, including PAH and tyre-wear additives, and can result in the in-situ formation of oxidation products. This study aimed to develop and validate a TSOD for UFP sampling that (i) removes O₃ effectively, (ii) does not induce measurable particle losses across the UFP size range, and (iii) selectively scrubs O₃ from the sampling air without interfering with the gas phase or introducing additional artefacts.

Laboratory experiments conducted under controlled relative humidity (~50 %) showed near-complete O₃ removal for inlet concentrations up to 200 ppb, with outlet levels indistinguishable from reference baselines. Particle-loss tests using secondary organic aerosol confirmed that the TSOD introduced UFP losses within the range of the instrument's uncertainty across relevant flow rates.

Field deployment involved the TSOD in a dual-channel setup alongside an uncoated reference sampling line, positioned downstream of a reduced 120R MOUDI impactor. Continuous monitoring confirmed O₃ removal under ambient conditions. Chemical analyses of parallel filter samples revealed distinct results for organic marker compounds: PAH concentrations were higher in the denuded channel, indicating suppression of in-situ degradation, with relative artefacts of up to ~40–45 % for high-molecular-weight PAH. For tyre-wear markers, the antiozonant 6PPD was higher and its quinone oxidation product was lower in the denuded channel compared to the O₃-exposed channel. Mass-balance analysis indicated that ~15–20 % of 6PPD can be converted to 6PPD-quinone under O₃ exposure during UFP sampling. In contrast, biogenic organic acids showed no significant inter-channel differences, suggesting that the TSOD did not affect gas–particle partitioning for these semi-volatile species.

In summary, the TSOD achieved O₃ removal under both laboratory and field conditions, negligible UFP losses, and selective scrubbing of O₃ without introducing new biases for semi-volatile organic acids. These results demonstrate a field-ready, chemically selective solution for minimising oxidant artefacts during UFP sampling.

3.4 Summary of the submitted article – Objective III

Submitted article III: Sampling and Chemical Characterisation of Ambient Ultrafine Particles: A Case Study in Augsburg, Germany

Chemical characterisation of UFP is frequently constrained by their low mass. In this study, a daily, automated UFP sampling protocol was implemented at an urban background site in Augsburg, combining an upstream TSOD with a reduced ultraMOUDI (cut-points 2.5/1.0/0.1 μm). Two sampling campaigns were conducted in spring (March 2023) and autumn (September 2023) to capture seasonal variability. Samples were analysed by direct thermal desorption (DTD)-GC $\times$ GC-TOFMS for ten targeted PAH and by non-target analysis to classify broader compound families, including oxygenated PAH, alkylated PAH, and hopanes. Meteorology, air quality, particle size distributions, and back-trajectories supported source interpretation.

A method comparison was performed prior to data interpretation to validate GC $\times$ GC results. Quantification of PAH by DTD-GC $\times$ GC-TOFMS was evaluated against HPLC-FLD using the NIST SRM 2786 reference material. The two methods demonstrated strong agreement, with high correlations observed (e.g., $\Sigma[\text{BaP}, \text{BeP}]$ slope = 0.83, $R^2 = 0.98$ for the standard; slope = 1.02, $R^2 = 0.93$ for ambient samples), thereby confirming the robustness of the GC $\times$ GC approach and its comparability to established reference techniques.

The PAH data revealed distinct seasonal and short-term variability. In March, PAH concentrations remained relatively stable (e.g., BaP 9–14 pg m^{-3}). In contrast, September was characterised by a lower-pollution period (Sep-1) and a short high-pollution episode (Sep-2), during which the total PAH concentration increased to $\sim 270 \text{ pg m}^{-3}$ and BaP levels rose more than fourfold. The latter coincided with stagnant, low-altitude easterly flow and elevated combustion tracers, suggesting a strong local influence.

Non-target GC $\times$ GC analysis identified compositional changes in UFP composition. March UFP samples contained a higher proportion of oxygenated PAH, consistent with more aged or regionally transported aerosol. In contrast, September samples exhibited stronger hopane signals, indicative of traffic and lubricating-oil contributions. During the high-pollution episode in September, increased concentrations of parent and alkylated high-ring PAH were observed, suggesting fresh combustion sources. Hopane source ratios further supported these findings, indicating additional heating-related sources in March and predominantly traffic-related sources in September.

Overall, the findings demonstrate that both seasonal and short-term meteorological conditions substantially affect the molecular fingerprint of ambient UFP. The integration of non-target GC $\times$ GC analysis, cross-validation against targeted HPLC-FLD and certified reference material, yields a chemically resolved molecular composition that distinguishes aged, regionally transported aerosol from

fresh, traffic-related emissions. This approach offers a methodological framework for future long-term UFP monitoring studies.

3.5 Summary of the published article – Objective IV

Published article IV: About the Variability of Tire and Road Wear Marker Components in Air: From Emissions to Atmospheric Deposition

Tyre wear emits a complex mixture of rubber additives, the diagnostic value of which as molecular markers is determined by their persistence and transformation from emission to deposition. Two HPLC-MS methods with complementary gradients and SIM detection, validated using internal standards, were developed and applied to quantify six widely discussed TRWP markers (DPG, IPPD, 6PPD, IPPDq, 6PPDq, DPPD) throughout the entire tyre-to-atmosphere pathway. Detection limits for air samples ranged from ~ 15 to 54 pg m^{-3} . QA/QC procedures included calibration with a reference tyre material, blanks, and repeatability assessments.

Samples encompassed the entire lifecycle of a tyre: (i) reference tyre compounds and shredded bulk in three size classes to assess extraction efficiency and particle-size effects; (ii) worn tyre surface sections to evaluate in-use variability; (iii) controlled abrasion emissions from two tyres, including size-resolved ELPI measurements ($0.094 - 3.6 \text{ }\mu\text{m}$); (iv) on-road emissions from the ZEDU-1 demonstrator vehicle; (v) ambient UFP at six Bavarian sites, ranging from alpine background to urban traffic locations, sampled with an ozone denuder, ultraMOUDI impactor and 24 h automated filter changer; and (vi) monthly total atmospheric deposition at an urban site over one year.

Results showed directional changes in marker composition along the source-atmosphere pathway. Abrasion caused a loss of parent 6PPD by roughly an order of magnitude, accompanied by the appearance of 6PPDq, indicating oxidative transformation during wear. However, the measured 6PPDq accounted for only a small fraction of the lost 6PPD, suggesting additional transformation pathways and/or volatilisation. Smaller particle sizes yielded higher oxidised marker concentrations per mass, consistent with greater surface oxidation.

In ambient UFP, 6PPD was detectable at all sites, scaling with urban intensity. Atmospheric deposition fluxes showed seasonal trends, with 6PPD peaking in winter and quinones dominating ($> 50 \%$ of total PPD markers) in summer. The proportion of 6PPD-quinone relative to total 6PPD + 6PPD-quinone increased systematically from tyre material ($\sim 1\text{--}15 \%$) to emissions ($\sim 26 \%$), to ambient UFP ($\sim 46\text{--}51 \%$), to deposition ($\sim 63 \%$ in spring-summer), indicating progressive oxidation during atmospheric transport and ageing.

The unified analytical approach reveals a coherent pattern of PPD-based marker transformation from tyre to environment: abrasion initiates chemical shifts, while ambient processing further alters the chemical composition. This dual dynamic enhances the potential for tracing TWP emissions using parent/product pairs, but also complicates mass apportionment due to variability in tyre composition, emission conditions, and atmospheric ageing. The dataset also quantifies non-negligible environmental loading of PPDqs via atmospheric deposition, relevant for exposure and fate assessments.

4. Outlook

This thesis examined how measurement methodology, atmospheric processing, and source-specific emissions jointly influence the molecular fingerprint of airborne UFP.

One key finding is that uncertainty in UFP characterisation already arises at the sampling stage. Furthermore, challenges in the characterisation of UFP arise due to their low mass, as measurements are frequently near detection limits and require long sampling durations, which further increases susceptibility to methodological bias. Thus, cross-study comparability is limited, as different studies use different methods for UFP sampling and characterisation. Consequently, it is even more difficult to establish a comprehensive link between UFP composition and their potential effects on human and environmental health, despite increasing toxicological evidence. The WHO Global Air Quality Guidelines (2021) have emphasized that the lack of standardized and comparable exposure data remains a primary barrier to deriving health-based limit values for UFP.

A key example of such methodological sensitivity is size-segregated UFP sampling with cascade impactors, which remains a standard collection approach for subsequent offline chemical characterisation. In the UFP range, small performance differences in the separation method can systematically bias the recovered mass and chemical composition. Without explicit quantification and awareness of these artefacts, chemically resolved UFP compositions obtained with different impactors are difficult to compare, and apparent “source” or “seasonal” differences may partly reflect methodological effects. Consequently, future UFP research should focus on sampling strategies that explicitly account for chemical biases during UFP collection.

This thesis also demonstrates that selective artefact mitigation (e.g., ozone denuding) is capable of improving the integrity of the chemical composition of UFP samples. To contextualize these findings, a systematic assessment should be conducted to determine the extent to which UFP studies may have been affected by such impactor- and denuder-induced artefacts. The next step would be the widespread implementation of such denuder concepts in long-term field studies. This would not only minimise sampling biases but also provide an operational basis to continuously quantify oxidant-driven changes in UFP under varying realistic conditions.

While particle number concentrations are increasingly regulated, the chemical complexity and low mass of UFP requires high-resolution analytical methods. The success of GC×GC fingerprinting in yielding patterns across different pollution episodes suggests a proof of concept in observing chemical UFP patterns during varying seasons and pollution events. However, to make these complex datasets comparable across different studies, establishing a harmonised, CEN-style protocol for UFP chemical measurements is essential. Such a protocol should include standardized methods as well as cross-

calibration against established reference methods to ensure that "molecular fingerprints" are reproducible and comparable on a global scale.

Regarding TRWP, future research must treat atmospheric transformation as a defining feature rather than a complication. This thesis identified coherent, directional changes in tyre-related marker profiles along the source-to-atmosphere continuum. Future studies investigating TRWP in the environment based on organic tyre additives should therefore move away from single-compound analysis, which can be misleading, toward parent-product relationships. Investigating these relationships in controlled environments, such as chamber studies linked to chassis dynamometers, would further refine our ability to back-extrapolate environmental findings to primary emissions.

Ultimately, the goal should be to provide a reliable evidence base that bridges the gap between UFP measurement and potential effects. Although UFP have been regulated by particle number concentration since 2024, this contrasts with historical air-pollution monitoring and much of the toxicological evidence base, which are largely mass-based. In order to determine what truly matters for human and environmental health, we must first ensure that the methodology to characterise UFP is reproducible and comparable, and that their chemical fingerprints are fully resolved.

5. Published and submitted articles

Published Article I

Performance evaluation of four cascade impactors for airborne ultrafine-particle (UFP) collection: the influence of particle type, concentration, mass, and chemical nature



Performance evaluation of four cascade impactors for airborne ultrafine-particle (UFP) collection: the influence of particle type, concentration, mass, and chemical nature

Elisabeth Eckenberger¹, Andreas Mittereder², Nadine Gawlitta^{3,4}, Jürgen Schnelle-Kreis^{3,4}, Martin Sklorz⁴, Dieter Brüggemann², Ralf Zimmermann^{3,4}, and Anke C. Nölscher¹

¹Bayreuth Center of Ecology and Environmental Research (BayCEER),
University of Bayreuth, Bayreuth, Germany

²Department of Engineering Thermodynamics and Transport Processes,
University of Bayreuth, Bayreuth, Germany

³Comprehensive Molecular Analytics (CMA), Helmholtz Munich, Munich, Germany

⁴Institute of Chemistry, Division of Analytical and Technical Chemistry,
University of Rostock, 18059 Rostock, Germany

Correspondence: Elisabeth Eckenberger (elisabeth.eckenberger@uni-bayreuth.de) and Anke C. Nölscher (anke.noelscher@uni-bayreuth.de)

Received: 8 August 2024 – Discussion started: 9 August 2024

Revised: 17 November 2024 – Accepted: 5 December 2024 – Published: 27 January 2025

Abstract. Ultrafine particles (UFPs) have aerodynamic diameters of 100 nm or less. As UFPs potentially impact human and environmental health, their chemical composition is of interest. However, their small mass presents challenges for sampling and chemical characterization methods. Therefore, we conducted a comprehensive characterization and comparison of four cascade impactors suitable for separating and collecting UFPs – namely, the 120R Micro-Orifice Uniform Deposit Impactor (120R MOUDI-II), ultraMOUDI, electrical low-pressure impactor (ELPI), and personal nanoparticle sampler (PENS) – under controlled laboratory conditions and in a field application.

In the laboratory, we evaluated pressure drops, cutoff diameters, the steepness of the cutoff curve, losses, particle bounce, and transmitted particle mass. We observed that the performance of the impactors varied between 59 and 116 nm in cutoff diameter (electromobility diameter), depending on the impactor's design and the type of test aerosol mixture – salt particles (NaCl), simulated secondary organic aerosol (SimSOA), or soot. All impactors separated UFPs, with the best agreement in cutoff diameters for SimSOA, which showed maximum deviations of about 4 nm. The cutoff curve was steeper for soot compared to SimSOA and NaCl. Pressure drops were measured at 260 ± 1 hPa (PENS), 420 ± 2 hPa (ultraMOUDI), 600 ± 3 hPa (120R MOUDI-II), and 690 ± 3 hPa (ELPI). Losses were assessed as maximum transmissions in the ultrafine fraction at 30 nm, yielding 83 ± 8 % for the PENS, 77 ± 8 % for the ultraMOUDI, 75 ± 8 % for the 120R MOUDI-II, and 69 ± 7 % for the ELPI. We compared two additional impactor-specific factors crucial for mass-based analyses of organic marker compounds: the evaporation of semi-volatile compounds due to a high-pressure drop across the impactor and material addition from larger particles bouncing off upper stages. “Bounce-off” was influenced by the particle number concentration in the sampled air and could be partially mitigated by applying a coating to the upper impaction plates.

In the field application, we deployed the four cascade impactors side by side under environmental conditions to sample urban air. We analyzed six markers representing typical UFP sources and various molecular

properties using HPLC-MS/FLD (high-performance liquid chromatography with mass spectrometry and fluorescence detection). These markers comprised benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), levoglucosan (Levo), pinic acid (PA), terpenylic acid (TA), and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD). The impactors showed the best agreement for BaP and BbF. BaP had an average mass concentration of $175 \pm 25 \text{ pg m}^{-3}$ across all impactors and sampling days. However, concentrations were about 29 % higher when sampled with the PENS and 30 % lower when sampled with the 120R MOUDI-II, indicating a maximum disagreement of nearly 60 %.

The mass concentrations of the semi-volatile markers (PA, TA, and Levo) decreased on average from the PENS to the ultraMOUDI, then to the 120R MOUDI-II, and finally to the ELPI. We attributed this tendency to the following two effects. (1) Evaporation losses of these markers were likely driven by the pressure drop within the impactor, which increased from the PENS to the ELPI. (2) Despite the applied coating, bounce-off might have affected the smallest impactors (i.e., the PENS and ultraMOUDI) the most as they have fewer stages for retaining larger particles and fragments.

1 Introduction

The characterization of ultrafine particles (UFPs) in the atmosphere is key to understanding the causes and impacts of air pollution. UFPs are defined as particulate matter with aerodynamic diameters of 100 nm or less. They have gained considerable attention due to their potential impacts on human health and the environment (Kumar et al., 2014, 2021; Schwarz et al., 2023). Furthermore, airborne UFPs are naturally linked to weather and climate as they might alter the Earth's radiative budget directly or indirectly when growing and activating to form cloud droplets (Junkermann et al., 2022). The size and chemical composition of UFPs are thus crucial properties for assessing their sources and atmospheric fate, as well as potential adverse effects.

Information about the size and chemical composition of airborne particulate matter can be collected via impactors. Impactors allow for the separation of particles in an air sample based on their aerodynamic diameter (d_a). The physical separation of particles within an impactor is based on the particles' inertia, which causes smaller particles to continue moving when the airflow bends sharply – for example, when forced through nozzles, orifices, or slits (Baron and Willeke, 2011). Upon separation, the particles can be collected on impaction plates or downstream of the impactor by using filter substrates, such as aluminum foil, PTFE, or quartz fiber filters. Particles caught on the substrate can be extracted and undergo chemical analysis to determine their composition (Bein and Wexler, 2014; Canepari et al., 2010; Daher et al., 2011). To describe the separation and collection efficiency, d_{p50} – the diameter at which particles are collected with 50 % efficiency – is used. Indeed, the d_{p50} value, or cutoff diameter, for a given impactor design will depend on the nozzle diameter and the flow rate.

A stack of impactors, consisting of impactor-plate–nozzle-plate pairs, forms a cascade impactor. Within the cascade impactor, the nozzles or slits become increasingly smaller, causing the air to move faster through these orifices. Large

particles impact earlier, while smaller particles travel further through the impactor and are collected at later stages. Cascade impactors were first employed in the 1860s to study the relationship between airborne particles and diseases (Marple, 2004). Later models enabled size classification in the sub-micrometer range (May, 1945; Berner et al., 1979; Brink, 1958; Mitchell and Pilcher, 1959). Examples include the Berner and Anderson impactors (Hata et al., 2012; Hillamo and Kauppinen, 1991); the electrical low-pressure impactor (ELPI), which can be used for real-time size distribution measurements (Keskinen et al., 1992; Marjamäki et al., 2000; Held et al., 2008); the Micro-Orifice Uniform Deposit Impactor (MOUDI), which is capable of capturing particles as small as $0.056 \mu\text{m}$ (Marple et al., 1991); miniaturized impactors, such as the personal nanoparticle sampler (PENS) (Tsai et al., 2012); and the novel development of small samplers for ultrafine particles (Thongyen et al., 2015; Kumsanlas et al., 2019; Gong et al., 2023).

Several recent studies have focused on airborne UFP chemical analyses using cascade impactor sampling. For example, the MOUDI has been used at Frankfurt Airport to analyze size-resolved UFP emissions from aircraft, identifying organic compounds such as esters from jet engine oils (Ungeheuer et al., 2021). In Rio de Janeiro, the MOUDI was used to collect ultrafine and coarser particles from vehicular emissions in an urban area, and the trace element composition was analyzed across various particle sizes, detecting cadmium, nickel, lead, chromium, and iron, particularly in the UFP ranges (de Souza et al., 2021). The ELPI can be used for the simultaneous real-time sampling of particle size distributions and offline chemical analysis, as demonstrated, for example, by Kim et al. (2013), who classified and characterized airborne particulate matter from a rubber manufacturing plant. In the surroundings of a former electronic waste recycling facility, the ELPI was used to detect real-time airborne particles in the size range of $0.03\text{--}10 \mu\text{m}$ (Guo et al., 2023). Moreover, a size-resolved chemical characterization of airborne particles from indoor sources, such as candles, mosquito coils,

and cooking activities, highlighted heavy metals and polycyclic aromatic hydrocarbons (PAHs) in the ultrafine fraction (Caracci et al., 2024). Similarly, other working environments were characterized in terms of personal exposure via the application of a portable PENS (e.g., Pomata et al., 2023; Young et al., 2013). The PENS has also been employed in air quality studies, such as those conducted in rural and urban China during winter, for the chemical analysis of biomass-burning tracers (e.g., levoglucosan) (Zhu et al., 2017). While not exhaustive, these examples underscore the growing number of applications of, as well as the increasing interest in, diverse types of target analytes. This raises the question of comparability between cascade impactor applications for the chemical analysis of atmospheric ultrafine particles.

The challenge, particularly when it comes to the separation and collection of UFPs from the atmosphere using cascade impactors, is unequivocally associated with the remarkably small mass of UFPs. This small mass, as opposed to fine particulate matter (PM_{2.5}), presents a substantial hurdle in conducting gravimetric or chemical analyses. Specifically, UFP collection with cascade impactors is sensitive to the following aspects:

1. The cutoff diameter for UFPs from the last impactor stage ($d_{p50} = 100$ nm, referring to aerodynamic diameter) depends on the impactor's design and operational characteristics, such as the diameter, nozzle size, flow rate, distances between plates, and shape. Moreover, real atmospheric particles, with various shapes and densities, will vary in impaction behavior and thus potentially influence the separation.
2. The loss of UFPs on walls or in earlier stages could result in the retention of particulate material.
3. During collection, either larger particles bounce or break into fragments and experience re-entrainment, adding mass to the filter substrate dedicated to UFPs, or target UFPs bounce off the collection substrate and are lost from the analysis.
4. Semi-volatile particle-bound components may evaporate from already collected particulate surfaces during ongoing sampling due to reduced pressure within the impactor and continuous ventilation. This can result in alterations in the chemical composition due to interactions with the gaseous phase.

Therefore, in this study, we explored cutoff diameters, potential losses, artifacts due to “bounce-off”, and evaporation with respect to four different cascade impactors capable of separating and sampling UFPs. Our overall aim was to identify and quantify organic marker compounds in the collected UFPs. The four cascade impactors differed in terms of design, flow rate, the number of stages, and other factors. We expected that these differences would significantly impact the abovementioned aspects and, therefore, lead to different

results for the analyzed mass concentrations of the selected organic marker compounds within the collected UFPs.

2 Methods

2.1 Impactors for UFP sampling

Today, several cascade impactors exist that are either commercially available or newly developed (Crazzolaro and Held, 2024; Ngagine et al., 2022; Järvinen et al., 2014; Romay and García-Ruiz, 2023; Marple et al., 2014; Tsai et al., 2012). For our comparison, we selected four commercially available models for sampling atmospheric UFPs that have different designs, flow rates, and stage numbers. Additionally, we aimed to sample all particles ≤ 100 nm on one substrate without further separation. Moreover, we envisioned the use of an automated filter changer in future applications, which is possible with all selected models. Some of these selected impactors required minor adjustments to make them suitable for achieving the final cutoff diameter of 100 nm. Aside from these adjustments, which are outlined in the following, the cascade impactors were operated as described by the manufacturers.

For each impactor and measurement, the aerosol flow was regulated between the impactor and its pump. The flow rate was determined at the impactor's inlet with a Gilibrator-2 bubble flow meter and rechecked following each collection interval.

Rotating 10-stage 120R MOUDI-II. The MOUDI utilizes numerous micro-orifice nozzles to reduce jet velocity, pressure drop, particle bounce, and re-entrainment while enhancing collection efficiency and enabling a uniform deposition on the impaction plate (Marple et al., 1991). Each pair of nozzle and impaction plates is called a stage. The uniform deposition prevents particle buildup and allows for a greater collection mass without overloading. It is further supported by rotating the impaction plates relative to the nozzles while distributing the sampled particles over the sampling substrates. Earlier MOUDI models (Models 110 and 115) achieve relative rotation between the impaction and nozzle plates by rotating alternate impactor stages using external gears and hooks that mesh with an external drive shaft powered by an electric gear motor. In contrast, the newest model (120R MOUDI-II, MSP Corp., Shoreview, MN, USA) has impaction plates that are directly mounted onto miniature stepper motors, which are housed within a chamber situated in the center of each stage. Therefore, the 120R MOUDI-II model offers an undisturbed flow path from the impaction plate to the following stage's nozzle plate. This design is expected to show relatively low particle losses compared to previous models (Marple et al., 2014).

In this study, we modified the 120R MOUDI-II by removing the 0.56 μ m stage (including the nozzle and impaction plates) located below the 100 nm cutoff diameter stage. This modification allowed us to collect all particles ≤ 100 nm

in the original “after-filter” holder mounted at the impactor outlet. As recommended, we operated the 120R MOUDI-II model at a flow rate of 30 L min^{-1} . It separated airborne particulate matter into nine fractions with nominal cutoff diameter (d_{p50}) values of 0.10, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, and $10 \mu\text{m}$. We equipped all upper stages with pieces of aluminum foil with a 47 mm diameter, which were greased at a later stage of the experiments. We placed a 47 mm quartz fiber filter (QFF; Whatman QM-H) in the after-filter holder for the collection of UFPs.

Non-rotating three-stage MOUDI (ultraMOUDI). In contrast to the 10-stage 120R MOUDI-II model, this compact MOUDI model has three non-rotating stages (MOUDI 100-2.5-1-0.1, MSP Corp., Shoreview, MN, USA). The internal construction of these stages is similar to that of Models 110 and 115 and shares the same inlet and outlet design. We asked the manufacturer for three stages with cutoff diameters of 0.1, 1, and $2.5 \mu\text{m}$. Here, we employed the ultraMOUDI with pieces of aluminum foil (47 mm diameter) on the impaction plates. The after-filter holder was equipped with a 47 mm quartz fiber filter (Whatman QM-H). The flow rate through the impactor was 30 L min^{-1} . Due to its reduced size and weight, this impactor could be integrated into an automated sampler for independent long-term observations of UFPs.

ELPI. The ELPI (Dekati Ltd., Tampere, Finland; Keskinen et al., 1992) separates and counts particles simultaneously in the respective stages while sampling. In this way, the ELPI determines particle size distributions ranging from 30 nm to $10 \mu\text{m}$. Sampled particles are first charged to a predetermined level. These charged particles are then classified by aerodynamic diameter within the cascade impactor. Lastly, a multichannel electrometer simultaneously measures the charges carried by the collected particles to each stage, providing a measurement for the particle number concentration. The particle classification is achieved using a multi-jet impactor, where stage 1 has the smallest cutoff diameter and stage 13 has the largest (diameters: 0.03, 0.06, 0.09, 0.17, 0.26, 0.40, 0.65, 1.0, 1.6, 2.5, 4.4, 6.8, and $10 \mu\text{m}$). The jet orifices are symmetrically drilled in rings around the center of each stage. Stage 1 of the impactor serves as a critical orifice, regulating the flow rate to 30 L min^{-1} and creating a low pressure, which is thought to ensure the impaction of even the smallest particles (Marjamäki et al., 2000).

For this study, we extracted the cascade impactor component from the ELPI and treated it as a standalone impactor, excluding the charger and electrometer. For the collection of UFPs, we removed the stages with cutoff diameters of 0.03 and $0.06 \mu\text{m}$ to achieve a final cutoff size of $0.09 \mu\text{m}$ for stage 3. To maintain the flow characteristics, secure the impaction plates in the built-in tensioner, and ensure appropriate spacing between the nozzle and collection plates, place-holders were inserted. The flow was adjusted with a valve. On the upper stages, aluminum foil filters (25 mm, Dekati Ltd.) were installed. For the collection of UFPs, a 37 mm

QFF was installed in the after-filter holder provided by the manufacturer.

PENS. The PENS (Haze Control System Inc., Taiwan) was recently designed by Tsai et al. (2012) as a three-part system for the collection of airborne particles. The first part is a respirable cyclone that separates particles larger than $4 \mu\text{m}$ in aerodynamic diameter. The second part is a micro-orifice impactor, where particles sized from 0.1 to $4 \mu\text{m}$ impact on an impaction plate. The final part consists of a filter holder containing a 37 mm quartz fiber filter, which collects UFPs. Compared to the previously described devices, the PENS is compact, with dimensions of 107 mm in length and 44 mm in width, as well as a total weight of 240 g. This makes the PENS portable and useful for personal exposure studies (Young et al., 2013). The manufacturer modified the PENS used in this study to separate the particles into fractions of 2.5 and $0.1 \mu\text{m}$ and to operate at a sampling flow rate of 4 L min^{-1} . The impaction plate itself is not suitable for installing a filter. For the collection of UFPs within the after-filter, we utilized a 37 mm quartz fiber filter (Whatman QM-H).

2.2 Overview of laboratory tests for evaluating the performance of the four impactors for UFP separation and collection

To test the four cascade impactors under controlled conditions, we conducted a series of laboratory tests. Our objective was to determine the pressure drop, transmission, UFP cutoff diameter, and potential artifacts of each impactor. Therefore, we generated three types of test aerosols and used reference instrumentation to quantify UFPs. In this way, we detected the particle number size distribution before and after the test aerosol passed through the impactors.

2.2.1 Detection of particle number size distributions

We monitored the particle number size distributions for the four cascade impactors with two complementary instruments. For accurate and sensitive observations, a mobility particle size spectrometer (MPSS) was deployed. However, the analysis of cutoff performance for impactors with a pressure drop of several hundred hectopascals (hPa) posed a challenge to the MPSS flow regulation. Thus, for fast and repetitive measurements recorded under low pressure, a real-time differential mobility spectrometer (DMS) was used. However, this instrument has comparatively low sensitivity.

MPSS

The MPSS (manufactured by TROPOS, Leibniz Institute for Tropospheric Research) classifies and quantifies airborne particles based on the principle of the mobility of charged particles in an electric field (Wiedensohler et al., 2012, 2018). Sampled particles are neutralized to achieve a Fuchs equi-

librium charge distribution and then classified by a differential mobility analyzer (DMA) based on electrical mobility and detected with a condensation particle counter (CPC). The particle number size distribution is obtained by scanning the voltage applied to the DMA, typically covering a range of 10 to 800 nm. The MPSS is capable of detecting down to 10 particles per cm^3 per scan (Wiedensohler et al., 2012). The MPSS data were processed following the protocol by Wiedensohler et al. (2012), including corrections for particle losses and CPC counting efficiency. The MPSS measurements had an uncertainty of $\pm 10\%$.

DMS500

The DMS500 (Cambustion) uses a corona diffusion charger and a classification column with electrometers to detect particle concentrations across a size range of 5 nm to $2.5\ \mu\text{m}$, with a time resolution on the order of milliseconds (Symonds et al., 2007). The air sample is diluted twice before classification, leading to a comparatively low sensitivity of $170\ \text{cm}^{-3}$ for 80 nm particles. The DMS500 was calibrated using polystyrene latex spheres (3320A/3495A, Thermo Scientific, National Institute of Standards and Technology (NIST)), and data were processed using DMS software (DMS 6.09 complemented by DMS Excel Utilities 7.49). The overall uncertainty in the instrument was $\pm 23\%$, calculated based on the relative standard deviation for the test particle mixtures (Cambustion Ltd., 2019; Symonds et al., 2004; see Sect. 2.2.2).

2.2.2 Test particle generation

To determine the cutoff characteristics of the individual impactors under controlled conditions, we used a laboratory test bed consisting of a defined particle source, the test impactor, and a reference instrument (such as the MPSS or DMS500), which determined the particle number size distributions. If needed, the impactors were modified to have a cutoff diameter of 100 nm at the last stage (see Sect. 2.1.). Furthermore, we removed the after-filter holder in order to directly assess the transmitted particles with the online reference instruments. Instead, following the impactor, a “Y” piece made of stainless steel (inner diameter: 15 mm) was installed, directing the airflow to the detector and a pump. The pump was adjusted to achieve the correct overall sampling flow for the impactor. The test impactor was then connected to one of three different particle sources. The setup is presented in Fig. 1.

NaCl particles

First, we generated salt particles from sodium chloride (NaCl). The particles were generated using a commercially available nebulizer, i.e., PARI LC SPRINT (Type 023). The nebulizer was filled with a saturated solution of NaCl in Mil-

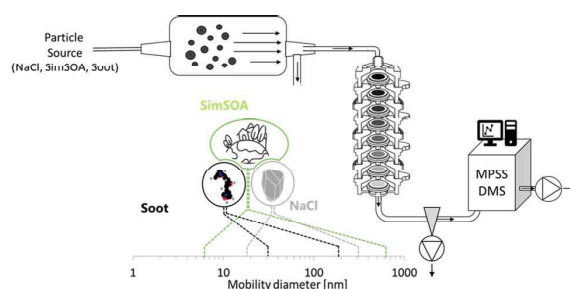


Figure 1. Schematic experimental setup used to evaluate the cutoff characteristics of various impactors: the 120R MOUDI-II, ELPI, PENS, and ultraMOUDI. Three different types of particles were generated: (1) NaCl (produced by spraying a saline solution), (2) simulated secondary organic aerosol (SimSOA) (generated through a chamber experiment involving particle formation from α -pinene and ozone, including seed particles), and (3) soot (produced by a diesel engine) (Sect. 2.2.2).

lipore water. We connected synthetic compressed air from the house line to the nebulizer and regulated it with a needle valve to $4\ \text{L min}^{-1}$. This aerosol flow was directed into a 30.5 L quartz glass flow tube for dilution, mixing, aging, and drying. Since the majority of the impactors have a flow rate of $30\ \text{L min}^{-1}$, an additional $40\ \text{L min}^{-1}$ of synthetic air was fed into the flow tube for dilution. At the flow tube outlet, the test impactor was connected in line with the reference instrument and the pump. This setup allowed us to run tests for a time period of about 6–8 h with a stable and relatively broad test particle number size distribution (Fig. 2).

With estimates of the density ($\rho_p = 2.16\ \text{g cm}^{-3}$) and shape ($\chi = 1$) of the NaCl particles, we converted the electrical mobility diameter (d_m) given by the reference instruments to an aerodynamic diameter (d_a) (Baron and Willeke, 2011). The aerodynamic diameter is the basis for the size-based separation of particles in the impactors and thus the critical value for evaluation and comparison.

Soot particles

Secondly, we tested the four impactors with diesel exhaust particles containing soot, following the experimental setup previously described by Mühlbauer et al. (2016). For our investigation, we employed a contemporary four-cylinder diesel engine supplied by Daimler AG (OM651, Mercedes-Benz, Germany). This engine is equipped with a common-rail system and features direct-acting piezoelectric injectors from Delphi Automotive PLC (United Kingdom). This production engine, equipped with a particle filter, complies with the European exhaust emission standard Euro 5. The engine was run at a speed of 1200 rpm (revolutions per minute), with an injection pressure of $7 \times 10^7\ \text{Pa}$, using a throttle position maintained at 15 %, and at an exhaust gas recirculation (EGR) rate of 45 %. The engine emissions were directly

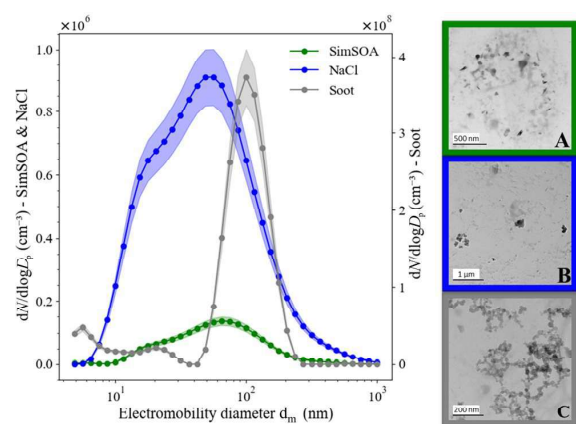


Figure 2. Particle number size distributions of three particle types for physical impactor testing, averaged over the duration of the experiments and displayed with standard deviations for each particle type. The data for SimSOA (green) and NaCl (blue) correspond to the left axis, while the soot data (black) correspond to the right axis. The particle size distribution is expressed as the number of particles (dN) per logarithmic diameter interval ($d\log D_p$). SEM (scanning electron microscopy) images of the test particles are displayed in plots A (SimSOA), B (NaCl), and C (soot).

channeled from the exhaust pipe to the impactor to achieve a stable particle number size distribution around the 100 nm diameter range (Fig. 2).

Simulated secondary organic aerosol (SimSOA)

Thirdly, we tested the impactors' performances with atmospherically simulated secondary organic aerosol (SimSOA). In order to conduct our tests with a stable mixture for several hours, we used a chamber from the Bayreuth ATmospheric simulation CHambers (BATCH) infrastructure (Ofner et al., 2011). Before each measurement, a 700 L cylindrical glass chamber was flushed with outdoor air to introduce real environmental particles and trace gases. Subsequently, 0.05 mL of α -pinene was injected into the airflow, while a nebulizer delivered seed particles (saturated ammonium sulfate solution) into the chamber at a flow rate of 3 L min^{-1} for 3 min. After an additional 5 min, the pump supplying outdoor air was switched off, and a UV solar simulator (HMI 4000 W, Osram (filtered with a water-cooled glass plate); Ofner et al., 2011; Zhao et al., 2008) was turned on for 15 min to stimulate ozone production and the subsequent formation of SimSOA. Prior to commencing the impactor measurements, the reference instruments were directly connected to the chamber to ensure suitable particle concentrations and number size distributions (Fig. 2).

2.2.3 Determining physical parameters as evaluation criteria

To comprehensively characterize the four cascade impactors for UFP sampling, we focused on determining the pressure drop and cutoff properties, evaluating potential particle losses, and identifying any measurement artifacts that may arise. For each impactor, we followed the same protocol: determine the particle number size distribution of the test particles (step 1), insert the (modified) impactor and monitor the transmitted particles as described (step 2), and conduct an *empty* measurement (step 3). For the empty measurements, all nozzle stages and impaction plates were removed, meaning that no size classification occurred, and the inlet and outlet of the impactor were connected as in step 2. Step 3 allowed for baseline measurements without the influence of impaction stages while maintaining a setup comparable to that of the transmission measurements in step 2.

Pressure drop assessment. The pressure drop across each impactor was measured using a differential pressure gauge. This measurement encompassed the total pressure loss through the impactor, including the quartz fiber after-filter that was integrated into the system. For this measurement, T-junctions were installed at both the inlet and outlet of the impactor. Branches from these junctions were connected to the differential pressure gauge (26 PCCFA6D (differential pressure sensor, relative, ± 15 psi), Honeywell) to record the pressure drop across the entire impactor and the quartz fiber filter on which the UFPs were collected. The pressure drop was determined at the same flow rate as that used for each impactor under operating conditions.

Cutoff diameter determination. To derive the transmission of particles through the impactor as a function of the particles' diameter, the ratio of the number concentration between the impactor (step 2) and the empty measurement (step 3) was calculated for each size bin. The resulting transmission curve was subsequently normalized for each impactor to the maximum transmission. From this, the d_{p50} values were deduced from a linear regression in the range of $30 < d_m < 110$ nm for NaCl and SimSOA particles and from a linear regression in the range of $60 < d_m < 110$ nm for soot. Additionally, we determined the steepness of the cutoff curve, as well as the d_{p90} and d_{p10} values, which describe the diameters at which 90 % and 10 % of particles are deposited and not transmitted, respectively.

Evaluation of losses. We analyzed the transmission curves for the ultrafine section of the particle size distribution to evaluate the losses of each impactor. Due to the larger uncertainties in the reference instruments for very small diameters, i.e., $d_m < 20$ nm, we decided to evaluate the particle number concentration at 30 nm to determine the losses in the ultrafine fraction. At this size, all impactors showed a peak in the transmission curve, which we used as a reference for determining the losses, calculated as 1 minus the derived transmission.

Observation of other artifacts. We also evaluated the transmission curves for other possible artifacts, such as the transmission of larger particles, which could potentially occur as a result of particle bounce.

2.3 Overview of the field application of the four cascade impactors for the chemical analysis of organic markers in UFPs

To assess the performance of the impactors under real environmental conditions, we operated all impactors simultaneously at the same location for the same duration in a side-by-side comparison. We took three samples of ambient aerosol on 24, 25, and 30 January 2023 in Bayreuth, Germany, with each sample collected over a 24 h period. The impactors and their respective pumps were positioned indoors in the laboratories of the Bayreuth Center of Ecology and Environmental Research (BayCEER; 49.9305° N, 11.5881° E). The location is characterized by nearby manufacturing industries, road traffic, and proximity to a highway but is also adjacent to residential areas of the city of Bayreuth, which has around 75 000 inhabitants (Bayerisches Landesamt für Statistik, 2022). Ambient air was drawn into each impactor through antistatic inlet lines, each 1.2 m long (9.525 mm, TSI). The lines, impactors, and pumps were maintained at a constant temperature of about 21 °C. Each inlet line was equipped with honeycomb ceramic bodies measuring 25.4 × 50 mm (620 000 cells m⁻², Rauschert, Germany), coated with sodium thiosulfate (ReagentPlus® (99 %), Merck), positioned right in front of the impactor's inlet. The coated ceramic body was contained inside a stainless-steel housing and served as an ozone denuder, preventing potential oxidation reactions on the already collected particles during sampling. The ozone scrubbers had been previously evaluated for their capacity to scrub ozone from the sampling air and for potential losses (≤ 6 % for particles with diameters smaller than $d_m = 200$ nm and ≤ 11 % for particles with diameters larger than $d_m = 200$ nm). Thus, up to an ozone concentration of 250 ppb over 72 h, ozone levels were reduced to below 5 ppb behind the ozone denuder. The flow rate was adjusted before each measurement for each impactor.

All upper stages of the impactors were coated with a thin layer of vacuum grease (Apiezon L Grease, M&I Materials Ltd., Manchester, England) to ensure the adherence of deposited particles and minimize bounce. To achieve this, we first dissolved the vacuum grease in *n*-hexane (ReagentPlus® (≥ 99 %), Merck) and applied approximately 0.05 mL of this solution onto aluminum foil using a syringe. We allowed the solvent to evaporate for a minimum of 12 h before mounting the treated foils onto all existing stages of the 120R MOUDI-II, ultraMOUDI, and ELPI. For the PENS, which does not have an impaction plate suitable for filter installation, the grease was applied directly to the plate following the evaporation process. After each 24 h sampling period, all impactor

and nozzle plates were cleaned using an ethanol–water mixture, dried with synthetic compressed air, and recoated before the next measurement. For the collection of UFPs, we inserted pre-baked quartz fiber filters (Whatman QM-H (47 or 37 mm)) into the after-filter holder of each impactor, which had been pre-baked at 300 °C for 24 h. These were stored at -20 °C immediately after collection.

To compare the results of the chemical analysis of the sampled UFPs between the four impactors, we selected six organic marker components to represent a mixture of anthropogenic sources (benzo[a]pyrene (BaP) and benzo[b]fluoranthene (BbF)) (Hussain et al., 2018) and biogenic sources (pinic acid (PA) and terpenylic acid (TA)) (Vestenius et al., 2014)). Furthermore, we analyzed levoglucosan (Levo) as a marker for biomass burning (Simoneit et al., 1999) and N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) as a marker for tire wear material (Klöckner et al., 2021). The marker components were selected to provide a diverse range of molar masses, volatilities, and mass abundances.

2.3.1 Extraction of samples

We extracted the selected marker components from the filters using a soft, solvent-based, and optimized protocol. (1) The filter loaded with particles was divided into two equal parts. One part was extracted, while the other was used as a backup. (2) The filter half used for extraction was spiked with 50 μ L of each internal standard, namely 3-methylcholanthrene (3-MC; 0.4 μ M) and nicotinic acid (NA; 10 μ M), and cut into small fragments. (3) These filter fragments were then transferred into a glass container with a screw cap, and 2 mL of extraction solvent (e.g., analytical-grade dichloromethane (DCM; 99.8 %, Fisher Chemical) and methanol (MeOH; ≥ 99.9 %, Carl Roth)) was introduced. (4) The samples underwent extraction through agitation in a closed flask for a duration of 15 min using a vortex shaker (2000 rpm). (5) The filter residues were kept in a glass container. The extracts were filtered using specially designed glass frits with a diameter of 1 cm and a pore size of 20 μ m to eliminate any potential filter residue.

Steps 3 to 5 were repeated three times, each time using a different extraction solvent. The solvents were used sequentially in the following order: pure MeOH, 50:50 MeOH:DCM, and pure DCM. Subsequently, the solvent from the combined extracts was evaporated under a gentle flow of nitrogen (N₂; 99.99 %) while cooled with ice to prevent the loss of semi-volatile compounds. A droplet, approximately 0.5 μ L in volume, was kept as residue and dissolved in 1 mL of a 60:40 solution of acetonitrile (ACN; 99.95 %, Carl Roth) and water (H₂O; obtained from a Seralpur PRO 90 CN system with an electronics-grade Supor DCF filter (0.2 μ m)). This was transferred into a separate vial for subsequent analysis. Throughout the entire sample preparation process, the samples were stored in an ice-cooled environment.

2.3.2 High-performance liquid chromatography (HPLC) analysis for chemical marker profiling

The analysis of the sample extracts was performed using two high-performance liquid chromatography (HPLC) systems. For the detection of PA, TA, Levo, and 6PPD, an Agilent 1100 Series chromatograph equipped with an electrospray ionization mass spectrometer (ESI-MS; Agilent 6130 Single Quadrupole) was utilized. To determine the concentration of the polycyclic aromatic hydrocarbons (PAHs), BaP and BbF, an Agilent 1260 Infinity system coupled with a fluorescence detector (FLD; Agilent 1100 Series) was employed. For the mobile phase, HPLC-grade acetonitrile, water, and formic acid (HCOOH; p.a. $\geq 98\%$, Carl Roth) were used as a buffer. We applied three different methods, which are summarized in Table S1 in the Supplement.

To assess the efficacy of the sample preparation, including the extraction method, recovery experiments were conducted in triplicate. Half of the preheated quartz fiber filter (47 mm, Whatman QM-H) was spiked with 10 μL of a 10 μM standard solution encompassing all markers. Subsequently, the spiked filter was extracted as outlined previously. Each recovery (Rec) was ascertained utilizing external standard (ESTD) calibration and calculated by dividing the measured concentration of each marker by the expected (spiked) concentration.

$$\text{Rec} = \frac{c_{\text{measured}}}{c_{\text{expected}}} \cdot 100 \quad (1)$$

The obtained recoveries were as follows: $78 \pm 7\%$ (BaP), $74 \pm 7\%$ (BbF), $79 \pm 7\%$ (Levo), $84 \pm 8\%$ (PA), $85 \pm 8\%$ (TA), and $75 \pm 7\%$ (6PPD). As these recovery rates describe the average systematic loss of the marker compounds during extraction, we corrected our data using the following equation:

$$c_{\text{sample,corrected}} = c_{\text{sample,measured}} \times \left(\frac{100}{\text{Rec}} \right) \quad (2)$$

The recovery-corrected results were then validated against the NIST Standard Reference Material (SRM) 2786 ($< 4\mu\text{m}$), which was applied to a filter, extracted, and analyzed according to the methods described herein for validation. The results showed agreement within the uncertainty of the measurement, even in the presence of a particulate matrix. The limit of detection (LOD) was determined based on the standard deviation (σ) of the response from a modified calibration solution, targeting a signal-to-noise ratio of approximately 3 for each analyte, as well as the response factor (RF) from the ESTD calibration.

$$\text{LOD} = \frac{3 \cdot \sigma}{\text{RF}} \quad (3)$$

The LOD was calculated across four replicates. Furthermore, the LOD for airborne concentrations (LOD_{Air} ;

pg m^{-3}) was calculated by dividing the LOD by the sampling volume. For the MOUDI and ELPI devices, sampling for 24 h at 30 L min^{-1} resulted in a sampling volume of 43.2 m^3 . For the PENS, which has a sampling flow of 4 L min^{-1} , the sampling volume was 5.76 m^3 . The LOD values ranged from around 1–2 and 40–186 pg m^{-3} for target markers measured using high-performance liquid chromatography with fluorescence detection (HPLC-FLD) and mass spectrometry (HPLC-MS), respectively. The LOD increased by a factor of 7.5 when sampling a smaller volume, as was the case with the PENS, compared to all other impactors (Table S2 in the Supplement). Additionally, we estimated impactor-specific overall measurement uncertainties using Gaussian error propagation, with uncertainties ranging from 13.8 % to 17.8 % (Sect. 1.1 in the Supplement). This uncertainty estimate includes the instrumental variability for repeated analysis (2 %), reference material uncertainty (0.5 %), preparation of stock solutions (5 %), dilution errors (5 %), and inaccuracies in volume determination (1 %). Additionally, it accounts for impactor-specific factors, including flow adjustment errors (3 %–10 %) and handling errors (10 %–15 %).

3 Results and discussion

3.1 Physical characterization I: pressure drops, cutoff diameters, and the steepness of the cutoff curve

The pressure drop across an impactor, including the quartz fiber filter, can significantly influence collection efficiency and the chemical composition of the captured particles. The greater the pressure drop across the impactor and quartz fiber filter, the higher the rate of potential evaporation of semi-volatile compounds. For the four tested impactors, the pressure drops corresponded to $260 \pm 1\text{ hPa}$ (PENS), $420 \pm 2\text{ hPa}$ (ultraMOUDI), $600 \pm 3\text{ hPa}$ (120R MOUDI-II), and $690 \pm 3\text{ hPa}$ (ELPI).

Figure 3 shows the normalized transmission curves obtained from testing the four impactors with the three test particle mixtures. Cutoff diameters were calculated as d_{p50} values for the electromobility diameter. They increased consistently for all impactors – from NaCl particles to SimSOA to soot particles ($59\text{--}68 < 70\text{--}74 < 102\text{--}116\text{ nm}$). The best agreement between the individual impactors' cutoff diameters was found for SimSOA. For SimSOA, the ultraMOUDI and 120R MOUDI-II had the smallest cutoff diameters, with electromobility diameters of 71 ± 7 and $70 \pm 7\text{ nm}$, respectively. Contrastingly, for soot, the largest deviations among the impactors' cutoff diameters were observed, showing that the devices deviated by about 14 nm at most. Here, the two MOUDI models had the highest cutoff diameters, while the PENS had the smallest one ($102 \pm 10\text{ nm}$). For NaCl and SimSOA particles, we compared the aerodynamic cutoff diameters, which were 86 ± 9 and $84 \pm 8\text{ nm}$ (ultraMOUDI), 89 ± 9 and $85 \pm 9\text{ nm}$ (120R MOUDI-II), 99 ± 10

and 89 ± 9 nm (PENS), and 100 ± 10 and 85 ± 9 nm, respectively. For these calculations, a shape factor of 1.0 and a density of 2.165 g cm^{-3} were used for NaCl, while a shape factor of 1.2 and a density of 1.21 g cm^{-3} were applied for SimSOA.

Generally, the transmission curves were steeper for soot than for SimSOA and steeper for SimSOA than for NaCl particles. This trend is strongest for the ELPI and PENS, which have the greatest steepness for soot, with transmission curve slopes of -1.1 nm^{-1} , and the least sharp cutoff curves for NaCl, corresponding to -0.52 and -0.56 nm^{-1} , respectively. The sharpness of the cutoff curves for the 120R MOUDI-II and ultraMOUDI seems to be less sensitive to the type of test particle as the steepness of the transmission curves varied by about 9 % at most between the different test particles. The four impactors showed the best agreement regarding the steepness of the transmission curve for SimSOA, with a relative difference between the maximum and minimum slopes of about 26 %.

The d_{p10} and d_{p90} values represent the diameters at which 10 % and 90 % of the test particles, respectively, were deposited on the impaction plates of the impactor. An impactor with closely spaced d_{p10} and d_{p90} values would have a steeper transmission curve, indicating more precise segregation of particles by size. For all impactors, the lowest d_{p10} values were observed for NaCl particles ($d_{p10\text{ave}} = 34$ nm, averaged across all impactors). The d_{p90} values did not vary systematically between the test particles and impactors, ranging from 125 ± 13 nm (for NaCl particles collected with the ultraMOUDI) to 183 ± 18 nm (for SimSOA collected with the 120R MOUDI-II). As this general trend might be driven by the relatively sticky nature of NaCl particles and SimSOA, leading to a relatively smeared cutoff curve, it is interesting to observe the sharpest cutoff curve for the soot particles, which exhibits the most complex shape among the curves of the three tested particle types. This can also be seen from the difference between the d_{p90} and d_{p10} values, which was smallest for soot particles across all four impactors.

SimSOA is likely the most representative type of test particle for environments ranging from urban to suburban to rural, provided they are not coastal, curbside, or subject to nearby combustion sources. For the tests with SimSOA, the four impactors performed comparably in terms of cutoff diameter, transmission curve steepness, and d_{p10} and d_{p90} values (Table 1). We observed a tendency for a sharper separation of UFPs with the PENS and ELPI compared to the two MOUDI models. However, larger deviations between the four impactors were observed for soot particles, both in terms of cutoff diameter and steepness. The estimated aerodynamic cutoff diameters for SimSOA and NaCl overlap for all the impactors within their uncertainties and in the range of 84–100 nm. Typically, the UFP range includes the nucleation mode and marks the “shoulder” of the accumulation mode. From the perspective of a mass-based analysis, the particle composition of these two modes would be reflected in the

results. However, as the mass of particles around 100 nm is small, the observed variations in cutoff diameters likely do not diminish their comparability.

3.2 Physical characterization II: losses and particle bounce

To determine potential losses within the impactors, we compared the transmission curves for SimSOA generated in the atmospheric simulation chamber (Fig. 4). The maximum transmission in the ultrafine fraction at 30 nm was 84 ± 8 % for the PENS, 77 ± 8 % for the ultraMOUDI, 75 ± 8 % for the 120R MOUDI-II, and 69 ± 7 % for the ELPI. These results indicate that the ELPI had the highest losses of SimSOA UFPs during sampling compared to the other tested impactors. However, considering the overlap of the uncertainties, these differences are not significant. Losses can be either wall losses or interstage losses, which retain particles on surfaces other than the impaction plate. In addition, losses can also occur through the evaporation of (semi-)volatile particles, especially under a high-pressure drop during “flow-through” (Marple and Willeke, 1976; Won Kim, 2010).

Ideally, the transmission should ultimately reach zero for particles with larger diameters as these particles should be retained in the upper stages of the impactor. However, the elevation above zero for diameters between 200 and 1000 nm suggests the occurrence of particle bounce (Fig. 4). The ELPI detected very few particles at the larger diameters, with minimal transmission observed for these particle sizes. Thus, within the uncertainty, no particles with an electromobility diameter larger than 177 nm passed through the last impaction stage. A similar observation was made for the 120R MOUDI-II, where very few particles were detected at larger diameters, with minimal transmission being approached at an electromobility diameter of 562 nm. For larger particles, the transmission remained at zero. This is in line with the comparably flat slope of the transmission curve of the 120R MOUDI-II, indicating a broad separation of particle sizes rather than a sharp cutoff curve (Table 1). However, both the PENS and ultraMOUDI devices exhibited notable bounce effects. For the PENS, the transmission dropped to a local minimum at 133 nm (electromobility diameter) and remained at approximately 38 % for larger particles. For the ultraMOUDI, the local minimum of transmission occurred at an electromobility diameter of 273 nm, amounting to 13 %, but then increased again to about 19 % for larger particle diameters.

Overall, the impactor design seems to critically impact potential losses and particle bounce. The ELPI and 120R MOUDI-II have a higher number of stages and impactor-plate–nozzle-plate pairs before ultimately separating UFPs (stages 13 and 9, respectively) compared to the ultraMOUDI and PENS (stages 3 and 2, respectively). The increased number of stages appears to reduce the bounce effect (Fig. 4). This is likely because particles have more opportunities to

Table 1. Summary of the performance test results for the four impactors and the three test aerosol mixtures. The particle diameter (d_p) values are provided in terms of electromobility diameter (nanometers). The steepness describes the slope of the transmission curve at particle diameters of around 100 nm. Values of d_{p50a} (the aerodynamic particle diameter at 50 % collection efficiency) are calculated as aerodynamic cutoff diameters, derived from the salt particle tests.

Impactor	Aerodynamic cutoff (nm) (manufacturer)	Aerosol type	d_p value (nm)			Steepness (nm ⁻¹)	d_{p50a} (nm)
			10	50	90		
120R MOUDI-II	100	NaCl	34 ± 4	61 ± 6	182 ± 18	−0.55	89 ± 9
		SimSOA	41 ± 4	71 ± 7	183 ± 18	−0.55	85 ± 9
		Soot	78 ± 8	116 ± 12	175 ± 18	−0.86	–
PENS	100	NaCl	30 ± 3	67 ± 7	177 ± 18	−0.52	99 ± 10
		SimSOA	42 ± 4	74 ± 7	148 ± 15	−0.64	89 ± 9
		Soot	69 ± 7	102 ± 10	153 ± 15	−1.1	–
ELPI	90	NaCl	39 ± 4	68 ± 7	162 ± 16	−0.56	100 ± 10
		SimSOA	39 ± 4	71 ± 7	148 ± 15	−0.65	85 ± 9
		Soot	72 ± 7	106 ± 10	162 ± 16	−1.1	–
ultraMOUDI	100	NaCl	32 ± 3	59 ± 6	125 ± 13	−0.67	86 ± 9
		SimSOA	35 ± 4	70 ± 7	162 ± 16	−0.58	84 ± 8
		Soot	76 ± 7	112 ± 11	166 ± 17	−0.95	–

impact as they traverse through multiple stages, with each stage being less loaded with particles, reducing the probability of bounce. As both the ELPI and MOUDI devices are modular cascade impactors, they allow us to include different numbers of stages with different cutoff diameters, which, in turn, might result in different sampling characteristics – not only for the ultrafine particles but also for the upper stages. However, including a higher number of upper stages could come at the cost of comparably increased losses in the UFP range.

Here, the losses in the UFP range were similar for the ELPI, 120R MOUDI-II, and ultraMOUDI. This contrasts with the PENS, which had the smallest loss amongst all the tested models (about 6 %), likely due to its design, which features a cyclone pre-separator and only one nozzle plate. We can compare our results to those of a few other studies that experimentally determined the loss rate of the MOUDI. Liu et al. (2013) showed a total loss for a MOUDI device (Model 110) in the range of 2.9 %–26.1 %, which increased with decreasing d_{p50} values and was attributed mostly to convective diffusion. Similarly, Durand et al. (2014) observed losses due to convective diffusion in cascade impactors featuring stages designed for ultrafine particles with diameters below 100 nm. Ungeheuer et al. (2022) measured losses of 28 % and 40 % in the Nano-MOUDI (Model 110) for particles with aerodynamic diameters of 32–56 nm and 18–32 nm, respectively. It is thought that diffusion deposition becomes increasingly significant for smaller particles, which can lead to substantial particle losses. As high uncertainties are associated with both the MPSS and the DMS when measuring particles with diameters below 20 nm, we could not test this behavior within our setup. However, a mass-based analysis of UFPs might be

less affected by such losses than the measurement of number concentration.

It has been reported that particle bounce becomes particularly significant for lower cutoff stages due to the gradual reduction in pressure at each stage, which subsequently leads to a decrease in relative humidity (RH). The reduction in RH, in turn, can intensify the particle bounce effect (Chen et al., 2011). Pressure dropped most drastically throughout the ELPI, which may have been problematic for collecting semi-volatile organic marker compounds (Yao et al., 2022). Knowing that the diameter of the cutoff and the effective sharpness of the separation between fine and ultrafine SimSOA particles were comparable for all tested impactors, the impact of losses and particle bounce on mass-based chemical analyses might be significant and is therefore further investigated below. Considering the mass of UFPs compared to the mass of potential artifacts, we aimed to understand the relative impact of particle bounce. Even a few larger particles or fragments bouncing onto the UFP collection substrate could heavily skew the results, leading to an overestimation of the UFP mass concentration and a misrepresentation of its chemical composition. This is particularly problematic because UFPs can have different chemical properties and health impacts compared to larger particles (Abdillah and Wang, 2023; Müller et al., 2012). Particle bounce-off can be influenced by the impaction surface; the presence, type, and depth of a coating; particle types; particle loading; sampling conditions; and the impaction substrate. Particularly during long-term sampling with heavy particle loads, deposited particles have been found in excessive layers (Kulkarni et al., 2011; Marple et al., 1991; Pak et al., 1992; Turner and Her-

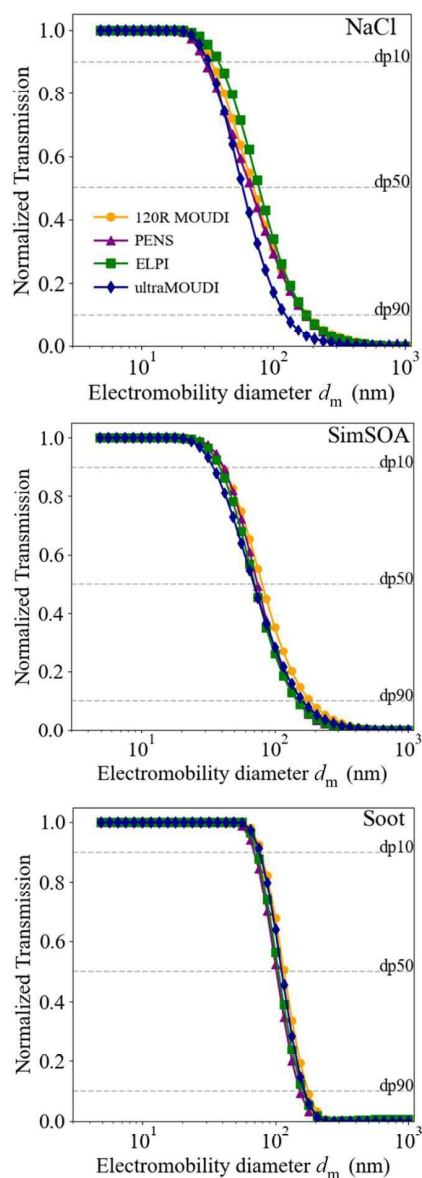


Figure 3. Normalized transmission curves for three test particle types (NaCl, SimSOA, and soot), as captured by different impactors: the 120R MOUDI-II (orange circles), PENS (purple triangles), ELPI (green squares), and ultraMOUDI (blue diamond-shaped markers). Each plot displays the transmission versus the electromobility diameter (nanometers) on a logarithmic scale. Lines are included to guide the eye.

ing, 1987; Chang et al., 1999; Newton et al.; Lai et al., 2008; Rao and Whitby, 1978).

To test whether an increased particle load leads to more severe particle bounce, we varied the particle number concentration in the chamber for SimSOA from a maximum of

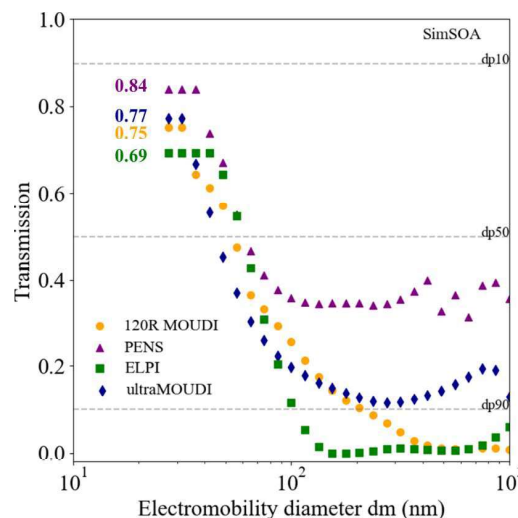


Figure 4. Transmission curves for the four tested impactors collecting SimSOA generated within the atmospheric simulation chamber. Note that all tests were performed without applying any coating. The four impactors are labeled follows: 120R MOUDI-II (orange circles), PENS (purple triangles), ELPI (green squares), and ultraMOUDI (blue diamond-shaped markers).

about $200\,000\text{ cm}^{-3}$ to a more realistic maximum of about 5700 cm^{-3} (see Fig. 5). As a wide range of number concentrations were covered, we measured the particle number size distributions with both the DMS500 (level 1 in Fig. 5a) and the MPSS (levels 2, 3, and 4 in Fig. 5a). Additionally, Fig. 5b presents an exemplary number size distribution (level 4) for ambient particles, which were collected during a period of environmental sampling when the impactors were deployed side by side (see Sect. 2.3). For each of these levels, Fig. 5b shows the transmission through the PENS impactor as an example. Indeed, reducing the particle number concentration resulted in a decreased bounce effect, although it still remained noticeable. Compared to the highest particle load (level 1), transmission was reduced in level 2 for particles sized 150–200 nm, while particles $> 500\text{ nm}$ still exhibited transmission rates of up to 34 %. Level 3a had the lowest particle load, which decreased transmission to about 5 %–9 %, remaining relatively consistent across the diameter range of 170–800 nm.

Furthermore, greasing the upper stages is a method that has previously been suggested and applied to reduce particle bounce (Baron and Willeke, 2011; Ungeheuer et al., 2021). To test this method, we greased the upper stages of the PENS (level 3b in Fig. 5b). Applying a coating on the impactor further reduced the bounce effect, lowering transmission rates to 0 %–6 % within the same particle size range. The duration of these measurements was notably brief (20 min), in contrast to the typical collection times employed with impactors

(e.g., 24 h). Thus, we also greased the upper stages of the 120R MOUDI-II and monitored the transmission over 3 consecutive days while sampling ambient air. While greasing improved the sharpness of the cutoff curve, the transmitted fraction of particles around a size of about 200 nm increased over the 3 d from about 0 % to 15 %. These tests highlight the variations in the observed bounce effects over short and extended collection periods, which may be highly dependent on particle load and nature. However, greasing the upper impactation stages generally improved UFP sampling as it reduced the fraction of larger particles being transmitted.

3.3 Physical characterization III: transmitted particle mass

Typically, UFP collection using impactors is followed by analyses of chemical composition, which have a mass-based focus. Breakthroughs of coarser particles into the UFP range can significantly distort mass-based analytical results as particle mass increases in cubic proportion to the diameter. As an example, Fig. 6 illustrates the transmission of particles through the PENS based on their respective masses. The density of the α -pinene particles was measured by Zelenyuk et al. (2008) to be 1.20 g cm^{-3} . We used this value to calculate the mass of the particles transmitting through the impactor according to the measured number size distributions, assuming spherical shapes for the SimSOA particles. We separated the data into two size classes (based on the electromobility diameter of the particles): (1) the entire recorded range (10–800 nm) and (2) the UFP range (10–74 nm), which is below the previously determined d_{p50} value (Sect. 3.1).

The set of measurements includes particle mass as measured directly from the chamber, the empty PENS, the uncoated PENS, and the coated PENS (Fig. 6). The total mass of all particles in the chamber, ranging from 10 to 800 nm, calculated directly from the measured particle number size distribution, was $220.2 \mu\text{g m}^{-3}$. Due to losses in the lines and the empty PENS, the mass was reduced to $205.87 \mu\text{g m}^{-3}$. Upon separation, $21.4 \mu\text{g m}^{-3}$ of the mass was transmitted through the PENS when no coating was applied. Through the coated PENS, a particle mass of $3.3 \mu\text{g m}^{-3}$ was transmitted. This highlights the coated impactor's capability to retain over 98.5 % of the test particle mass, whereas the uncoated impactor captured only approximately 90.3 %. The differences are artifacts due to the bounce and fragmentation of larger particles sampled as UFPs. Figure 6 also shows that the transmitted ultrafine fraction, as detected by the MPSS, remained comparable between the coated and uncoated tests. For these tests, we chose a reduced particle number concentration compared to the aforementioned cutoff characterization experiments and SimSOA particles in the context of environmental measurements. Due to the nature of SimSOA, the particles are likely not representative of a worst-case scenario for particle bounce.

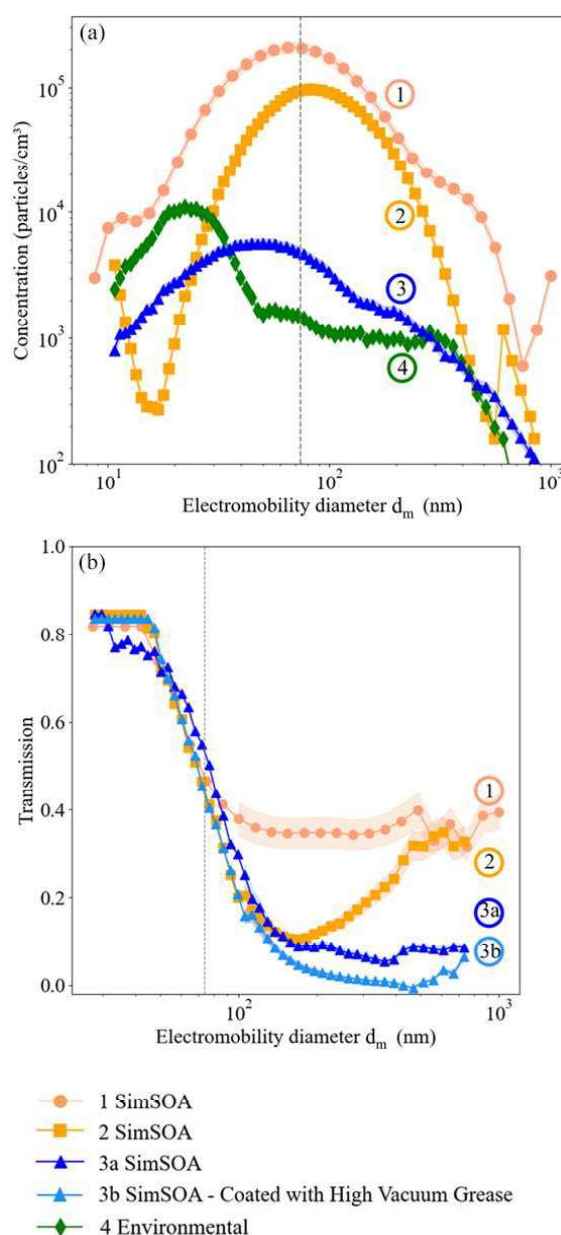


Figure 5. Panel (a) illustrates particle number size distributions in units of particles per cubic centimeter for SimSOA (detected at its highest concentrations by the DMS500 (1) and at relatively lower concentrations by the MPSS (2 and 3)) and environmental secondary organic aerosol (SOA) (4). Panel (b) presents the transmission curves of the PENS for the respective particle size distributions. Data labeled with “3a” and “3b” display uncoated measurements and coated measurements using high-vacuum grease, respectively.

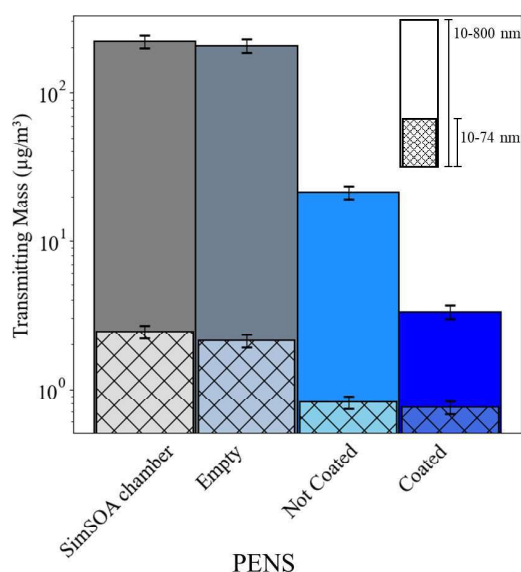


Figure 6. Comparative bar chart displaying the masses of transmitting particles in $\mu\text{g m}^{-3}$ for coated and uncoated PENS tests, compared with the original aerosol mixture (SimSOA) and the empty PENS. The two segments represent the entire observed electromobility diameter range (10, ..., 800 nm) and the ultrafine fraction (10, ..., 74 nm), respectively. The chart uses a logarithmic scale for the y axis.

3.4 Field application: chemical analysis of organic markers

We evaluated the performance of the four cascade impactors under environmental conditions using six selected markers (see Methods):

- *Polycyclic aromatic hydrocarbons (PAHs)*. PAHs have a potential impact on human and environmental health (Hussain et al., 2018; Kim et al., 2013; Wang et al., 2006). Benzo[a]pyrene (BaP; $M = 252.31 \text{ g mol}^{-1}$) and benzo[b]fluoranthene (BbF; $M = 252.31 \text{ g mol}^{-1}$) are high-molecular-weight PAHs with five aromatic rings and low volatility. They are predominantly found in fine particulate matter originating from incomplete combustion.
- *Levoglucosan (Levo)*. Levo ($M = 162.14 \text{ g mol}^{-1}$) is a well-studied tracer for cellulose combustion (Bhattacharai et al., 2019; Simoneit et al., 1999). Its presence is indicative of sources such as residential wood burning, agricultural fire practices, and wildfire emissions. Levoglucosan is semi-volatile and can partition between gas and particle phases (Xie et al., 2014).
- *Pinic acid (PA) and terpenylic acid (TA)*. PA ($M = 186.21 \text{ g mol}^{-1}$) and TA ($M = 198.24 \text{ g mol}^{-1}$) are representative of secondary organic aerosols (SOAs) of

biogenic origin, produced through the oxidation of terpenes (e.g., α -pinene and β -pinene), which are emitted by vegetation (Claeys et al., 2013; Grieshop et al., 2007).

- *6PPD.N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD; $M = 268.40 \text{ g mol}^{-1}$)* is an additive in tire wear materials and has recently been proposed as a tracer for non-exhaust traffic-related particles (Chen et al., 2023; Hu et al., 2022).

We analyzed UFPs sampled in an urban, semi-industrial environment. The observed average mass concentrations are presented in Fig. 7a. Furthermore, we evaluated the relative deviation of each impactor compared to the average of all impactor results (Fig. 7b). Overall, the best agreement between all impactors was found for the two PAHs. For BaP, the average mass concentration was highest for the PENS, amounting to $227.2 \pm 97 \text{ pg m}^{-3}$ (the average $\pm$ the standard deviation over 3 consecutive days), which is 29 % above the average of 175.65 pg m^{-3} when considering all impactors. The ELPI and ultraMOUDI agreed within approximately 4 % above and 3 % below the average, respectively. The 120R MOUDI-II had the lowest average concentration ($122.6 \pm 74 \text{ pg m}^{-3}$), which was 30 % below the overall average. For BbF, the tendencies were the same but less pronounced. We can highlight two findings here for the analysis of the two PAHs. Firstly, the maximum disagreement may be as large as 59 % between the PENS and 120R MOUDI-II. Secondly, the two PAHs, originating from the same sources and found in > 90 % of the particle phase, exhibit the same sampling tendencies across the impactor models. This is likely due to their identical molecular weights and very comparable boiling points.

As the results from the PENS seemed to be consistently at the higher end for all marker compounds, we calculated the averages across all impactors, both including and excluding the PENS, and then compared them (Fig. 7b). The PENS exceeded the average of the remaining impactors by a factor of 1.3 for BaP, 1.2 for BbF, 2.0 for Levo, 1.5 for PA, 1.7 for TA, and 2.3 for 6PPD. Our cutoff characteristic tests indicate three potential reasons for this overestimation. Firstly, the PENS had the lowest pressure drop of all the impactors (260 hPa), which might have affected the gas–particle partitioning of semi-volatile compounds in a way that, for example, resulted in Levo, TA, and PA having comparably higher mass concentrations in PENS samples. Secondly, the bounce effect was more pronounced in the PENS and dependent on the particle number concentration of the SimSOA. Possibly, and despite the applied coating, the overestimation in marker mass concentrations by the PENS could be due to a bounce effect, which increases with rising ambient mass concentrations. Thirdly, the physical loss in the UFP range was relatively small in the PENS compared to the other impactors (Fig. 4). The losses, however, were similar across all impactors and likely less impactful from a mass-based viewpoint.

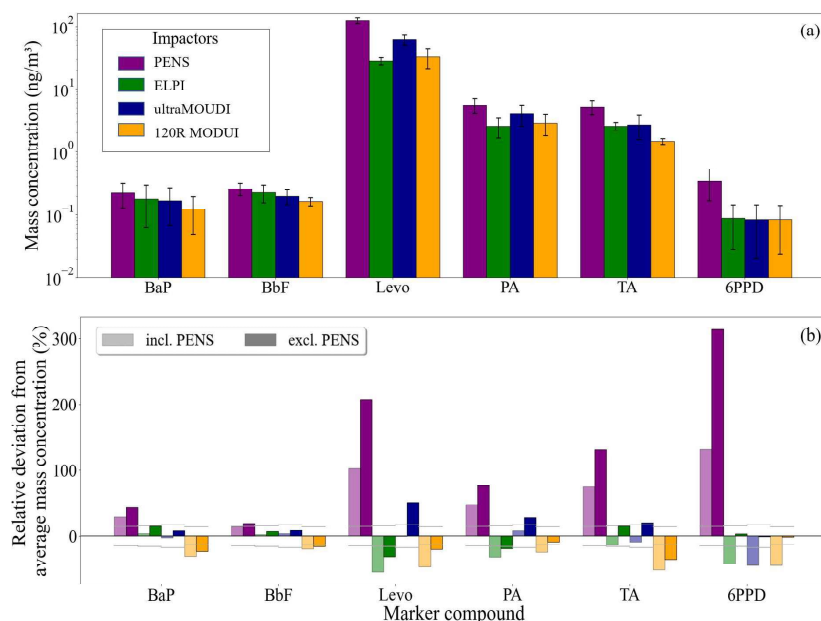


Figure 7. (a) Bar chart showing the average mass concentrations of selected organic marker compounds in UFPs collected with the PENS (purple), ELPI (green), ultraMOUDI (dark blue), and 120R MOUDI-II (orange) over 3 d, expressed in units of ng m^{-3} on a logarithmic scale. The error bars indicate standard deviations. (b) Relative deviations (percentages) in the mass concentrations of BaP, BbF, Levo, PA, TA, and 6PPD in UFPs, calculated using the average of all impactors (incl. PENS; transparent bars) and the average of all impactors minus the PENS (excl. PENS; opaque bars). For comparison, horizontal gray lines represent the estimated overall errors for each marker and impactor (Sect. S1.1 in the Supplement). A logarithmic representation of panel (b) can be found in Fig. S1 in the Supplement.

A comparison of the remaining impactors showed the best agreement in the results for 6PPD. Here, in the sampled UFPs, the two MOUDI models measured, on average, $83 \pm 30 \text{ pg m}^{-3}$ of 6PPD, and the ELPI measured $86 \pm 48 \text{ pg m}^{-3}$ of 6PPD. The differences amongst the 120R MOUDI-II, ELPI, and ultraMOUDI varied for the different markers as follows (presented in increasing order): 6PPD (−2 % to +3 %), PAHs (BaP and BbF; +8 % to −22 %), organic acids (PA and TA; +20 % to −35 %), and Levo (+51 % to −31 %). Thus, the range of deviation increased with the average observed mass concentration: 6PPD ($84 \pm 30 \text{ pg m}^{-3}$), BaP ($158 \pm 25 \text{ pg m}^{-3}$), BbF ($199 \pm 23 \text{ pg m}^{-3}$), PA ($3144 \pm 620 \text{ pg m}^{-3}$), TA ($2231 \pm 541 \text{ pg m}^{-3}$), and Levo ($40\,660 \pm 17\,148 \text{ pg m}^{-3}$).

It should be noted that the differences among the impactors fall within the same order of magnitude as the overall uncertainty for most markers (BaP, BbF, TA, and PA). Yet, these differences are systematic and seem to depend not only on the impactor design but also on the properties of the analyzed compounds (see Sect. 2.3.2).

3.5 Influence of physical factors on the results of marker mass concentration analyses of UFPs

We systematically analyzed the influence of the previously examined physical factors on the results of marker concentrations in UFPs with respect to the markers' properties. While the cutoff diameter, cutoff curve steepness, and losses do not seem to vary significantly between the four tested impactors, the pressure drop (mass loss) and the effect of particle bounce (mass gain) have the potential to drive the observed differences in the mass-based UFP analysis.

We expected the pressure drop to primarily affect the semi-volatile markers (PA, TA, and Levo) due to evaporation losses during sampling. Figure 8a illustrates the dependency of the absolute deviation of the average mass concentration on the pressure drop for all samples and impactors. The absolute deviation of the average mass concentrations of PA, TA, and Levo decreased with the increasing pressure drop, more so than for the less volatile markers, BaP and BbF. We categorized these two groups of markers – semi-volatile and mostly particle-bound – and compared the change in concentration for the two extremes: the PENS with the smallest pressure drop ($260 \pm 1 \text{ hPa}$) and the ELPI with the largest pressure drop ($690 \pm 3 \text{ hPa}$). The lower-volatility markers (BaP and BbF) decreased in average concentration

by about 15 %. In contrast, the average mass concentration of the higher-volatility markers (PA and TA) decreased by about 52 %. These findings seem to confirm that a larger pressure drop in the impactors leads to evaporation and, thus, a mass loss of the semi-volatile substances. The evaporative loss likely also depends on the collection substrate. When sampled using a QFF, for example, UFPs are exposed individually and ventilated efficiently. However, QFFs were used in all impactors during UFP sampling. Furthermore, we initially noted differences between the 120R MOUDI-II and ELPI, despite there being a comparable pressure drop. Secondly, mass concentrations of 6PPD were comparable across all impactors except the PENS. These observations indicate that additional influencing factors, beyond the pressure drop alone, could potentially affect the analysis more significantly.

Despite the application of a coating, we suspected particle bounce and thus tested whether the absolute deviation from the impactor average mass concentration was dependent on the ambient marker mass concentration (Fig. 8b). While we expected an increasing effect with higher mass concentrations, the potential dependency became more apparent only at the highest daily average concentrations, particularly above 1 ng m^{-3} . Below this level, the data primarily exhibited scatter, suggesting that any systematic influence of particle bounce may be less pronounced at lower concentrations.

While the nature of the particles may play a role in their efficiency of being captured by the filter substrate – as evident when comparing sticky, spherical SOA particles to combustion particles with complex shapes (Boskovic et al., 2005; Matthew et al., 2008; Huang et al., 2004) – the design of the impactors likely determines the potential for particle bounce. The main differences between the PENS and the other impactors are the cyclone and the number of stages used for separating and impacting larger particles. The larger number of stages – and, thus, the larger number of coated surfaces in the two MOUDI models and the ELPI – is likely beneficial for reducing the impact of particle bounce. The rotating stages of the 120R MOUDI-II potentially played a more significant role in the field study, with longer sampling times, than in the laboratory tests. Over time, the rotation resulted in an even loading of the upper stages, which, in addition to the coating, likely reduced particle bounce. Thus, we observed almost no dependency of the 120R MOUDI-II deviations on average mass concentrations with increasing mass concentration (Fig. 8b). However, as the marker compounds with high observed mass concentrations are, at the same time, semi-volatile, we cannot completely separate the two effects of pressure-drop-driven losses and mass gain due to particle bounce within this study.

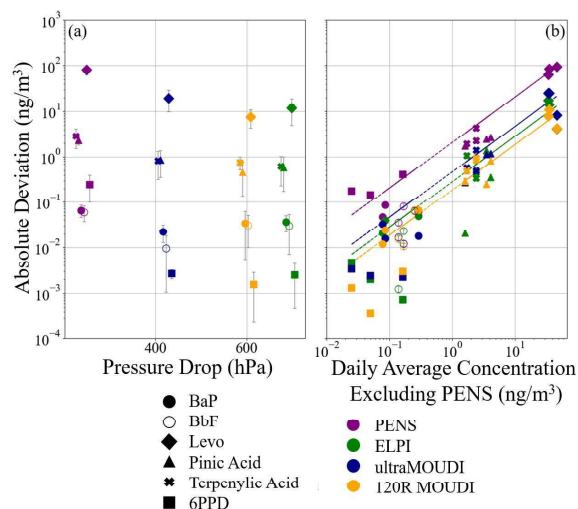


Figure 8. (a) Absolute deviations of the average mass concentrations of BaP, BbF, Levo, pinic acid, terpenylic acid, and 6PPD, as determined by the four impactors, are presented as functions of the pressure drop across the impactors. Data points are displaced horizontally around each impactor's nominal pressure drop value for illustrative purposes, allowing for comparison while avoiding overlap. The markers denote different substances: BaP (filled circles), BbF (unfilled circles), Levo (diamonds), pinic acid (triangles), terpenylic acid (crosses), and 6PPD (squares). (b) Absolute deviations from the mass concentration averages for the PENS (purple), ELPI (green), ultraMOUDI (dark blue), and 120R MOUDI-II (orange) with respect to the selected organic marker compounds in UFPs are shown. Linear regressions through the origin are included for each impactor.

4 Conclusions

This study provides a detailed characterization and comparison of the performance of four impactors: the 120R MOUDI-II, ultraMOUDI, ELPI, and PENS. To understand the impact of the impactors' designs on their ability to collect UFPs, we examined them with respect to pressure drops, cutoff diameters, the steepness of the cutoff curve, losses, and particle bounce. Under controlled conditions using three test particle mixtures, we showed that not only the impactor design but also the nature of the particles contribute to differences in the observed results. This was confirmed when we applied the four impactors to ambient air to examine the mass concentrations of six organic markers in UFPs. In summary, all four impactors were capable of separating and collecting UFPs as they all have a cutoff diameter of about 100 nm. More explicitly, they can be characterized as follows:

- The PENS is compact and lightweight, making it portable and suitable for field studies or personal exposure studies that require mobility. With a sampling flow rate of 4 L min^{-1} , a smaller air volume is probed

compared to other impactors. This affects the detection limits while keeping the pressure drop within the device low (about 260 hPa). Thus, the evaporation and mass loss of semi-volatile compounds are comparably low. The PENS showed an impact from particle bounce, particularly at higher particle concentrations. We showed that the application of a coating largely reduced the transmission of larger particles in the laboratory tests. However, when markers were present at high mass concentrations, we observed a significant deviation from the results of the other impactors in the field comparison. This is likely due to the design of the PENS, which features a cyclone for pre-separation and only one stage for the impaction of larger particles, which could be used for applying a coating. However, for particle-bound BaP and BbF, as well as moderate marker mass concentrations, the PENS compared well with the other impactors.

- The ELPI was simplified for this study. When operated in its original setup, it offers the advantage of parallel online monitoring of the number size distribution. Here, the ELPI showed a sharp cutoff curve for UFPs and effectively no transmission of larger particles. This is likely due to its design, featuring 13 nozzle–impactor pairs, which can retain larger particles and prevent fragments from cascading through the device. However, this comes with an overall loss in the ultrafine fraction ($31 \pm 7\%$) and a pressure drop of 690 hPa. The reduced pressure on the filter substrate can lead to the evaporative loss of semi-volatile substances during sampling, while non-volatile, particle-bound compounds in UFPs (e.g., metals and plastics) may be unaffected by this effect.
- The 120R MOUDI-II features a rotating design that distributes particles evenly across the impaction surface, reducing particle buildup and re-entrainment. Indeed, no transmission of particles larger than about 500 nm was observed in our test, and the bounce effect remained comparably small. However, the cutoff curve was relatively broad, as can be seen, for example, from the d_{p90} value, which was about 180 nm – the highest among the four tested impactors. Interestingly, in our tests, the sharpness of the cutoff curve for the 120R MOUDI-II was not impacted by the particle type. The 120R MOUDI-II features a pressure drop of 600 hPa. Thus, for semi-volatile substances, evaporative losses are likely. In future studies, it would be interesting to determine the long-term efficacy of the rotation in minimizing the bounce effect.
- The ultraMOUDI is a non-rotating, simplified variant of the 120R MOUDI-II. As it features a pressure drop of 420 hPa, evaporation loss of semi-volatile compounds is less likely compared to the ELPI and 120R MOUDI-II.

Due to a reduced number of nozzle–impactor pairs, it showed fewer losses in the ultrafine range compared to the ELPI and 120R MOUDI-II. When compared based on the mass concentrations in ambient UFPs, the ultraMOUDI agreed well within the measurement uncertainty for the mostly particle-bound BaP, BbF, and 6PPD markers, and it found slightly higher concentrations for the semi-volatile TA, PA, and Levo markers. Similar to the PENS, we observed the transmission of larger particles due to potential particle bounce; however, we showed that this effect was reduced with the application of a coating. The ultraMOUDI is smaller and simpler to handle than the 120R MOUDI-II and, thus, can be integrated, for instance, into automated, standalone low-volume samplers.

Our findings indicate that separating and collecting UFPs for mass-based chemical analysis is challenging. Numerous factors affect the separation and collection of UFPs, complicating the comparability of studies. The nuanced performance differences among the impactors underscore the need for careful consideration of the intended application and the potential artifacts that may arise during sampling and analysis. Each impactor offers unique advantages and limitations, making it essential to match the impactor to the specific research goals and the properties of the particles being studied. Furthermore, the variability in the performance of the impactors in the analysis of the six selected organic markers suggests that factors such as chemical composition, particle morphology, and physical interactions with the impactor significantly influence the results as well.

Code and data availability. The code and data used in this study are available upon request from the corresponding authors.

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/ar-3-45-2025-supplement>.

Author contributions. EE: measurements, data analysis, and writing (original draft, review, and editing). AM and DB: DMS500 measurements, data analysis, and writing. NG, JSK, MS, RZ, and ACN: funding acquisition, conceptualization, supervision, writing (review and editing), and funding acquisition.

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

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Acknowledgements. We thank Wolf-Ulrich Palm and Klaus Kümmerer from Leuphana University Lüneburg for providing us with the fluorescence detector. Additionally, we extend our gratitude to the KeyLabs at the Bavarian Polymer Institute (BPI), University of Bayreuth, for providing the scanning electron microscopy images.

Financial support. This research has been financed by the Bayerisches Staatsministerium für Umwelt und Verbraucherschutz (grant no. TLK01L-77229).

Review statement. This paper was edited by Aladar Czitrovsky and reviewed by two anonymous referees.

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Supplement of

Performance evaluation of four cascade impactors for airborne ultrafine-particle (UFP) collection: the influence of particle type, concentration, mass, and chemical nature

Elisabeth Eckenberger et al.

Correspondence to: Elisabeth Eckenberger (elisabeth.eckenberger@uni-bayreuth.de) and Anke C. Nölscher (anke.noelscher@uni-bayreuth.de)

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Table S1: Overview of HPLC methods applied for mass based chemical analysis applied on the environmental UFP samples.

Parameter	HPLC-MS neg	HPLC-MS pos	HPLC-FLD
Analytical column	Gemini 5u C18 110A (150 mm x 4.6 mm, 5 µm)	Gemini 5u C18 110A (150 mm x 4.6 mm, 5 µm)	EC 125/4 Nucleosil 100-5 C18 HD (125 mm x 4 mm, 5 µm)
Column temperature	40 °C	30 °C	30 °C
Injection volume	20 µL	20 µL	25 µL
Autosampler temperature	–	–	-5 °C
Flow rate	0.5 mL/min	0.3 - 0.5 mL/min	1 mL/min
Gradient	A) 80% ACN, B) 4 mM HCOOH 0 min 5% A 1 min 5% A 18 min 50% A 21 min 100% A 29 min 100% A 31 min 5% A	A) 80%MeOH, B) 4 mM HCOOH 0 min 50% A 3 min 80% A 12 min 100% A 18 min 90% A 20 min 50% A 25 min 75% A	A) ACN, B) H₂O (Milli-pore) 0 min 60% A 5 min 70% A 8 min 70% A 12 min 80% A 15 min 80% A 19 min 90% A 22 min 60% A
Detector	MSD Time ESI(-)-m/z-ions 0 min 207 8 min 111, 157, 171, 185 18 min 121, 135, 183 25 min 193, 217	MSD Time ESI(+)-m/z-ions 0 min 212, 227, 269 12 min 257, 261, 299	FLD Time λ_{ex} / λ_{em} [nm] 0 min 259 / 386 3.3 min 242 / 388 5.8 min 250 / 370 7.5 min 270 / 390 13 min 290 / 430

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Table S2: Summary of Considered Uncertainties and Their Contributions

Source of Uncertainty	Relative Uncertainty (%)
Relative Standard Deviation of Repeated Analysis	2
Errors from Reference Material	0.5
Errors from Self-Prepared Stock Solutions	5
Dilution Errors	5
Calibration Uncertainty	5
Inaccuracies from Balance and Pipette	1

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Table S3: Specifications regarding the different marker compounds that were analyzed and chosen for this study.

Marker	Method	Recovery	LOD _{Air} [pg/m ³]		LOD _{Instrument} [pg]	External standard calculation	
			43.2 m ³	5.76 m ³		Response factor [AU/μg/L]	R ²
Levo	HPLC-MS neg	86 ± 9%	130.09	975.67	5619.89	442.68	0.99
PA	HPLC-MS neg	84±6%	186.57	1399.28	8059.82	4415.4	0.99
TA	HPLC-MS neg	85±6%,	171.76	1288.20	7420.03	3352.9	0.99
6PPD	HPLC-MS pos	75±7%	40.17	301.26	1735.34	26766	0.98
BaP	HPLC- FLD/UV	78±5%	1.62	12.15	69.98	10.116	1.00
BbF	HPLC- FLD/UV	74±4%	1.16	8.70	50.11	12.15	1.00

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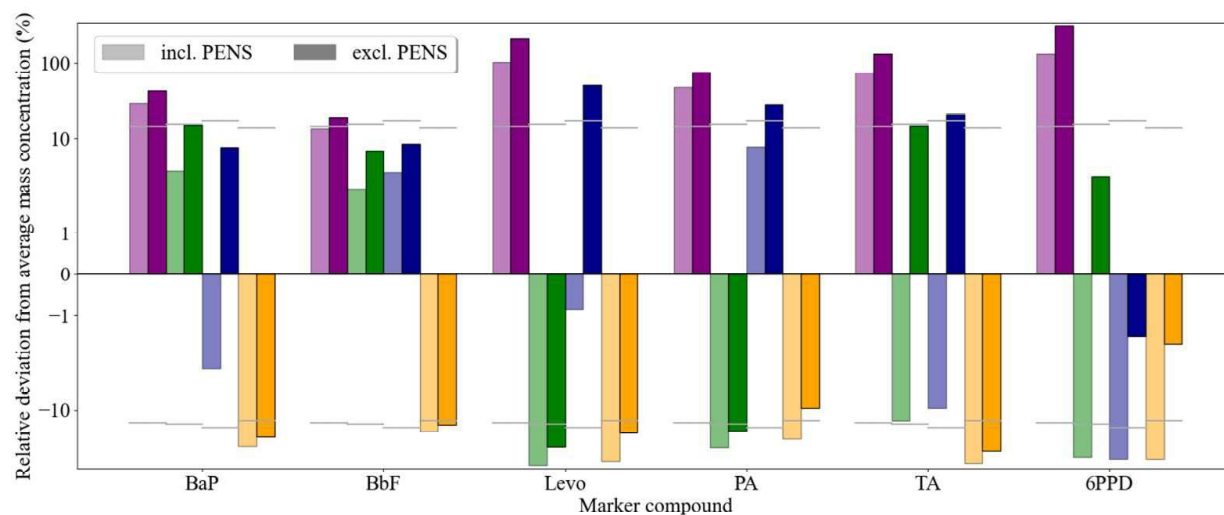


Figure S1: logarithmic representation of Fig. 6b.

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Sect.S1.1 Estimation of Impactor Uncertainties

To accurately assess the overall measurement uncertainty associated with the various impactors used in our study, we applied Gaussian error propagation. The overall chemical analysis error was 9% for all impactors. For the Ultra MOUDI impactor, in addition to the analysis error, the flow error was 10% and the handling error was increased to 10%. This adjustment leads to a total measurement uncertainty for the Ultra MOUDI of approximately 16.76%. The ELPI impactor had a flow error of 3% and an increased handling error of 15%, resulting in a total measurement uncertainty of around 17.75%. For the 120R MOUDI impactor, the flow error was 3% and the handling error was increased to 10%, leading to a total measurement uncertainty of approximately 13.78%. For the PENS impactor, the flow error was 5% and the handling error was increased to 10%, resulting in a total measurement uncertainty of approximately 14.35%.

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Published Article II

Sodium Thiosulfate-Coated Ceramic Denuders for Ozone Removal in Ultrafine Particle Sampling



Sodium thiosulfate-coated ceramic denuders for ozone removal in ultrafine particle sampling

Elisabeth Eckenberger¹, Andreas Mittereder², Nadine Gawlitta^{3,4}, Martin Sklorz^{3,4}, Dieter Brüggemann², Ralf Zimmermann^{3,4}, and Anke Christine Nölscher^{1,a,b}

¹Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Bayreuth, Germany

²Department of Engineering Thermodynamics and Transport Processes, University of Bayreuth, Bayreuth, Germany

³Joint Mass Spectrometry Centre (JMSC) at Comprehensive Molecular Analytics, Helmholtz Zentrum München, Neuherberg, Germany

⁴JMSC at Chair of Analytical Chemistry, Institute of Chemistry, University of Rostock, Rostock, Germany

^anow at: Institute of Climate and Energy Systems – Troposphere (ICE-3),

Forschungszentrum Jülich GmbH, Jülich, Germany

^bnow at: Institute of Geophysics and Meteorology, University of Cologne, Cologne, Germany

Correspondence: Elisabeth Eckenberger (elisabeth.eckenberger@uni-bayreuth.de) and Anke Christine Nölscher (a.noelscher@fz-juelich.de)

Received: 17 December 2025 – Discussion started: 23 January 2026

Revised: 21 May 2026 – Accepted: 29 May 2026 – Published: 22 June 2026

Abstract. Ozone (O₃) remaining in sampling air can artefactually alter the chemical composition of collected ultrafine particles (UFPs), biasing quantitative analysis of the chemical composition. In this study, we developed and evaluated a sodium-thiosulfate O₃ denuder (TSOD) specifically tailored for UFP sampling and assessed its O₃ scrubbing efficiency, particle losses, and chemical selectivity. In laboratory tests under controlled relative humidity and inlet O₃ levels up to 200 ppbV, the outlet concentration remained consistently below the limit of detection, demonstrating the O₃ removal efficiency of the TSOD. During an urban field deployment over 5 d O₃ downstream of the TSOD consistently remained below the detection limit while ambient O₃ varied between 0 and 65 ppbV. Moreover, for particles with mobility diameters ranging from 10 to 1000 nm, we did not observe any significant losses in particle number concentrations. Using a parallel two-channel UFP sampler (with vs. without upstream TSOD), we quantified O₃-driven sampling artefacts in UFP mass focussing on three types of organic markers. (1) Firstly, we targeted polycyclic aromatic hydrocarbons (PAHs), particularly chrysene (Chry), benz[a]anthracene (BaA), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), benzo[k]fluoranthene (BkF), and benzo[b]fluoranthene (BbF). Without upstream

O₃ removal, the individual concentrations of the PAHs were $15 \pm 3\%$ – $46 \pm 6\%$ lower. (2) Secondly, for the tire and road wear marker, the antioxidant N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) and its oxidation product 6PPD-quinone (6PPDq), we observed in-situ ozonation of 6PPD to 6PPDq with transformation yields of about $13 \pm 4\%$ to $20 \pm 8\%$. (3) In contrast, biogenic organic acids (BOAs) did not show differences when sampled with or without O₃, as their O₃ reactivity is much lower than the one of the PAHs. Moreover, this test indicated that the TSOD did not perturb the gas–particle partitioning of these semi-volatile species. Our results demonstrate that the TSOD (i) efficiently scrubs atmospheric O₃ at relevant mixing ratios, (ii) does not introduce measurable particle losses across 10–1000 nm, and (iii) preserves semi-volatile partitioning.

1 Introduction

Tropospheric ozone (O₃) is ubiquitous and highly reactive. Close to the Earth's surface, O₃ typically exhibits mixing ratios of up to 80 ppbV, occasionally exceeding 90 ppbV during strong photochemical episodes (Gaudel et al., 2018; Monks et al., 2015). Its tropospheric lifetime is on the order of days

to weeks, typically 6–27 d depending on altitude and chemical environment (Prather and Zhu, 2024; Young et al., 2013). O₃ can damage leaf tissues, irritate eyes, and harm the respiratory system, making it an air pollutant with short and long-term effects on ecosystems and human health (Emberson, 2020; Zhang et al., 2019). In the atmosphere, O₃ reacts with a wide range of atmospheric organic compounds. While being an important oxidant and initiating the oxidative removal of unsaturated organic gaseous molecules, O₃ poses a challenge in sampling when these O₃-reactive molecules are targeted in the chemical analysis (Ernle et al., 2023; Monks et al., 2015). If O₃ remains in the sampling air, it can continue to react with other atmospheric compounds bearing O₃-reactive unsaturated functional groups during the collection, thus leading to sampling artefacts. Such O₃-induced artefacts have been long recognized in atmospheric science and especially aerosol sampling (Balducci et al., 2018; Grosjean, 1992; Van Vaecck and Van Cauwenberghe, 1984). In filter-based aerosol samplers, particles often reside on filters from several hours up to several days, providing enough time to react with O₃ of the sampling air streaming through filters and already collected particles (World Meteorological Organization (WMO), 2023). Consequently, collected particles may undergo oxidative reactions with O₃, resulting in distortion of their chemical composition.

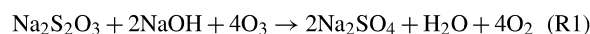
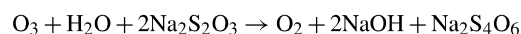
To mitigate O₃-induced sampling artefacts, upstream O₃ denuders or scrubbers are recommended for the sampling of particulate matter (e.g. PM_{2.5} and PM₁₀) by regulatory standards such as CEN EN 15549:2008. Particularly for O₃-reactive species like PAH (European Committee for Standardization (CEN), 2008), those denuders are used to remove O₃ from the sampling air stream and thereby prevent O₃ induced reactions on the filters before analysis.

There are different materials which have been deployed in O₃ denuders, which offer various mechanisms to scrub O₃ (Fick et al., 2001). Common approaches include potassium iodide (KI) coatings, manganese dioxide (MnO₂) catalysts, activated carbon (charcoal) adsorbents, silver-coated surfaces, and sodium thiosulfate (Na₂S₂O₃) impregnation (Ernle et al., 2023; Fick et al., 2001; Liu et al., 2014; Williams and Grosjean, 1990).

KI based denuders remove O₃ via stoichiometric redox reactions, thereby iodide oxidation products are generated. But the release of those reactive by-products such as I₂ and OH[−], could interact with the atmospheric samples. For example, iodinated compounds and hydroxide from KI based O₃ scrubbers have been shown to degrade derivatization agents that might be used during the extraction procedure, and introduce secondary artefacts in sampling of carbonylic compounds (Ho et al., 2013). MnO₂-coated denuders function via catalytic O₃ removal and have proven to prevent O₃ induced reactions of organic marker compounds in particulate matter. Yet, studies showed that the strong oxidizing surface of the MnO₂ coated denuders itself can react with components of the sampling air. In particular, while the use

of a MnO₂ denuder prevented the loss of particle-bound PAH during sampling, it also led to degradation of some PAH and concurrent formation of oxygenated PAH on the denuder surface (Liu et al., 2006). Activated carbon and silver traps offer broad O₃ removal through adsorption or catalysis, but these materials are relatively non-selective and thus may adsorb other gas-phase species or alter trace constituents in the sampling air (Fick et al., 2001; Helmig and Greenberg, 1995; Liflick, 1970). In contrast, Na₂S₂O₃ offers a well-characterized stoichiometric reaction with O₃ yielding in unreactive inorganic products.

Thiosulfate reacts with O₃ via stepwise oxidation, yielding tetrathionate and, under excess O₃, sulfate as stable products. The reaction effectively removes O₃ without generating gaseous radical by-products (Reaction R1, Takizawa et al., 1973):



Na₂S₂O₃ coated denuders (TSOD) have been successfully employed in gas-phase sampling to protect analytes (e.g. volatile organic compounds, VOC, such as terpenoids and carbonyls) from O₃ reactions. In one comparative study, both KI and Na₂S₂O₃ O₃ filters achieved > 90 % removal efficiency for about 50 ppbV O₃, although KI showed slightly higher performance and less humidity sensitivity. For Na₂S₂O₃, O₃ removal increases with relative humidity (RH) and declines in very dry air, while robust elimination is obtained at ~ 50 %–80 % RH (Rynek et al., 2025). Crucially, unlike KI, the thiosulfate method does not introduce organic reactive by-products, offering a potential advantage for preserving the organic composition of particle samples (Fick et al., 2001). Despite that, sodium thiosulfate O₃ denuders have seen little application in particulate-matter sampling compared with established O₃-denuders to date, and their performance in that context remains largely unexplored.

This knowledge gap is particularly relevant for ultrafine particles (UFPs, diameter < 100 nm), which are of special interest due to their many, diverse sources and health implications (Balmes and Hansel, 2024; Haddad et al., 2024; Li et al., 2023; Marval and Tronville, 2022). Among others, UFPs distinguish from coarser particles because of their small mass, high number concentration and high surface-area-to-mass ratio and high diffusional mobility. Thus, UFPs can readily adsorb gases, like O₃ and other oxidants, and undergo rapid surface chemistry. These properties not only facilitate heterogeneous reactions, altering particle composition, but also influences toxicological behaviour (Kwon et al., 2020; Oberdörster et al., 1992).

A particularly relevant example is the enrichment of polycyclic aromatic hydrocarbons (PAH) in UFPs. PAH are ubiquitous environmental pollutants originating from anthropogenic activities such as biomass burning and fossil fuel combustion (Abdel-Shafy and Mansour, 2016). They are of

concern due to their persistence, potential for long-range transport, and the formation of toxic transformation products in the atmosphere (Ravindra et al., 2008). Their atmospheric lifetime and toxicity profiles are governed by multi-phase oxidation pathways involving gas-phase radicals and O_3 . Among others, the higher-molecular-weight PAH (≥ 5 rings; benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), indeno[1,2,3-cd]pyrene (IcdP), together with four-ring PAHs such as chrysene (Chry) and benz[a]anthracene (BaA), are known to undergo heterogeneous ozonolysis on particle surfaces, especially under conditions of elevated O_3 exposure (Ji et al., 2024).

Another prominent example is *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD), a widely used tire antiozonant that protects rubber surfaces through reactive scavenging of O_3 . During tire wear, 6PPD is released into the environment and oxidized via O_3 to 6PPD-quinone (6PPDq). This transformation product has recently shown to exhibit acute aquatic toxicity, particularly toward coho salmon (Hu et al., 2022; Zhao et al., 2023).

A further compound class of interest are biogenic organic acids (bOAs), secondary oxidation products of monoterpenes that serve as markers for biogenic secondary organic aerosol (SOA) formation and ageing (Christoffersen et al., 1998; Denjean et al., 2015; Mutzel et al., 2016). This includes pinic acid (PA), pinonic acid (POA), terpenylic acid (TPA), and terebic acid (TA), which span a broad range of volatility: while PA is mainly particle-bound, POA, TPA, and TA remain partly in the gas phase (Kristensen et al., 2016a; Yu et al., 1999). Because of their semi-volatile nature, non-specific adsorption of gas-phase bOAs or disturbance of the gas–particle equilibrium are known artefact pathways in denuder-based sampling, which can alter the measured particle-phase concentrations (Subramanian et al., 2004; Yatavelli et al., 2014, 2012). This issue is particularly relevant for UFP sampling, where the high surface-area-to-mass ratio enhances adsorption and desorption processes and thus amplifies potential denuder artefacts (Kristensen et al., 2016b; Kuwabara et al., 2016; Shiraiwa et al., 2011).

Given the emerging significance of UFPs as important contributors to air pollution in atmospheric chemistry and human health, being linked to oxidative stress, respiratory and cardiovascular diseases (Das et al., 2024; Pantzke et al., 2023), such artefacts can bias the interpretation of UFP chemical composition and reactivity, underscoring the need for artefact-free sampling when assessing their environmental and health relevance (Schraufnagel, 2020).

To address this, we designed a study combining laboratory and field experiments to assess the performance of TSOD for UFP composition analysis under controlled and ambient conditions. Specifically, we focused on three representative classes of marker compounds: (1) PAHs to quantify O_3 -induced losses; (2) tire-derived *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD) and its quinone (6PPDq) as a parent–product pair indicative of in-

sampler ozonation; and (3) biogenic organic acids (bOAs) to test the selectivity and potential disturbance of gas–particle equilibrium.

2 Methods

2.1 O_3 denuder preparation

As O_3 denuder body, we used ceramic bodies ($\emptyset$ 25.4 $\times$ 50 mm; squared channels with 400 cells per square inch, Rauschert, Germany) that were impregnated with $Na_2S_2O_3$ (Merck, 99 %). Before coating the ceramic bodies, they were heated to 500 $^{\circ}C$ for 5 h, then cleaned in water (H_2O , obtained from Seralpur PRO 90 CN system with Supor DCF filter, Electronics Grade, 0.2 μm), subjecting them to ultrasonication for two cycles, each for 10 min. Subsequently, the bodies were manually dried with vigorous shaking to remove bulk water from the honeycomb channels. Next, the bodies were placed in a 5.6 mol L $^{-1}$ solution of $Na_2S_2O_3$ and H_2O , and ultrasonicated for an additional 10 min. After ultrasonic impregnation, excess solution was removed by vigorous shaking while holding the monolith vertically to allow drainage of bulk liquid from the honeycomb channels. Afterwards, bulk solution within the channels, which was not removed by shaking, was blow-dried with nitrogen (N_2 , 99.99 %). This was a critical step to prevent the growth of crystals within the ceramic matrix and the subsequent occlusion of the channels. The drying process was finished by baking the TSODs at a temperature of 120 $^{\circ}C$ for a duration of 60 min. For equilibration, the TSODs were placed in a sealed container with a separate water reservoir at the base to maintain a high humidity environment. This setup was left to rest overnight, for 12 h, to achieve an even coating of $Na_2S_2O_3$ on the ceramic body. Afterwards the TSODs were stored under N_2 atmosphere in a closed glass vessel.

2.2 Laboratory test-bed for determining the denuder efficiency for O_3 removal under controlled conditions

To assess the O_3 removal efficiency of the TSODs, we set up an experimental test-bed in the laboratory. O_3 was produced in variable levels with a generator (Teledyne, T750U), diluted with zero air at a flow rate of 4 L min $^{-1}$, and passed through the TSOD. Upstream of the TSOD, humidified air was added to the sample flow by bubbling 4 L min $^{-1}$ of zero air through a suction flask filled with H_2O , yielding a total flow of 8 L min $^{-1}$ through the TSOD (Fig. 1a). We measured the RH upstream of the TSOD, which remained constant at about 50 %. Downstream of the TSODs, the O_3 mixing ratio was measured using an O_3 -analyzer (Thermo Scientific, MLU, Model 49i). We tested the TSOD over an O_3 mixing ratio range of 5 to 200 ppbV. To assess the practical zero-level response of the instrument, separate zero-air measurements were performed, yielding an analyzer signal

of 4.6 ± 0.5 ppbV under O_3 -free conditions. The variability of this baseline signal resulted in a limit of detection (LOD) of 1.5 ppb, calculated as three times the standard deviation of the zero-air measurements ($k = 3$).

2.3 Assessment of particle losses within the O_3 denuder

To examine potential particle losses due to the TSOD, we conducted loss tests with simulated atmospheric organic aerosol (SimOA) using the Bayreuth Atmospheric simulation Chambers (BATCH). To maintain a stable aerosol mixture for several hours, we flushed the 700 L cylindrical glass chamber with ambient air for several hours. Subsequently, 0.05 mL of alpha-pinene ($\geq 98.0\%$, Carl Roth) was injected into the airflow, while a nebulizer delivered seed particles (from spraying saturated ammonium sulfate solution and drying) into the chamber at a flow rate of 3 L min^{-1} for 3 min. After an additional 5 min, the pump supplying ambient air was switched off, and the solar simulator (UV Osram HMI, 4000 W, filtered with a water-cooled glass plate) (Ofner et al., 2011; Zhao et al., 2008), was ignited for 15 min to produce first O_3 and subsequently SimOA. We connected three TSOD bodies in line to the chamber. Downstream the TSOD, a Y-connector was attached splitting the flow into two channels. One channel end led to a pump which allowed to adjust to variable flows through the denuder ($4\text{--}30 \text{ L min}^{-1}$). The other channel end led to a particle size spectrometer to record the particle size distribution after the TSOD (Cambustion, DMS500). As a control, the setup was also operated without the TSOD installed in the stainless-steel cylinders.

2.4 Field deployment and UFP sampling for offline chemical characterization

To evaluate the performance of the TSOD under real environmental conditions, a novel setup was installed in a measurement container at an urban field site of the University of Applied Sciences in Augsburg, Germany (48.358°N , 10.907°E) in September 2023. The site is dominated by domestic heating and traffic which are likely sources for PAH and 6PPD/6PPDq. Streetside and campus vegetation emitted monoterpenes, providing biogenic precursors for SOA. Air was drawn through a PM_{10} sample inlet from the roof of the air-conditioned container at a height of 4.2 m. A stainless-steel sampling tube ($2.1 \text{ m} \times 28 \text{ mm}$) led into the container, where it was connected to a modified 120 R Microorifice Uniform Deposit Impactor (MOUDI, TSI). The 120R-MOUDI was reduced to sample with cut-off sizes of 2.5, 1.0, and $0.1 \mu\text{m}$. The impactor plates were coated with high-vacuum grease to minimize bounce effects. Behind the reduced MOUDI unit, the After Filter Stage, intended to collect particles smaller than $0.1 \mu\text{m}$, was omitted, and instead, a Y-connector ($30 \text{ cm} \times 28 \text{ mm}$) was installed, leading to an automated filter changer (HYDRA Dual Sampler, FAI instruments), thereby introducing a two-channel filter collec-

tor. Here, UFP samples were collected from both channels in parallel on pre-baked quartz fiber filters (47 mm Whatman, QM-A) and, following a weekly change, stored at -20°C in Analyslides (Cytiva) until analysis. In one of these channels (Channel A), the TSOD was installed, while the other channel (Channel B) was operated with an uncoated ceramic body as reference (Figs. S1 and S2 in the Supplement). For control measurements, both channels were operated with a ceramic body without coating. The total flow through the impactor was set to 30 L min^{-1} according to the manufacturer's specifications, with a corresponding collection of 15 L min^{-1} per channel. Ambient O_3 mixing ratios were measured after channel A (41M, UV Photometric O_3 analyzer, ansysco, Environnement S.A.) and cross-checked against values reported by the local governmental monitoring station (Landesamt für Umwelt, LfU). This field setup was intended to serve (i) as assessment of the O_3 removal efficiency under real-world conditions over a longer time period, and (ii) the effect of O_3 removal during collection of UFP samples for subsequent offline chemical analysis.

2.5 Chemical marker compounds

UFP samples obtained during the field campaign were analyzed offline to investigate the effect of upstream O_3 removal via TSOD on the concentrations of selected organic marker compounds. The following target compounds were analyzed: (i) PAHs: BaP, BbF, BkF, IcdP, Chry, and BaA; (ii) parent-product (ozonolysis) pair: 6PPD and 6PPDq; and (iii) BOAs: PA, POA, TPA, and TA. Internal standards were 3-methylcholanthrene (3-MC, Merck, 98.0% , $0.4 \mu\text{M}$) and nicotinic acid (NA, Merck, 99.5% , $10 \mu\text{M}$). Reagents, solvents, and standards were sourced from LGC Standards, Merck, Carl Roth, ASCA-Berlin, and Fisher Chemical (purities $> 95\%$ – 99.99%). HPLC-grade acetonitrile (ACN, 99.95%), methanol (MeOH, 99.99%), water (H_2O ; Seralpur PRO 90 CN, electronics grade, $0.2 \mu\text{m}$), and formic acid ($HCOOH$, $\geq 98\%$) were used as mobile-phase components; dichloromethane (DCM, 99.8%) and high-purity nitrogen (N_2 , 99.999%) were used for extraction/solvent handling and evaporation.

2.6 Extraction

We extracted the selected marker components from the filters via a soft, solvent-based and optimized protocol: (1) the filter loaded with particles was divided into two equal parts. One part was extracted, the other one used as backup. (2) The filter-half for extraction, was spiked with $50 \mu\text{L}$ of each internal standard, namely 3-methylcholanthrene (3-MC, $0.4 \mu\text{M}$) and Nicotinic acid (NA, $10 \mu\text{M}$) and cut into small fragments. (3) These filter fragments were then transferred into a glass container with a screw cap, and 2 mL of extraction solvent (e.g. analytical-grade dichloromethane (DCM, Fisher Chemical, 99.8%) and methanol (MeOH, Carl Roth,

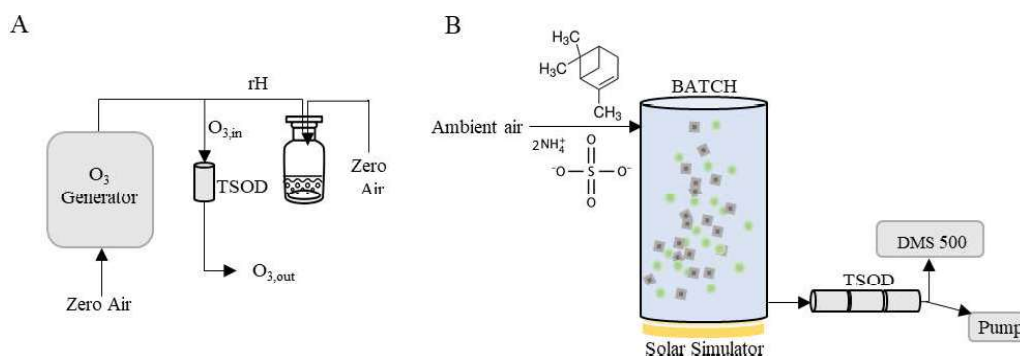


Figure 1. Schematic of the laboratory test-bed for assessing the O₃ removal efficiency (A) and potential particle losses of TSODs (B). (A) O₃ was generated, diluted with zero air, humidified to ~50 % relative humidity, and passed through the TSOD. Downstream O₃ mixing ratios were measured using an O₃ analyzer. (B) For particle loss tests, the setup was connected to the BATCH, where SimOA was generated from α -pinene oxidation with ammonium sulfate seed particles and ambient air. The aerosol flow was directed through three TSODs, and particle size distributions were measured downstream using a DMS500.

$\geq 99.9\%$)) were introduced. (4) The samples underwent extraction through agitation within a closed flask for a duration of 15 min using a vortex shaker (2000 rpm). (5) Filter residues were kept in the glass container. Extracts were filtered using custom-designed glass frits with a diameter of 1 cm and a pore size of 20 μm to filter any potential filter residue.

Steps (3) to (5) were repeated three times, each time employing a different extraction solvent. The sequential solvents used were, in order, pure MeOH, 50 : 50 MeOH : DCM, and pure DCM. Subsequently, the solvent from the combined extracts was evaporated under a gentle flow of nitrogen while cooled with ice to avoid loss of semi-volatile compounds. A droplet was kept as residue which was dissolved in 1 mL of a 60 : 40 solution of acetonitrile (ACN, Carl Roth, 99.95 %) and Millipore water (H₂O obtained from Seralpur PRO 90 CN system with Supor DCF filter, Electronics Grade, 0.2 μm). This was transferred into two separate vials for subsequent analysis. Throughout this entire sample preparation process, the samples were consistently stored in an ice cooled environment to avoid losses.

2.7 HPLC methods

The extracts of the collected UFPs were analyzed using two complementary high-performance liquid chromatography (HPLC) systems, adapted to the specific analytical requirements of the target compounds. PAHs were quantified using an Agilent 1260 Infinity system equipped with a fluorescence detector (Agilent 1100 Series FLD). bOAs and tire-derived antioxidants, including 6PPD and its transformation product 6PPDq, were analyzed on an Agilent 1100 Series HPLC coupled to an electrospray ionization mass spectrometer (ESI-MS; Agilent 6130 Single Quadrupole).

All analyses were conducted using HPLC-grade solvents: acetonitrile, ultrapure water, and formic acid ($\geq 98\%$, Carl

Roth). Chromatographic separation and detection settings were optimized for each compound class. A detailed summary of the applied methods is provided in our previous publication and in the Supplement (Eckenberger et al., 2025; Table S1).

To assess the overall analytical recovery, spiking experiments were performed in triplicate. One half of a pre-baked quartz fiber filter (47 mm, Whatman QM-H) was spiked with 10 μL of a 10 μM standard solution containing all target compounds and subsequently extracted following the same procedure used for ambient samples. Recoveries were calculated using external calibration and expressed as the ratio of measured to expected concentrations:

$$\text{Rec} = \frac{C_{\text{measured}}}{C_{\text{expected}}} \times 100 \quad (1)$$

Average recoveries ranged from 70 % to 101 % and were consistent across compound classes. Specifically, recoveries for PAHs were $78 \pm 5\%$ for BaP, $74 \pm 4\%$ for BbF, $89 \pm 6\%$ for BkF, $70 \pm 4\%$ for IcdP, and $97 \pm 5\%$ for $\sum(\text{Chry} + \text{BaA})$. 6PPD and its transformation product 6PPDq yielded recoveries of $75 \pm 7\%$ and $81 \pm 7\%$, respectively. Among the bOAs, PA was recovered at $84 \pm 6\%$, while POA, TA, and TPA showed recoveries of $101 \pm 6\%$, $85 \pm 6\%$, and $96 \pm 6\%$, respectively. Uncertainties represent 1σ standard deviations (SD) obtained from triplicate spiking experiments.

To account for analyte-specific losses, all sample concentrations were corrected for recovery using the following equation:

$$C_{\text{sample,corrected}} = C_{\text{sample,measured}} \times \left(\frac{100}{\text{Rec}} \right) \quad (2)$$

Validation of the analytical procedure was performed using the NIST Standard Reference Material SRM 2786 (Fine Atmospheric Particulate matter with mean diameter $< 4 \mu\text{m}$),

which was applied to a quartz filter and processed identically to the environmental samples. Specifically, $107 \pm 4\%$ of the certified BaP concentration was recovered. BbF, BkF, $\Sigma(\text{Chry} + \text{BaA})$, and IcdP showed recoveries of $96 \pm 5\%$, $94 \pm 7\%$, $89 \pm 5\%$, and $99 \pm 7\%$, respectively. The results agreed with the certified concentrations within their stated uncertainty, confirming the reliability of the method even in the presence of a complex particulate matrix. Limits of detection (LOD) were determined for each compound from four replicate injections of a diluted calibration standard, targeting a signal-to-noise ratio of 3. The LOD was calculated as:

$$\text{LOD} = \frac{3 \times \sigma}{\text{RF}} \quad (3)$$

where σ is the standard deviation of replicate peak areas and RF denotes the compound-specific response factor derived from external calibration. For comparison with ambient concentrations, airborne detection limits LOD_{Air} were calculated by normalizing the LOD to the sampling volume (Table S2).

Instrument and field blanks were routinely collected and processed alongside samples using the identical preparation. Instrument blanks consisted of pure-solvent injections between runs. Field filter blanks were prepared by placing clean quartz filters in the sampler holders but without drawing air. Blank signals were subtracted on a per-compound basis when reproducible across replicate blanks and clearly below sample signals. If blank values varied strongly within a batch or exceeded expected background levels, affected samples were excluded from further analysis.

Last step to calculate mass concentrations of the marker compounds in UFPs was to convert the blank-corrected extract concentrations to air concentrations by multiplying the corrected concentration by the final extract volume (1 mL), correcting for recovery and the analyzed filter fraction (only half filter was analyzed), and normalizing to the sampled air volume (21.6 m^3).

3 Results and Discussion

3.1 Laboratory evaluation of denuder performance

To evaluate the O_3 removal efficiency of the TSOD under controlled conditions, we first conducted a laboratory test. Previous studies have shown that RH plays a critical role in the reactivity of sodium thiosulfate toward O_3 (Ernle et al., 2023). Specifically, at 80 % RH, the lifetime of the sodium thiosulfate scrubber increases dramatically, enabling complete O_3 removal from the sample air, in contrast to its performance under dry conditions. As a reference for typical ambient conditions at our field site in Augsburg, daily data from the nearest German Weather Service (Deutscher Wetterdienst, DWD) climate station for the meteorological summer 2023 yield an average RH of $69\% \pm 11\%$ (Data source: DWD). We therefore intentionally conducted our laboratory

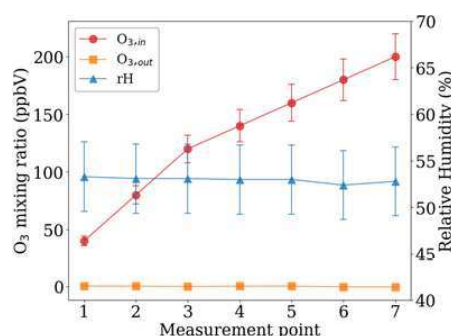


Figure 2. Average O_3 mixing ratios upstream (“ O_3 , in”, red) and downstream (“ O_3 , out”, orange) of the TSOD during consecutive laboratory measurement intervals with stepwise increasing inlet O_3 mixing ratios (40–200 ppbV). RH was simultaneously monitored and remained constant. Lines are included to guide the eye.

experiments under distinctly drier conditions (reported as $\text{RH} = 52.4\%–53.3\%$), in order to test TSOD performance near the lower end of the humidity range expected during field operation. Previous studies indicate that thiosulfate-based ozone removal decreases under drier conditions, consistent with reduced water availability at the denuder surface (Ernle et al., 2023; Rynek et al., 2025).

In urban and suburban environments, O_3 levels frequently peak between 70 and 100 ppbV and can surpass 120 ppbV during intense pollution events (Bell et al., 2007; Cooper et al., 2014; World Health Organization, 2021). Thus, the inlet O_3 mixing ratio was incrementally increased to up to 200 ppbV in a sequence of discrete measurement intervals. As depicted in Fig. 2, the outlet O_3 mixing ratios (4.4–5.0 ppbV) were indistinguishable from this zero-air baseline, indicating that ozone downstream of the denuder was below the LOD of the measurement setup.

This indicates that, even at comparably high mixing ratios, O_3 was removed from the air in this experimental setup. However, it is important to note that this experiment was conducted under controlled laboratory conditions with constant temperatures, RH, and zero air. Furthermore, the duration of the experiment does not match the typical collection duration required for UFPs, which, due to their low mass, must be collected over several hours or days for mass-based chemical analysis. To complement the controlled laboratory evaluation, a field deployment was conducted to assess the TSOD’s applicability under real-world sampling conditions. The results of this field implementation, including performance under ambient O_3 exposure and implications for UFP sampling, are discussed in detail in Sect. 3.2.

To assess if the sampling flow channelled through the TSOD is associated with particle losses, we compared particle number concentrations (PNC) measured with (wTSOD) and without (woTSOD) TSOD installed, where the woTSOD setup served as the reference using an empty TSOD hous-

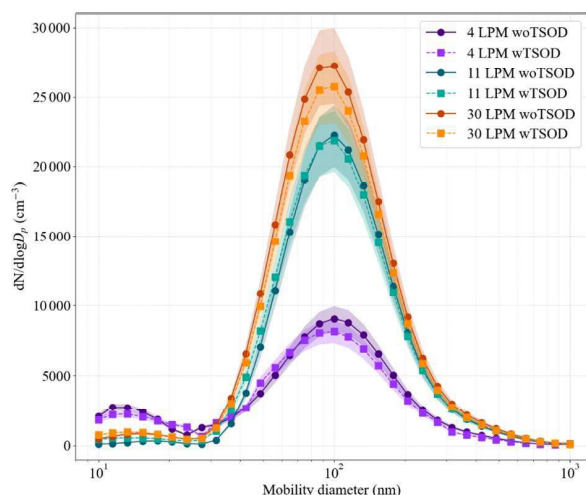


Figure 3. Particle size distributions recorded downstream of the TSOD and for reference without a TSOD at three different flow rates (4, 11, and 30 L min^{−1}). Purple tones refer to 4 L min^{−1} (light purple: wTSOD, dark purple: woTSOD), green tones to 11 L min^{−1} (medium green: wTSOD, dark green: woTSOD), and orange tones to 30 L min^{−1} (orange: wTSOD, dark orange: woTSOD). Shaded areas represent ±10 % uncertainty.

ing. The analysis was performed for two particle size ranges: 10–100 and 10–1000 nm. All measurements were repeated at three flow rates (4, 11, and 30 L min^{−1}), and an instrument uncertainty of 10 % was assumed. In the 10–100 nm range, relative differences between the wTSOD and woTSOD configurations ranged from 2 % to 7 % depending on the flow rate. At 4 L min^{−1}, the difference corresponded to a 2 % loss, increasing to 7 %, and 6 % at 11 and 30 L min^{−1}, respectively. Comparable results were obtained for the full-size spectrum (10–1000 nm). Measured losses amounted to 7 % (4 L min^{−1}), 3 % (11 L min^{−1}), and 6 % (30 L min^{−1}) (Fig. 3).

The average observed deviation between the wTSOD and woTSOD measurements was 5 % and falls within the measurement uncertainty of the particle size spectrometer utilized. Hence, we found no significant losses in particle number concentrations and the TSOD setup can be considered suitable for ambient UFP sampling. Since the measurements at 30, 11, and 4 L min^{−1} were conducted sequentially, the absolute particle number concentrations between the different flow-rate experiments vary and are not directly comparable.

3.2 Field performance of the denuder and chemical composition of UFPs

The O₃ removal performance of the TSOD was further evaluated under ambient conditions during a five-day deployment at an urban field site. Due to the lack of a second O₃ analyzer, the experiments were conducted using only one device. Ini-

tially, measurements were taken with the O₃ analyzer without the installed coated ceramic body. Subsequently, these measurement results were compared with publicly available data on O₃ mixing ratios from a nearby site monitored by the Bavarian Environment Agency (Bayerisches Landesamt für Umwelt (LfU), 2025).

The hourly averaged data are compared in Fig. 4a. A linear regression yielded a slope of 1.04 and a coefficient of determination (R^2) of 0.90, confirming the comparability of both datasets within the uncertainty of the measurement. The near-unity slope indicates that the inlet, impactor, hose system, and uncoated denuder did not cause substantial systematic O₃ losses under the field conditions. Therefore, no correction was applied to either dataset before subsequent analysis. During the period when a TSOD, in channel A of the measurement setup, was installed, the O₃ mixing ratio behind the TSOD was consistently measured. In comparison to the measurements from the Bavarian Environment Agency, it was observed that the O₃ mixing ratio behind the TSOD remained below the LOD, while the outdoor O₃ mixing ratios fluctuated between 0 and 65 ppbV (Fig. 4b). Over the period of 5 d, the TSOD removed O₃ reliably from the sampled air. These results indicate the O₃ removal efficiency of the TSOD under environmental conditions and over an extended time period.

Chemical organic tracer analysis of UFPs

To assess the efficiency and selectivity of the TSOD under ambient conditions, we evaluated changes in particle-phase concentrations of selected organic tracer compounds. We analyzed representative compounds from three organic marker groups: PAHs, 6PPD and 6PPDq, and bOAs. All compounds are potentially susceptible to TSOD-induced sampling improvements or artefacts. This could be either by prevented degradation through O₃ oxidation or by shifts in gas-particle partitioning through removal of gaseous components. In the following, we present compound-specific mass concentrations measured in Channel A (with O₃ removal via TSOD) and Channel B (without O₃ removal comparing to an uncoated ceramic body). We assess the TSOD performance for each class of marker compounds.

First, to verify the performance and internal consistency of the dual-channel sampling setup, all targeted marker substances were analyzed under reference conditions in which neither sampling line contained an upstream-coated ceramic body. The measured mass concentrations of all compounds in UFPs sampled through Channel A and Channel B agreed within the uncertainties. Regression slopes were close to unity for PAHs (BaP: 0.97, BkF: 0.83, BbF: 1.18, IcdP: 1.05, $\sum(\text{Chry} + \text{BaA})$: 0.92), demonstrating the absence of systematic differences between the two channels. Similarly, mass concentrations of 6PPD (slope = 1.01) and 6PPDq (slope = 1.04) and the bOAs, including PA (slope = 1.00), POA (slope = 0.94), TA (slope = 1.003), and

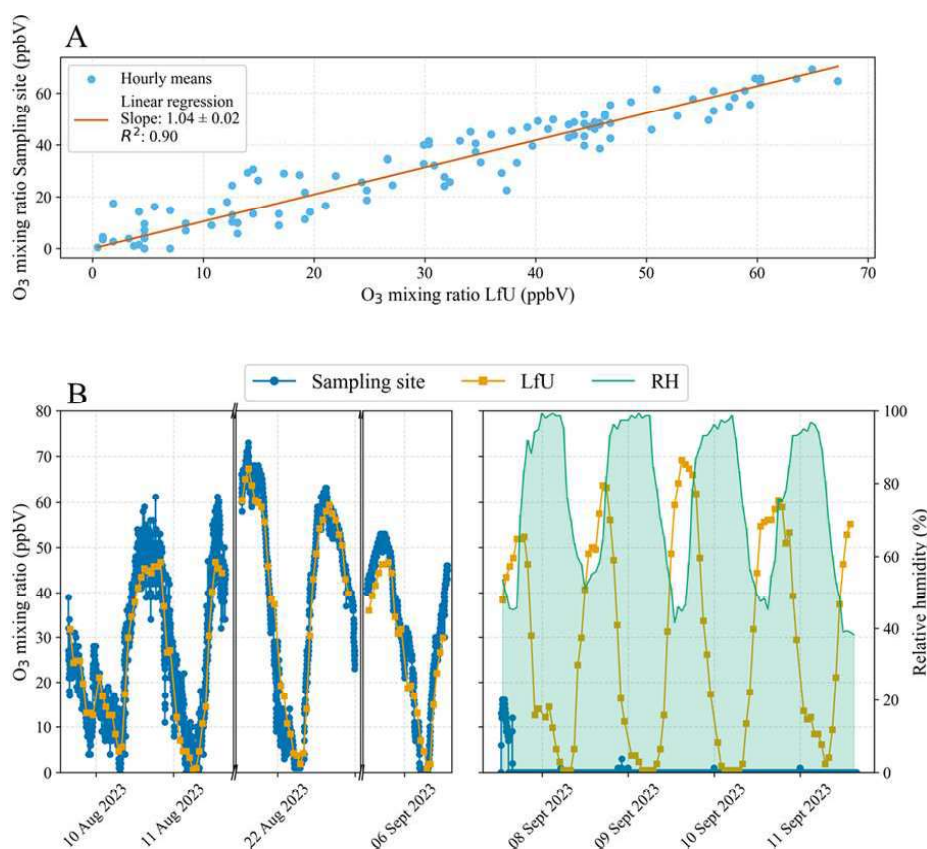


Figure 4. (A) Correlation between hourly averaged O₃ mixing ratios from the sampling site and the LfU monitoring station. A linear regression through the origin (red line) yields a slope of 1.04 and $R^2 = 0.90$. (B) Time line of ambient O₃ mixing ratios before and during the field campaign in Augsburg. Measurements before the campaign were taken from a setup without a TSOD, allowing comparison with reference data from the LfU monitoring station. After the start of UFP sampling, measurements were taken downstream of the TSOD (blue, “Sampling site”) and compared to the LfU reference data (orange, “LfU”).

TPA (slope = 1.010) were comparable for both channels (Table 1). Detailed regression plots are provided in the Supplement (Fig. S2).

Deploying the TSOD in Channel A and regressing concentrations in Channel B (no O₃ removal) against Channel A provides a direct quantitative analysis of O₃ induced sampling artefacts. For PAHs, slopes of 0.54–0.85 (BaP: 0.60, BkF: 0.85, BbF: 0.66, $\sum(\text{Chry} + \text{BaA})$: 0.54, IcdP: 0.62; Table 1) indicate about 15 % to 46 % in-sampler losses when O₃ is present (Fig. 5a). For context, ambient BaP was on the order of about 9 pg m^{-3} with the deployment of a TSOD, without O₃ removal this would be 40 % lower. In contrast, 6PPD and its oxidation product 6PPDq show opposite behaviour (Fig. 5b, Table 1): 6PPD exhibits a slope of 0.52, indicating underestimation without O₃ removal, whereas 6PPDq shows a slope of 1.40, reflecting overestimation due to in-sampler ozonolysis. These findings are consistent with the oxidative conversion of 6PPD to 6PPDq, which is suppressed in-situ

when O₃ is scrubbed from the sampling air. Mechanistic and computational studies have shown that O₃ attacks the aromatic amine moiety of 6PPD, forming hydroxylated intermediates that subsequently oxidize to 6PPDq as the major transformation product (Cataldo, 2019; Rossomme et al., 2023; Zhao et al., 2023). In our dual-channel approach, we find that about 13 % to 20 % of the initial 6PPD was converted to 6PPDq. These transformation yields align with those reported by Zhao et al. (2023), who reported that 1 %–19 % of 6PPD was converted to 6PPDq during controlled ozonation of 6PPD.

Conversely, BOAs exhibited negligible inter-channel differences (slopes about 0.95 to 1.09, Fig. 5c, Table 1), indicating that the TSOD effectively removes O₃ without perturbing gas–particle partitioning. Given their semi-volatile nature, any non-selective uptake or release by the TSOD would shift this equilibrium and drive evaporation or condensation, which is not observed (Kristensen et al., 2016a; Yu et al.,

Table 1. Linear regression slopes of marker compound concentrations between the two sampling channels during operation with ozone removal (TSOD installed in Channel A). For comparison, slopes obtained during reference operation, when both channels were equipped with uncoated ceramic bodies, are also shown (Reference, Fig. S3). Slopes were derived from linear regressions constrained through the origin. Values greater or smaller than unity indicate enhancement or loss of the respective compound in the presence of O₃ removal.

Compound	Slope	
	Relative change due to O ₃ exposure during sampling	Reference
BaP	0.60	0.97
BbF	0.85	1.18
BkF	0.66	0.83
IcdP	0.62	0.98
Σ(Chry + BaA)	0.54	0.92
PA	1.02	1.00
POA	0.94	1.01
TA	1.06	1.00
TPA	1.09	1.01
6PPD	0.52	1.01
6PPDq	1.40	1.04

1999). This indicates that the sodium thiosulfate coating does not disturb gas-particle equilibrium.

Among the PAHs, the most pronounced O₃ related losses were observed for the Σ(Chry + BaA) (46 %) and for BaP (40 %), followed by IcdP (38 %), BkF (34 %), and BbF (15 %). These losses observed in the UFP fraction are consistent with sampling artefact studies focusing on O₃ related degradation in larger particle fractions.

For PM₁₀, Balducci et al. (2018) reported summer field BaP concentrations of about 0.022 to 0.028 ng m⁻³ and, in laboratory tests at 400 ppbV O₃ for 1–3 h, observed BaP losses of ~24 %–55 % (with smaller losses for BbF and BkF). Similarly, Liu et al. (2006) reported daily O₃ concentrations of 50–95 µg m⁻³ (≈ 25–48 ppbV at 290 K) and deployed a MnO₂ denuder into PM₇ sampling. The observed concentrations for particulate PAH rose from 0.16 to 0.20 ng m⁻³ (+25 %) for BaP and shifts for BaA (–7 %), chrysene (–14 %), and IcdP (+6 %), while BbF remained unchanged upon the removal of O₃. Consistently, the study of Liu et al. (2014) in Beijing summer showed averaged O₃ concentrations of 74.6 µg m⁻³ (≈ 37 ppbV). They sampled PM_{2.5} with a denuder-equipped method, which yielded higher particulate PAH concentrations than the conventional setup (Σ₉PAH = 42.3 ± 10.5 vs. 27.1 ± 13.8 ng m⁻³), and for BaP a corresponding underestimation from 49 % to 83 % without O₃ removal. While inter-channel artifacts such as gas-particle partitioning (“blow-on” or “blow-off”) might occur, our control measurements showed no inter-channel bias

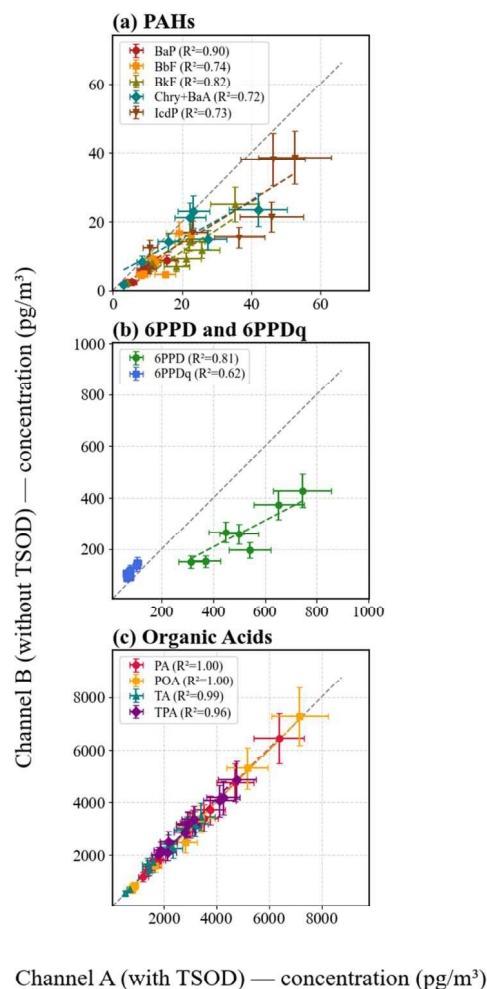


Figure 5. Comparison of analyte concentrations measured in sampling channel A (with TSOD, O₃ removed) and channel B (without TSOD, O₃ present). The sample in channel B was exposed to ambient O₃ mixing ratios during the 24 h sampling interval. Each data point represents the mass concentration of an analyte measured in parallel filters. Dashed lines show linear regressions constrained through the origin, while grey dashed lines represent the 1 : 1 relationship. (a) PAHs: BaP, BbF, BkF, IcdP, and Σ(Chry + BaA). (b) Tire wear antioxidants and their transformation product: 6PPD and 6PPDq. (c) bOA: PA, POA, TPA, and TA. The standard deviation used for the error bars is derived from three replicate measurements of three extracted filter samples.

in the absence of the TSOD. Therefore, we conclude that the observed differences are primarily driven by O₃-induced chemical transformation of particle-bound PAHs in the channel without the denuder.

To contextualize the relative O_3 -induced artefacts, we compared them with the heterogeneous pseudo-first-order rate constants (k') for O_3 loss of particle-bound PAHs reported by Bedjanian and Nguyen, (2010). In this study, soot from a premixed kerosene–air flame was exposed to an initial O_3 of $1.3 \times 10^{12} \text{ molec. cm}^{-3}$ ($\approx 51.4 \text{ ppbV}$ at 290 K) under dry, dark flow conditions. Figure 6 shows that our observed UFP degradation pattern generally follows the compound-specific reactivities described by Bedjanian and Nguyen (2010). Consistently with those compound-specific reactivities, our degradation pattern largely follows $\sum(\text{Chry} + \text{BaA}) > \text{BaP} > \text{BkF}$. Quantitatively, $\sum(\text{Chry} + \text{BaA})$ shows the highest k' ($7.3 \times 10^{-3} \text{ s}^{-1}$), followed by BaP ($6.8 \times 10^{-3} \text{ s}^{-1}$) and BkF ($6.0 \times 10^{-3} \text{ s}^{-1}$). BbF has a comparable k' ($5.5 \times 10^{-3} \text{ s}^{-1}$), about 80 % of BaP, yet its O_3 -related loss in our data is only $\sim 40\%$ of BaP. This discrepancy likely reflects particle-phase microphysics, specifically the partial embedding or molecular shielding within condensed organic matrices. These structural factors inherently reduce the effective surface accessibility of certain PAHs (Kwamena et al., 2007; Shiraiwa et al., 2011; Zhou et al., 2019). Furthermore, the elevated RH during sampling (74 %–84 %) may have further enhanced this effect, by increasing particle viscosity or forming hydrated amorphous surface layers which can act as transient diffusion barriers (Pöschl et al., 2001). Consequently, while the relative ranking of O_3 susceptibility among PAHs in UFPs is preserved, the overall magnitude of degradation is likely strongly influenced by particle-phase microphysics. This distinction underscores the critical importance of integrating such particle-phase effects when extrapolating laboratory kinetic data to realistic atmospheric conditions.

4 Conclusion

This study demonstrates the development and evaluation of a TSOD adapted for UFP sampling. Under controlled laboratory conditions, the TSOD removed O_3 effectively for O_3 mixing ratios of up to 200 ppbV and constant RH of 53 %. The same was observed during a 5 d field campaign, with varying ambient O_3 mixing ratios (0–65 ppbV) and RH (38 %–99 %). No significant particle losses were observed in the 10–100 and 10–1000 nm range across various flow rates, with relative average deviation of 5 %, remaining within instrumental uncertainty.

Utilizing a dual-channel approach, we compared the impact of upstream O_3 removal prior to filter based analysis of mass concentrations of selected UFP-bound marker compounds of diverse chemical properties and of well-known interest in atmospheric studies. O_3 -sensitive markers such as PAHs and 6PPD showed marked inter-channel differences: relative O_3 -induced losses reached 15 %–46 % for higher molecular weight PAHs and up to 48 % for 6PPD. In contrast, 6PPDq concentrations increased in the O_3 -exposed channel,

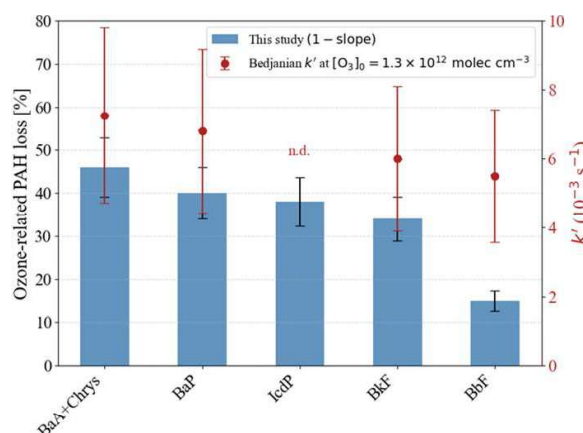


Figure 6. Compound-specific comparison of O_3 induced losses of particle-bound PAH. Blue bars (left axis) show the O_3 -attributable loss fraction from this study ($1 - \text{slope}$ of the O_3 -contrast regression). Red symbols (right axis) show first-order consumption rate constants k' ($\times 10^{-3} \text{ s}^{-1}$) from Bedjanian and Nguyen (2010) for soot exposed to $[\text{O}_3]_0 = 1.3 \times 10^{12} \text{ molec. cm}^{-3}$ at 290 K; red vertical whiskers indicate their reported variability. The red dashed lines simply connect compounds to guide the eye. “n.d.” = no k' reported (IcdP).

consistent with in-situ formation from 6PPD. Quantitative comparison of absolute concentrations suggests a 6PPD to 6PPDq transformation of about 13 % to 20 %, in agreement with previously reported laboratory yields. BOAs showed no inter-channel effect, implying that the TSOD did not induce a measurable change in particle reactivity or phase distribution of these semi-volatile species. Such change would need to be large enough to overcome analytical variability, which we do not observe.

Without an upstream O_3 denuder, systematic sampling artefacts occur: PAHs and 6PPD are systematically and significantly underestimated, while oxidation products such as 6PPDq are overestimated due to in-situ ozonolysis. Thus, O_3 removal is a methodological requirement for quantitative chemical UFP analysis. The TSOD meets the requirements by (i) efficiently scrubbing O_3 at atmospherically relevant mixing ratios, (ii) introducing no measurable particle loss across sizes from 10 to 1000 nm, and (iii) not perturbing the gas–particle partitioning of semi-volatile BOAs.

Data availability. The data presented here are available at <https://doi.org/10.5281/zenodo.20325619> (Eckenberger et al., 2026).

Supplement. The supplement related to this article is available online at <https://doi.org/10.5194/amt-19-4035-2026-supplement>.

Author contributions. EE: denuder design and preparation, laboratory and field deployment, measurements, chemical analysis, data processing and interpretation, and writing (original draft, review, and editing). AM, DB: DMS500 measurements, data analysis. NG: Filter collection and writing (review and editing). MS, RZ, ACN: funding acquisition, conceptualization, supervision, and writing (review and editing).

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

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Acknowledgements. We thank the Bavarian Environment Agency (LfU) and the German Weather Service (DWD) for providing ozone and meteorological data.

Financial support. This project is financed by the Bavarian State Ministry of the Environment and Consumer Protection.

The article processing charges for this open-access publication were covered by the Forschungszentrum Jülich.

Review statement. This paper was edited by Hans Osthoff and reviewed by two anonymous referees.

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Supplement of

Sodium thiosulfate-coated ceramic denuders for ozone removal in ultrafine particle sampling

Elisabeth Eckenberger et al.

Correspondence to: Elisabeth Eckenberger (elisabeth.eckenberger@uni-bayreuth.de) and Anke Christine Nölscher (a.noelscher@fz-juelich.de)

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Figure S1 Photograph of the ceramic honeycomb body (Ø 25,4 x 50mm) used as substrate for Na_2SO_3 coating in this study.

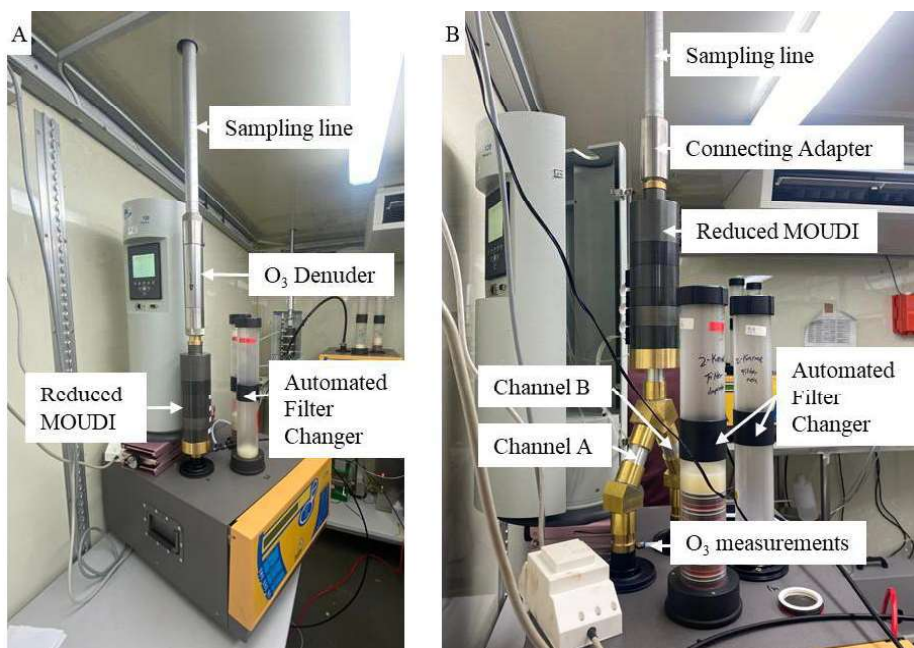


Figure S2 A Picture of one sampling setup, where the TSOD are in a stainless steel housing which is connected above the reduced MOUDI impactor. Such a housing is also used to connect the TSOD from the BATCH to the measurement devices as described in sections 2.2 and 2.3. B Picture of the sampling setup described in section 2.4. The uncoated or coated denuders (depending on the experiment) are behind the MOUDI impactor in channels A and B, directly placed above the UFP filter which was used for analysis.

Table S1: Specifications regarding the different marker compounds that were analyzed and chosen for this study.

Parameter	HPLC-MS neg	HPLC-MS pos	HPLC-FLD
Analytical column	Gemini 5u C18 110A (150 mm x 4.6 mm, 5 µm)	Gemini 5u C18 110A (150 mm x 4.6 mm, 5 µm)	EC 125/4 Nucleosil 100-5 C18 HD (125 mm x 4 mm, 5 µm)
Column temperature	40 °C	30 °C	30 °C
Injection volume	20 µL	20 µL	25 µL
Autosampler temperature	–	–	-5 °C
Flow rate	0.5 mL/min	0.3 - 0.5 mL/min	1 mL/min
Gradient	A) 80% ACN, B) 4 mM HCOOH 0 min 5% A 1 min 5% A 18 min 50% A 21 min 100% A 29 min 100% A 31 min 5% A	A) 80% MeOH, B) 4 mM HCOOH 0 min 50% A 3 min 80% A 12 min 100% A 18 min 90% A 20 min 50% A 25 min 75% A	A) ACN, B) H₂O (Milli-pore) 0 min 60% A 5 min 70% A 8 min 70% A 12 min 80% A 15 min 80% A 19 min 90% A 22 min 60% A
Detector	MSD Time ESI(-)-m/z-ions 0 min 207 8 min 111, 157, 171, 185 18 min 121, 135, 183 25 min 193, 217	MSD Time ESI(+)-m/z-ions 0 min 212, 227, 269 12 min 257, 261, 299	FLD Time λ_{ex} / λ_{em} [nm] 0 min 259 / 386 3.3 min 242 / 388 5.8 min 250 / 370 7.5 min 270 / 390 13 min 290 / 430

Table S2: Specifications regarding the different marker compounds that were analyzed and chosen for this study.

Marker	Method	Recovery	LOD _{Air}	External standard calculation	
			[pg/m ³] 21.6 m ³	Response factor [AU/μg/L]	R ²
POA	HPLC-MS neg	101±6%	268.06	1833	0.98
PA	HPLC-MS neg	84±6%	373.14	4415	0.99
TA	HPLC-MS neg	85±6%,	268.06	3352	0.99
TPA	HPLC-MS neg	96±6%,	343.52	2781	0.99
6PPD	HPLC-MS pos	75±7%	20.09	26766	0.98
6PPDq	HPLC-MS pos	81±7%	24.54	21767	0.99
BaP	HPLC-FLD/UV	78±5%	3.245	10.12	1.00
BbF	HPLC-FLD/UV	74±4%	4.025	12.15	1.00
IcdP	HPLC-FLD/UV	70±4%	3.052	3.29	1.00
Sum Chry BaA	HPLC-FLD/UV	97±5%	2.855	9.68	1.00
BkF	HPLC-FLD/UV	89±6%	2.679	11.80	1.00

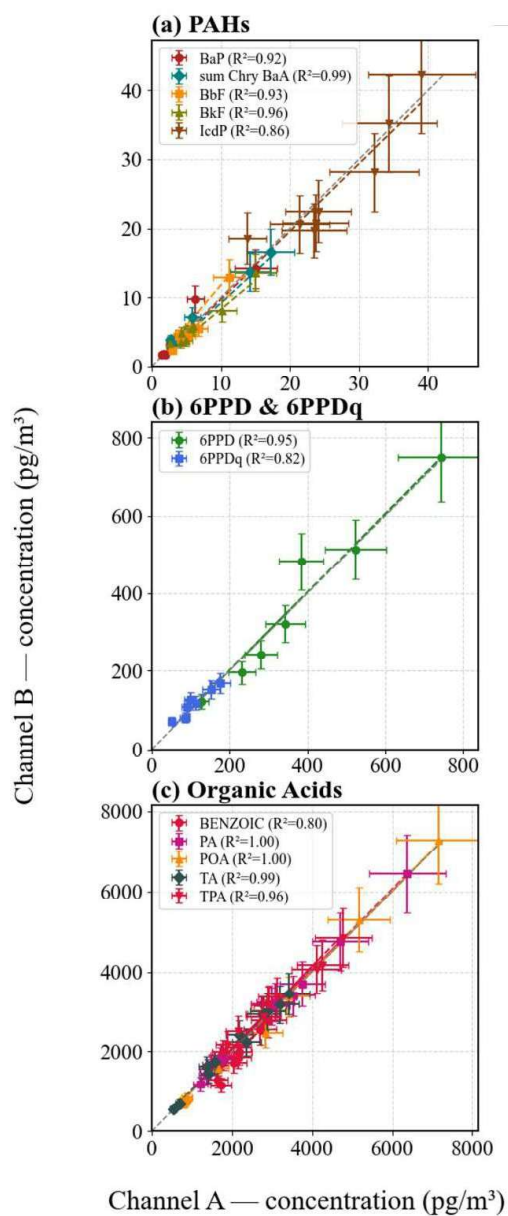


Figure S3 Comparison of PAH concentrations between Channel A and Channel B without the deployment of the TSOD. Regression slopes (s) and coefficients of determination (R^2) indicate high inter-channel agreement in the absence of O_3 removal.

Submitted Article III

Sampling and Chemical Characterization of Ambient Ultrafine Particles using Direct Thermal Desorption GC×GC-MS: A Case Study in Augsburg, Germany

1 Sampling and Chemical Characterization of Ambient Ultrafine 2 Particles using Direct Thermal Desorption GC×GC-MS: A Case Study 3 in Augsburg, Germany

4 Nadine Gawlitta^{1,2*}, Elisabeth Eckenberger³, Martin Sklorz⁵, Jürgen Schnelle-Kreis¹, Josef
5 Cyrys⁶, Anke C. Nölscher^{3,4}, Ralf Zimmermann^{1,5,7*}

6 *Co-corresponding authors: Nadine Gawlitta (nga@plen.ku.dk), Ralf Zimmermann
7 (ralf.zimmermann@uni-rostock.de)

8 ¹Joint Mass Spectrometry Centre (JMSC) at Comprehensive Molecular Analytics, Helmholtz
9 Zentrum München, Neuherberg, Germany

10 ²Now at: Analytical Chemistry Group, Department of Plant and Environmental Science, Faculty
11 of Science, University of Copenhagen, Frederiksberg C, Denmark

12 ³Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth,
13 Germany

14 ⁴Now at: Institute of Climate and Energy Systems, ICE-3: Troposphere, Forschungszentrum
15 Jülich GmbH, Jülich, Germany and Institute of Geophysics and Meteorology, University of
16 Cologne, Cologne, Germany

17 ⁵Joint Mass Spectrometry Centre (JMSC) at Chair of Analytical Chemistry, Institute of
18 Chemistry, University of Rostock, Rostock, Germany

19 ⁶Institute of Epidemiology, Helmholtz Zentrum München, Neuherberg, Germany

20 ⁷Department of Chemistry and Sustainable Technology, Faculty of Science, Forestry and
21 Technology, University of Eastern Finland, Finland

22

23 Abstract

24 Ultrafine particles (UFP) are recognized as emerging air pollutants, yet little is known about
25 their chemical composition. Their high surface area contrasts a low particle mass which
26 challenges current sampling and analysis methods. Herein, we present results from a field
27 study in the city of Augsburg, Germany. We sampled UFP during spring and autumn and
28 utilized direct thermal desorption two-dimensional gas chromatography coupled to time-of-
29 flight mass spectrometry to characterize the organic fraction of UFP. Ten known ubiquitous
30 polycyclic aromatic hydrocarbons (PAHs), including Benz(a)pyrene – as one of the most
31 abundant and cancerogenic PAHs – were targeted and quantified. The day-to-day variability of
32 the mass concentrations of the target PAHs was low during March, while higher variations
33 could be observed in September with concentrations ranging from 50 pg/m³ in the beginning
34 to about 310 pg/m³ at the end of the field study. Physico-chemical characterization of UFP
35 demonstrated no correlation between PM_{2.5}, PM₁₀ and PAH concentrations and only slight
36 correlations with Nitrogen Oxides (NO_x). In contrast, low altitude and low velocity winds seem
37 to accumulate near-ground emitted pollutants, leading to higher detected PAH concentrations.
38 Within a suspect screening approach, different patterns for compound classes such as
39 alkylated PAHs and hopanes between sampling campaigns were identified, e.g., calculated
40 hopane and homohopane indices suggest an influence of household heating emissions in
41 March compared to September. This research gives novel insights into the organic composition

42 of UFP from ambient urban environment influenced by seasonal differences and local
43 emissions.

44

45 **Introduction**

46 Ultrafine particles (UFP) are recognized as emerging air pollutants, yet little is known about
47 their chemical nature and their variability in the atmosphere. Due to their small size with
48 aerodynamic diameters of less than 100 nm, techniques for separating, sampling and analyzing
49 their chemical composition are challenged.^{1–4} In contrast, fine and coarse particulate matter
50 (PM_{2.5} and PM₁₀) are regulated air pollutants and widely monitored.⁵ It has been shown that
51 airborne PM can be composed of a large fraction of organic compounds. Molecular analysis of
52 this organic fraction can highlight the role of sources, the particles' atmospheric history and
53 impact.^{6–11} However, chemical composition or even molecular-level studies of ambient UFP
54 are rare. For this reason, among others, identifying the sources of UFP has proven difficult to
55 date. Therefore, no quantitative guideline values or exposure limits have been published by
56 WHO Global Air Quality Guidelines, highlighting the importance of further research on UFP
57 and their chemical composition.⁵ Some studies conducted on the sub-micron or quasi-
58 ultrafine particles composition cover different characteristic environments, ranging from
59 remote marine to forested to urban regions to hotspots close to airports and harbors.^{12–14}

60 Due to their low diameter and relatively high surface area, UFP can deeply penetrate into the
61 lung and can act as carrier of chemical substances.^{15–17} Das et al. (2024) recently demonstrated
62 the effect of organic chemical loading of UFP on distinct biological effects after cell exposure.
63 Zimmermann et al. (2023) studied the effect of UFP with subsequent allergen exposure and
64 revealed pro-inflammatory and xenobiotic-related responses potentially responsible for
65 adjuvant allergic effects. Moreover, some recent studies associated UFP exposure with adverse
66 health effects.^{20,21} For example, Schwarz et al. (2023) discovered delayed effects for
67 respiratory mortality within 1 week after UFP exposure. In order to understand their
68 environmental and health impact, more studies on UFP are essential.

69 Polycyclic aromatic hydrocarbons (PAHs) are a well-known compound class mainly derived
70 from anthropogenic sources. The US Environmental Protection Agency (EPA) specified 16 PAHs
71 frequently found in environmental samples to be monitored.^{23,24} As higher concentrations of
72 PAHs associated with UFP lead to distinct biological responses¹⁸, it is important to further
73 study the occurrence and determine the concentrations of PAHs found in real-life scenarios,
74 i.e. in ambient air samples. The focus on a few distinct target compounds allows conclusions
75 about their underlying emission, transport and aging in the air. Nevertheless, to gain insights
76 into the overall chemical composition of UFP, non-targeted screening (NTS) can uncover
77 potentially overlooked compounds and compound classes.^{25–28}

78 Herein, we present an approach for the sampling and chemical characterization of UFP in
79 urban air including targeted and non-targeted analytical methods. 10 higher molecular weight
80 PAHs usually bound to particulate matter and therefore associated with UFP were quantified
81 during two sampling periods in March and September 2023. Moreover, a suspect screening
82 approach was applied to compare compound classes including additional unsubstituted and

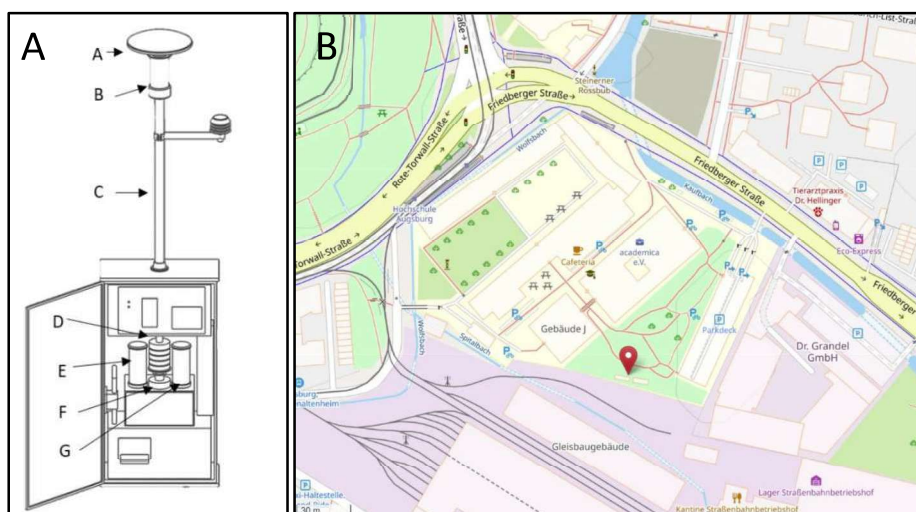
alkylated PAHs and hopanes. This research gives novel insights into the organic composition of UFP from an urban background environment and the impact of seasonality and meteorological conditions.

Methods

Field site and automated sampler

Urban air was sampled on the campus of the University of Applied Sciences in Augsburg approximately 1 km south-east of the city center (48°21'28.7"N 10°54'25.2"E). The sampling site represents an urban background site in the city of Augsburg as displayed by Fig. 1B. Several studies have previously described this sampling site, and more details can be found.²⁹ Within a radius of 100 m, the sampling location is surrounded by campus buildings, a yard, and a small company. Within a 200 m radius, mainly residential areas and a park north-west of the sampling location can be found. The closest main road is 100 m north-east. Samples were collected with a modified low volume sampler (DIGITEL, DPA-14) for two time periods during springtime (24.03. - 29.03.2023) and autumn (14.09. - 26.09.2023). First, air was drawn through a PM₁₀ inlet head and passed over an ozone denuder, consisting of two honeycomb ceramic bodies (25,4 x 50 mm; 400 CPSI, Rauschert) coated with sodium thiosulfate according to Eckenberger et al. (2026). Then, particles were classified with a three-stage cascade impactor (ultra MOUDI, MSP/TSI) with cut-off diameters at 2.5 µm, 1.0 µm, and 0.1 µm which was integrated into the sampling line within the device housing. The impactor's cut-off characteristics were evaluated in advance.⁴ The upper stages of the impactor were equipped with aluminum foils (47 mm, TSI) coated with high vacuum grease to prevent particle bounce effects. For the coating approximately 1 cm of high vacuum grease (Molykote) was dissolved in 20 mL of hexane and evenly applied to the aluminum foils with a syringe. Afterwards the filters were left for evaporation in a fume hood for 24 hours.

Figure 1A: Schematic representation of the unit for separating and sampling UFP from the atmosphere. From top to bottom, the unit consists of a PM₁₀ head as inlet (A), followed directly by a housing



containing ozone denuders (B). The ozone-free sampling air then flows downward through a sampling tube (C), where aerosols are separated into respective size classes using an impactor (D). At the bottom of the impactor, a QFF is positioned, which is automatically replaced every 24 hours. During the filter

112 replacement, the QFF is transferred from the storage housing (on the left side) (E) to the central
113 position (F) directly beneath the impactor, where it is exposed to the sampling air. The particle-laden
114 filter is then moved to the storage column on the right (G), where it remains until maintenance and
115 collection. **Figure 1B:** Sampling location in Augsburg, Germany (Credits: OpenStreetMap).

116 The after-filter holder was omitted, allowing particles smaller than 100 nm to pass through the
117 impactor unit and be collected on quartz fiber filters (47 mm, QFF, Whatman QMA), which
118 were automatically exchanged every 24 hours at midnight. The flow rate was set to 30 L/min,
119 resulting in a sampling volume of 43.2 m³. The filters were pre-heated at 550 °C for 5 hours
120 before use. Post sampling, the filters were stored at -20 °C until further analysis. Once a week,
121 the coated aluminum filters were renewed, the nozzle plates were cleaned, the ozone
122 denuders were replaced, and new QFFs were inserted. Respective field blanks were collected
123 by placing filters inside the sampler without any airflow, directly before and after the collection
124 period. Additionally, we verified that greasing did not impact the chemical analysis of the filter
125 dedicated for UFP-collection.

126

127 **DTD-GC×GC-TOFMS analysis**

128 Targeted and non-targeted analysis of the UFP samples was conducted using direct thermal
129 desorption comprehensive two-dimensional gas chromatography time-of-flight mass
130 spectrometry (DTD-GC×GC-TOFMS, Pegasus BT4D, Leco) according to Gawlitta et al. (2023). An
131 Optic-4 inlet system (GL Sciences) was utilized. For the DTD method a filter punch of 7 mm
132 diameter of each 24 h sample was used for analysis. The aliquot sample corresponded to
133 1.3 m³ of sampled air. 1 µL of deuterated standard solution (ISTD) was applied to the filter
134 sample prior analysis. A non-polar/polar column setup was installed for the GC×GC separation.
135 A pre-column was additionally installed. GC temperature was initially held at 50 °C for 5 min,
136 increased to 150 °C at a rate of 5 °C/min and from 150 °C at a rate of 3 °C/min up to 340 °C.
137 The final temperature was held for 15 min. Transfer line and ion source temperature were set
138 to 300 °C and 250 °C, respectively. Mass acquisition was performed in the range of 29 to
139 600 Da at an acquisition rate of 100 spectra/s. The applied electron energy was 70 eV. Data
140 acquisition and processing was performed using the ChromaTOF software (Version 5.5, Leco).
141 Peak picking was done at a signal-to-noise (S/N) of 50 and classification was conducted by
142 using distinct mass spectral filters. More information on the thermal desorption,
143 chromatographic and classification method can be found in the Supplementary Material (Table
144 S1, S2, S4). Quantification of ten different PAHs was performed by an external calibration of
145 the native equivalent and corrected by the corresponding internal deuterated standards.
146 Calibration curves and a list of the deuterated standards can be found in the Supplementary
147 Material (Table S3).

148

149 **Two-step method evaluation with HPLC-FLD and reference material**

150 For cross-checking the quantitative results of the target PAHs we chose HPLC-FLD, as a second
151 analytical tool, including a soft solvent-based extraction to analyse all samples (See
152 Supplementary Material). We verified the HPLC-FLD method with solid-phase dilutions of NIST

standard reference material (SRM 2786, <4 μ m). The two-step method evaluation was necessary as we could not analyse the NIST SRM with DTD-GC $\times$ GC-TOFMS due to the different matrix and sample handling which was not comparable to the ambient air samples. BaP and BeP, two ubiquitous PAHs, were chosen as target analytes for the method evaluation.

Figure 2A shows the concentrations of BaP and BeP measured by HPLC-FLD compared to the certified concentrations in the NIST standard reference material. In the HPLC-FLD, the two PAHs were not baseline separated and thus their sum Σ (BaP, BeP) is compared. The linear regression between the analysed and expected mass concentrations has a slope of 0.83 ($R^2=0.98$) indicating a slight underestimation, yet within the experimental uncertainty. Furthermore, the comparison between both analytical methods for the ambient UFP samples is shown in Figure 2B where the linear regression of the determined mass concentrations has a slope of 1.02 ($R^2=0.93$).

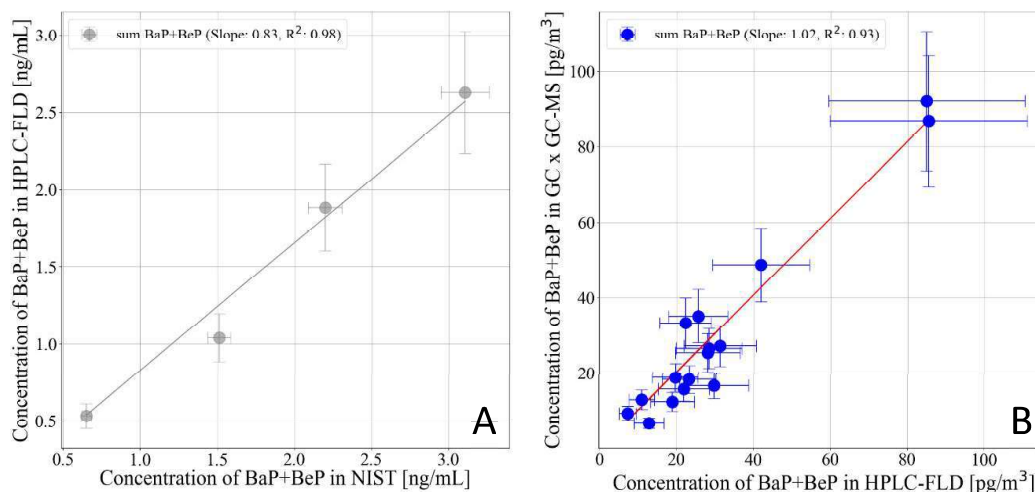


Figure 2: Scatterplot for the two-step method validation with HPLC-FLD and NIST standard reference material. **A:** Concentration of Σ (BaP, BeP) in the NIST standard reference material measured with HPLC-FLD compared to the theoretical values. **B:** Concentration of Σ (BaP, BeP) measured with DTD-GC $\times$ GC-TOFMS and HPLC-FLD.

Additional datasets

To complement the UFP composition analysis, we used additional datasets for meteorological and air quality parameters. For each day, we included the temperature (minimum, maximum, average), solar radiation period, the range of wind directions, average wind velocity, and precipitation as measured by the German Weather Service (Deutscher Wetterdienst, DWD) for Augsburg (Station ID232). Moreover, to understand the overall synoptic situation for the sampling days at a UFP-relevant timescale, we calculated 12-hour backward trajectories with HYSPLIT.^{32–36}

Additionally, the particle number size distribution was measured with a mobility particle size spectrometer (MPSS, SMPS+C 5420, GRIMM and TROPOS- type MPSS Wiedensohler et al., 2012) at the same site. At the air quality site of the Bavarian Environment Agency (Bayerisches

Landesamt für Umwelt (LfU)). LÜB – Messwertarchiv: hourly data, station Augsburg, LfU, 24th to 29th of March and 14th to 25th of September 2023. Accessed 8th of June 2025) particulate matter with maximum diameters of 2.5 µm and 10 µm (PM_{2.5}, PM₁₀) was monitored and the gaseous pollutants nitrogen oxides (NO_x=NO+NO₂) and ozone (O₃). Equivalent black carbon (eBC) was measured with an Aethalometer as absorption at the wavelength 880nm as well as the total particle number concentration with Condensation Particle Counter (CPC).

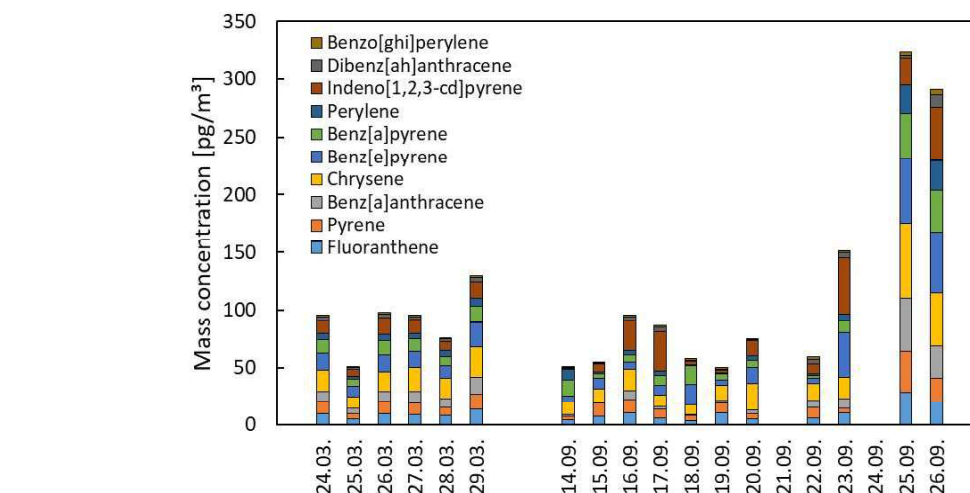
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187

188 Results

189 Air quality and quantification of target PAHs

190 Two sampling campaigns in March and September 2023 were conducted at this site. 10 PAHs associated with the particle phase were quantified in the UFP samples. Figure 3 presents the daily and seasonal variation in mass concentration for the sum (Σ PAH_{Target}) and the 10 individual PAHs. The mass concentrations indicate different trends between and within the sampling periods in March and September.



195 **Figure 3:** Mass concentration [pg/m³] of the 10 different PAHs quantified for each sampling day in
 196 March (24.03.-29.03.2023) and September (14.09.-26.09.2023). No data available on the 21st and 24th
 197 of September due to filter exchange and invalid data analysis, respectively. The concentration
 198 calculated for chrysene could be influenced by the closely eluting triphenylene which was not baseline
 199 separated.

200 In March, the average mass concentration of the Σ PAH_{Target} was about 90 pg/m³ and the
 201 relative contributions of the individual PAHs were comparable between sampling days (see SI
 202 Table S5). The most abundant PAH was chrysene with 11-26 pg/m³ accounting for about 20 %
 203 of the total mass determined for all quantified PAHs. In comparison, BaP accounted for about
 204 12 % ranging from 6 to 15 pg/m³ in Augsburg springtime UFP. The least abundant PAH during
 205 this measurement period was benzo[ghi]perylene with 1-2 pg/m³. Figure 4 demonstrates the
 206 corresponding meteorological and air quality data. An average temperature of 6.6 °C (daily
 207 averages: 2-11 °C) was recorded and it was rainy on five out of six sampling days. The prevailing

208 wind direction was southwest during the first three days, turning northwest to southeast for
 209 the last three days. Overall, lowest mass concentrations of PAH were observed on 25.03.,
 210 which was the day with highest wind speeds of about 7 m/s (compared to average wind speed
 211 of 5 m/s). Most air pollutants had low concentrations such as nitrogen oxides
 212 ($\text{NO}_{x\text{ave}}=10\pm 8\text{ }\mu\text{g}/\text{m}^3$, reported as average $\pm$ standard deviation of half-hourly values),
 213 equivalent black carbon ($\text{eBC}_{\text{ave}}=410\pm 270\text{ ng}/\text{m}^3$) and fine particulate matter (e.g.,
 214 $\text{PM}_{2.5\text{ave}}=3\pm 2\text{ }\mu\text{g}/\text{m}^3$). Interestingly, O_3 concentrations were high with an average of
 215 $53\pm 22\text{ }\mu\text{g}/\text{m}^3$ during the entire measurement period (Figure 4).

216 In September, our data seems to fall into two characteristic periods. While the summed mass
 217 concentration of all quantified PAHs remained below $150\text{ pg}/\text{m}^3$ (average $76\text{ pg}/\text{m}^3$) for the
 218 beginning of the measurement period, it increased to about $310\text{ pg}/\text{m}^3$ on September 25th and
 219 26th. This equals a rise of about a factor of ~ 4 . The rise was most pronounced for BeP and BaP
 220 with mass concentrations increasing from 12 and $8\text{ pg}/\text{m}^3$ to 54 and $38\text{ pg}/\text{m}^3$ (by a factor of
 221 ~ 4.5), respectively. The weather in September was sunny and warm with daily average
 222 temperatures of 16 to $27.5\text{ }^\circ\text{C}$. It rained on three days: September 18th (3.6 mm), 21st (3.5 mm),
 223 and 22nd (7.9 mm). The daily average wind velocity remained below 4 m/s. On September 25th
 224 and 26th it was below 2.5 m/s and mostly from the northeast. Yet, wind directions varied from
 225 southwest to northeast during the entire sampling period. Parallel to the increase of PAHs in
 226 UFP, a rise in other air pollutants can be observed. Most pronounced was an average increase
 227 in NO by a factor of ~ 5.2 from the first measurement days in September to September 25th and
 228 26th. Whereas PM_{10} , $\text{PM}_{2.5}$ and eBC increased by a factor of 1.3, 1.4, and 2.2, respectively.
 229 Interestingly, the total particle number concentration (PNC) only increased by a factor of 1.1.

230 Based on the significant differences in $\Sigma\text{PAH}_{\text{Target}}$ mass concentrations, we decided to divide
 231 the sampling campaigns into three distinct periods for the following discussions: March
 232 (24.03.2023-29.03.2023), Sep-1 (14.09.2023-23.09.2023), and Sep-2 (25.09.2023-
 233 26.09.2023). Figure S2 summarizes the average particle size distributions as measured by
 234 MPSS during these three periods. In March, the maximum PNC peaked between 20 and 30 nm,
 235 while in September the maximum mode was between 70 and 90 nm. Moreover, computing
 236 12-hour backward trajectories (see Figure S1) for all three periods showed the influence from
 237 air masses moving from central France, so from westerly directions to our sampling site for
 238 March and Sep-1. However, we can observe two exceptions: (1) Backward trajectories ending
 239 00:00 on 21.09.2023 (corresponding to sample 20.09. during Sep-1) are shorter and from both
 240 westerly and easterly directions. (2) Backward trajectories ending 25.09.2023 to 27.09.2023
 241 (corresponding to samples 24.09./25.09./26.09. during Sep-2) being even shorter, lower and
 242 arriving mostly from easterly directions. For the 26th of September, the air masses took 12 h
 243 to travel from Munich to Augsburg (about 50 km) staying at low altitudes (below 500 m AGL)
 244 close to the surface and thus passed very slowly over the region.

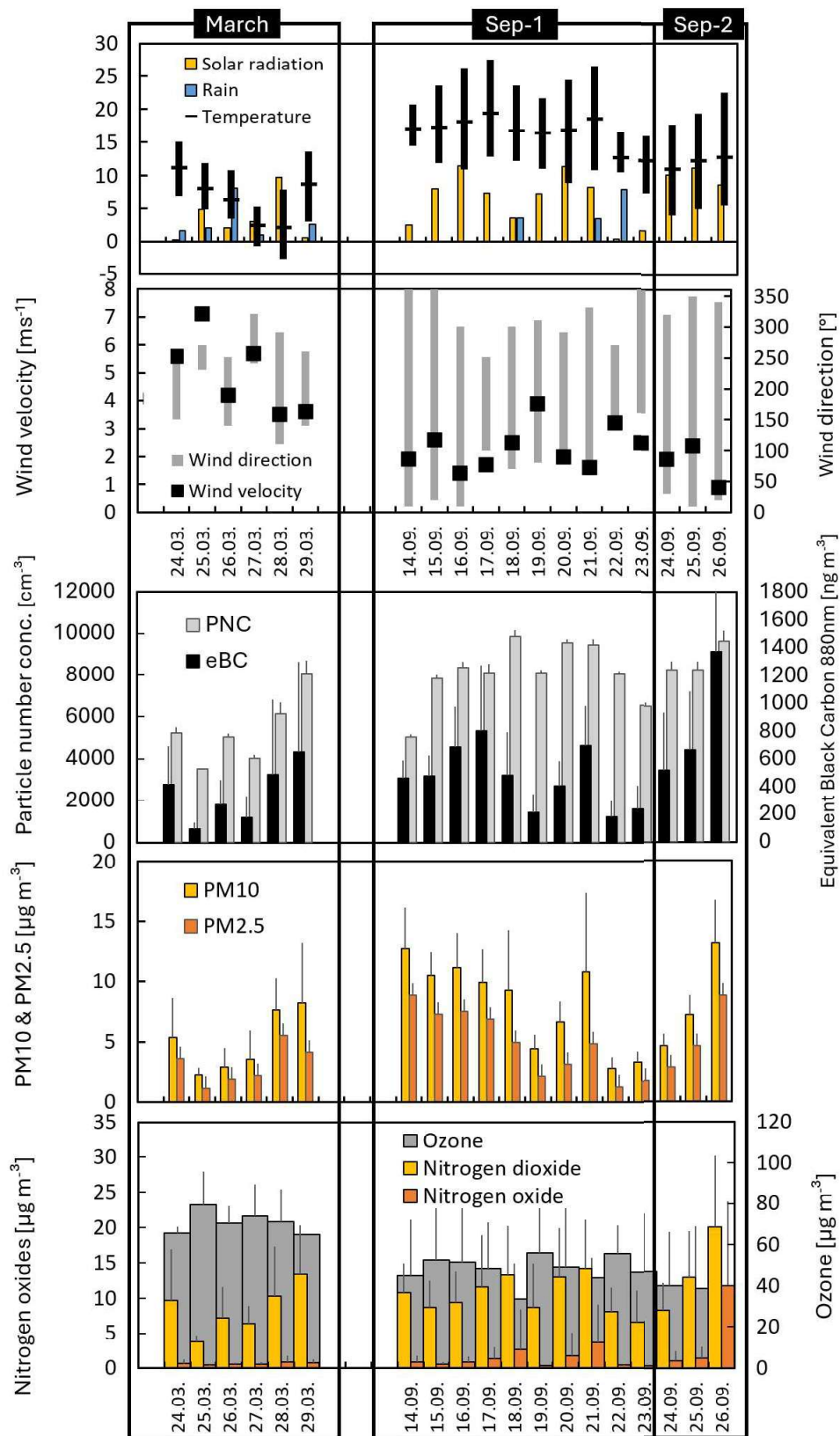


Figure 4: Characterization of air quality and weather data during the sampling periods. From left to right sampling days in March and September 2023 with a gap between the two main sampling periods and boxes highlighting the three characteristic periods (March, Sep-1 and Sep-2). From top to bottom: (1) temperature with daily minimum, average and maximum, solar radiation period in hours per day and rain per day in mm, (2) wind velocity and wind direction, (3) particle number concentration (PNC) and equivalent black carbon (eBC) as measured from absorption at 800nm with Aethelometer, (4) particulate matter PM10 and PM2.5, (5) ozone, nitrogen oxide and nitrogen dioxide. The error bars represent the relative standard deviation.

254

255 Suspect screening and classification

256 In order to identify other potentially important anthropogenic organic compounds associated
257 with UFP we screened for suspects expected in ambient air and grouped them according to
258 their chemical class. A two-dimensional chromatogram of one of the sampling days is
259 exemplified in Figure 5A. Each green dot represents a peak and thus an organic molecule
260 present in the sample. Volatile organic compounds (VOCs) elute first and can be found at low
261 retention times (RT < 3500 s). However, VOCs are barely adsorbed on particles but found in
262 the gas phase. As the gas phase was not stripped off before filter sampling, these compounds
263 likely reflect the equilibrium between gas- and particle-phase shortly before the end of the
264 sampling and are thus not representative for the entire sampling period. As the
265 characterization of these compounds is beyond the scope of this paper, they were not
266 evaluated. The second half of the chromatogram (RT > 3500 s) displays less volatile, mostly
267 particle-bound compounds, which are characteristic for the chemical composition of UFP. In
268 the total ion chromatogram (TIC, Figure 5A, top panel) mostly highly abundant peaks of alkanes
269 and alkenes can be seen. Using the base ion of

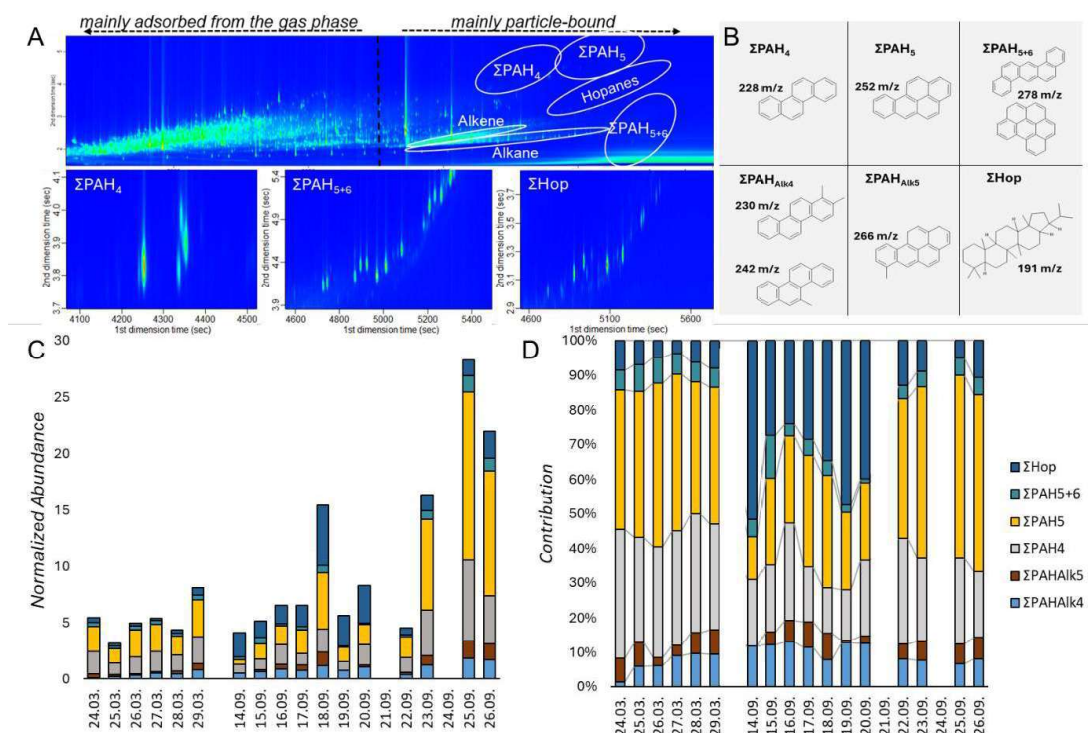


Figure 5. A: Example of a GC×GC-MS chromatogram of an ambient air UFP sample for a deeper analysis of particle-bound non-target analytes. Top: Example of a TIC of a GC×GC chromatogram. Bottom: Distinct compound classes and their EICs from left to right: ΣPAH_4 (m/z 226), ΣPAH_6 (m/z 278), ΣHop (m/z 191). **B:** Possible structural formula exemplified for each compound class and the EIC used for intensities. **C:** Normalized intensities of each compound class to the abundance of the internal standard BeP-d12 within each measurement. **D:** Relative contribution of the compound class based on the classified groups.

known air pollutants enables the filtering of the two-dimensional chromatogram for different chemical classes. Figure 5A, lower panel, exemplifies the zoomed two-dimensional chromatogram filtered for unsubstituted 4-ring PAHs (ΣPAH_4 , 226 m/z), 6-ring-PAHs (ΣPAH_6 , 278 m/z) and hopanes (ΣHop , 191 m/z).

In Figure 5B the different classes and their corresponding EICs are summarized, and possible structural formulas are exemplified for every class. These classes expand the list of the 10 target PAHs previously quantified to other unsubstituted PAHs with different ring number as well as alkylated PAHs and hopanes. For the comparison of the normalized absolute abundance of each compound class, we find relatively comparable values of all classes in March (Figure 5C). PAHs are comparable for March and Sep-1, while hopane intensities are higher in Sep-1. In contrast, Sep-2 shows increased levels of PAHs, especially, unsubstituted 5-ring PAHs (ΣPAH_5) followed by unsubstituted 4-ring PAHs (ΣPAH_4). This aligns with the results of $\Sigma\text{PAH}_{\text{Target}}$ for which BaP, BeP and chrysene concentrations increased at a factor of 3.4 and 4.2 compared to March and Sep-1, respectively, corresponding to ΣPAH_5 and ΣPAH_4 . While Sep-2 is recognized by an intense increase in PAHs, Sep-1 is characterized by highly abundant ΣHop (Figure 5C). In contrast to the high increase in abundance for Sep-2, the overall relative contribution is comparable to March, while the relative contribution of hopanes is significantly higher in Sep-1 (Figure 5D).

The comparison of different sampling days is unaffected and shows that, besides the high contribution of hopanes in Sep-1, we can also observe a pattern change from Sep-1 to Sep-2, already starting at the 22nd of September. While the pattern aligns well with the following days of Sep-2, the PAH concentration on this day (22nd of September) stays comparably low. An increase in PAH concentration can only be observed from the 23rd of September onwards (Figure 5D). While the contribution of alkylated 4- and 5-ring PAHs ($\Sigma\text{PAH}_{\text{Alk4}}$, $\Sigma\text{PAH}_{\text{Alk5}}$) were relative comparable between March, Sep-1 and Sep-2 (except for 24th of March with low contributions of $\Sigma\text{PAH}_{\text{Alk4}}$), the absolute intensities of $\Sigma\text{PAH}_{\text{Alk4}}$ and $\Sigma\text{PAH}_{\text{Alk5}}$ increased by a factor of 4.7 and 2.8 compared to March and Sep-1.

Hopanes are constituents of fossil fuels, i.e. coal, petroleum and lubrication oil, and can be used as molecular markers for source identification.⁷ Table 1 summarizes the 10 most abundant hopanes and their commonly used abbreviations identified in the samples from March and September. Their elution pattern in the GC×GC chromatogram is shown in Figure S3. Ratios of specific hopanoids can be utilized to indicate different source contributions.³⁸

Table 1: Summary of the most abundant hopanes detected and identified in all samples from March and September. Figure S3 shows their elution pattern in the GC×GC chromatogram.

Peak	Abbreviation	Compound
------	--------------	----------

1	Ts	17 α (H)-22,29,30-trisnorhopane
2	Tm	17 β (H)-22,29,30-trisnorhopane
3	27b	17 α (H),21 β (H)-30-norhopane
4	29ab	17 β (H),21 α (H)-30-norhopane
5	30ab	17 α (H),21 β (H)-hopane
6	30ba	17 β (H),21 α (H)-hopane
7	31abS	22S-17 α (H),21 β (H)-homohopane
8	31abR	22R-17 β (H),21 α (H)-homohopane
9	32abS	22S-17 α (H),21 β (H)-bishomohopane
10	32abR	22R-17 β (H),21 α (H)-bishomohopane

312

313 Table 2 summarizes the hopane and homohopane index, two strong indicators for source
314 contributions, and the ratio of Ts/Tm as a weaker index. The comparison of the different
315 sampling periods March, Sep-1 and Sep-2 shows that the hopane index is >0.9 for Sep-1 and
316 Sep-2 but below 0.9 for March.

317 *Table 2: Hopane, homohopane and Ts/Tm indices were calculated for the three sampling periods*
318 *(March, Sep-1, Sep-2). The hopane and homohopane indices are lower for March compared to Sep-1*
319 *and Sep-2. *One sample shows a significantly lower Ts/Tm value (0.89) compared to the other samples*
320 *of Sep-1 (Ts/Tm: 1.20-1.60).*

	Hopane index 30ab/(30ab+30ba)	Homohopane index 31abS/(31abS+31abR)	Ts/Tm index
March	0.81-0.89	0.18-0.39	0.92-1.17
Sep-1	0.90-0.99	0.46-0.60	0.89*-1.60
Sep-2	0.92-0.99	0.51-0.53	1.19-1.25

321

322 Moreover, the homohopane index ranges from about 0.2 to 0.4 for March, while it is 0.4 to 0.6
323 for Sep-1 and ~0.5 for Sep-2. The Ts/Tm index ranges from 0.9 to 1.2 for March, 0.9 to 1.6 for
324 Sep-1 and 1.2 to 1.3 for Sep-2 and is therefore overlapping for March and Sep-1. This can
325 mainly be explained by one sample of Sep-1 for which a ratio of 0.89 is calculated. If this sample
326 was excluded the range could clearly be differentiated from March as the next lowest sample
327 value is 1.2.

328 Discussion

329 In our study, we demonstrated a sufficient way of sampling ambient UFP for a longer time
330 frame by an automated daily exchange of filters, weekly collection of samples, preparation of
331 impaction plates and cleaning of nozzle plates. The use of DTD-GC×GC-TOFMS enabled the
332 direct volatilization of UFP-associated semi-volatile organic compounds and the quantification
333 of 10 target PAHs in the pg/m³ range. This target analysis revealed that environmental
334 conditions have a substantial impact on the composition of ambient UFP. Moreover, the
335 variation of PAH mass concentration was higher within September compared to March
336 emphasizing a higher daily variation in comparison to seasonal variances.

337 Interestingly, the concentration of air pollutants varied for different analyzed compound
338 classes within average sunny autumn days, i.e., between Sep-1 and Sep-2. PAH mass
339 concentrations in ambient UFP were elevated by a factor of 3.5 while hopanes were reduced
340 by a factor of 0.5 from Sep-1 to Sep-2. Other physico-chemical aerosol properties such as
341 concentrations of NO, eBC and PM_{2.5} increased from Sep-1 to Sep-2 by a factor of 5.2, 2.2 and
342 1.4, respectively.

343

344 Moreover, slow moving, low altitude airmasses from East characterized the period of Sep-2,
345 supporting the hypothesis that different local and regional sources dominated the organic
346 fingerprint of the analyzed UFP. Different sources, i.e. traffic (fresh and aged), nucleation and
347 aged secondary particles, stationary combustion, re-suspension, and long-range transport,
348 have previously been highlighted to impact particle number size distribution.^{39,40} Among
349 those, traffic and combustion emissions were dominated by UFP. PAHs are established
350 indicators for incomplete combustion⁴¹ and hopanes serve as tracers for petroleum-derived
351 lubrication oil in vehicle emissions.^{42–44} Here, we found that these compounds significantly
352 shape the observed UFP chemical fingerprint, with their relative contributions varying
353 according to prevalent source strength and environmental conditions.^{45,46}

354

355 Within our sampling campaigns, especially wind characteristics, such as velocity, altitude of
356 traveling air masses and direction, seem to highly impact UFP composition. The dominant wind
357 direction at our sampling site originates from southwest. The nearest busy road in this direction
358 is about 170 meters away, while the road closest to the sampling site is located about 100
359 meters to the northeast as further described in Cyrus et al. (2008).²⁹ While the wind is mainly
360 coming from southwest during our sampling campaign in March, and Sep-1, the wind direction
361 changes to northeast in Sep-2. Thus, likely the wind slowly passing the main road and
362 transporting traffic emissions to the site, leads to high PAHs concentrations in the sampled
363 UFP. Moreover, we observe an increase in NO_x at the same time, especially for the last sampling
364 day of Sep-2 underlining the previous assumption. The comparison of 12 h backward
365 trajectories (Figure S1) demonstrate low altitude and low velocity wind from Eastern direction
366 for Sep-2. Together with the exceptionally low wind speeds (< 1 m/s) and the warm, sunny
367 conditions (up to 27.5 °C), these stagnant conditions likely limited atmospheric dispersion and
368 promoted local accumulation of freshly emitted PAHs. This interpretation is consistent with Li
369 et al. (2018), who showed that reduced vertical mixing hampers dilution and is associated with
370 elevated PAH and other organic tracer concentrations. The concurrent increase in traffic-
371 related tracers (e.g., NO/NO₂) and a BaP/BeP ratio of ~1.4 further support a strong influence
372 of fresh, locally emitted aerosol with limited photochemical aging.⁴⁷ Notably, the near-stable
373 total particle number concentration (TPNC) suggests PAH enrichment on an existing particle
374 population and/or a shift toward PAH-rich emissions under limited dispersion rather than a
375 proportional increase in particle number. This period is as previously mentioned accordingly
376 characterized by high concentrations of PAHs, especially Chrysene, BaP and BeP, and it thus
377 seems that not only the local main road, but also other local emissions (highway, urban
378 background from the Munich area) impact the high concentrations of PAHs within Sep-2.
379 Overall, near-ground emitted pollutants like PAHs were accumulated by low altitude

trajectories with low wind velocities from east underlining the high impact of meteorological conditions on the composition of UFP.

Although lower average temperatures (5-15 °C) were measured in March, the PAH concentrations are comparable to Sep-1, underlining the greater impact of local sources compared to seasonal influences. Moreover, the negative correlation of higher temperature as found in September (11-20 °C, daily averages) might be equalized by lower O₃ levels in Sep-1 compared to March resulting in similar PAH concentrations for these two sampling periods. NO concentrations were comparable between all sampling periods but on average slightly lower for March, while NO₂ concentrations were on average higher in September with the highest concentration (20 µg/m³) on the 26th of September which also showed highest PAH concentrations, suggesting a potential correlation between NO₂ and PAH pointing towards fresh vehicle emissions as main source as described by Li et al. (2018). No difference in PNC between Sep-1 and Sep-2 but an increase in eBC can be observed for the last day of Sep-2. PM_{2.5} and PM₁₀ mass concentrations were on average lower in March compared to Sep-1 and Sep-2 and could not be correlated with PAH or hopane concentrations, demonstrating a weak correlation potential of PM_{2.5} and PM₁₀ with pollutant concentrations in the UFP fraction.

Hopanes are mainly found in particles smaller 0.49 µm rather than in larger sizes in urban and rural sites and over 96 % is attributed to the quasi-UFP mode (PM_{0.25}).⁴⁹ The ratio of different hopanoids can be utilized to identify their emission sources. The two main ratios are the hopane and homohopane index. The ratio of Ts to Tm hopane can additionally be used as source indicator but is a rather weak index compared to hopane and homohopane indices. Higher hopane, homohopane and Ts/Tm indices indicate higher contributions from lubrication oil, i.e. traffic related emissions. In Sep-1 and Sep-2 the hopane index was > 0.9 and the homohopane index was about 0.6. This indicates that vehicle emissions are the main source of the UFP associated hopanes. In contrast, in March the hopane index and the homohopane index were <0.9 and max. 0.4, respectively. Therefore, the contribution of an additional emission source of hopanes in March is expected. As the average temperatures in March were between 2 and 11 °C (Figure 3), it is likely that private households were heating during the sampling period. Residential heating with brown coal is still common in this part of Germany, likely explaining the difference in hopane pattern from March to September. Interestingly, absolute intensities are lower for March compared to September although we identified an additional source contributing to hopanes in the UFP fraction. In particular, the intensities in Sep-1 are comparably high. Li et al. (2018) used PMF analysis for source attribution of PM_{0.36} based on two hopanes (29ab and 30ab) at the same reference site and concluded that 92 % of hopanes could be linked to traffic. Moreover, traffic and traffic-related particles are mainly found in the UFP fraction, while coal-burning emissions likely also be found in larger size fractions. Size-resolved studies have consistently shown that while lower molecular weight PAHs can be found on ultrafine particles, the less volatile, higher molecular weight species, which are typically associated with residential solid fuel combustion, are predominantly enriched in the accumulation mode.^{46,50} Consistent with these findings, Schladitz et al. (2015) observed the highest concentrations of these PAHs in the accumulation mode during the heating period, attributed to residential wood and coal combustion.

423 However, the absolute contribution of hopanes to the UFP fraction appears to be low. For Sep-
424 1 the absolute and relative contributions of hopanes are higher than in Sep-2 contrasting the
425 results from increased PAH concentrations, particularly ΣPAH_5 , in Sep-2. As for Sep-2, the local
426 traffic seems to impact hopanes and PAH in UFP, we must consider additional sources of
427 hopanes in Sep-1.

428

429 The concentrations of hopanes and PAHs are more comparable between sampling days in
430 March while the concentrations and composition in Sep-1 varies daily. The lowest PAH
431 concentration was observed on March 25th, a rainy day with generally low concentrations of
432 air pollutants (see Figure 3), yet elevated O_3 . It is likely that local emissions got washed-out
433 and cleaner, rather aged air from higher altitudes mixed in. Contrastingly, Sep-1 was
434 characterized by comparably higher temperatures and sunny days, yet the PAH concentrations
435 in UFP did not significantly differ from March. Therefore, seasonal variations appear to be
436 lower than expected due to a complex interplay of different environmental conditions and
437 local sources.

438

439 Although meteorological conditions depend on the season, the daily variance of wind direction
440 and speed and thus the impact of local sources on the UFP composition seems to be
441 comparably higher than the influence of seasonality. Li et al (2018) came to a similar conclusion
442 when they attributed $\text{PM}_{0.36}$ composition to traffic sources, demonstrating that their
443 contribution was not only affected by the traffic load but also wind direction and wind speed
444 at the sampling site. Moreover, they advised to not conclude chemical variability and
445 consequently health-related effects of exposure studies solely on PNC. Our study can underline
446 this conclusion as high chemical variability could hardly be correlated to any physico-chemical
447 parameters but was rather dependent on local point sources influenced by wind direction,
448 velocity and altitude.

449 Conclusion

450 Within this work, we automatically sampled airborne UFP for two measurement periods in
451 spring and autumn. Within the sampled UFP mass, we quantified 10 of the 16 EPA PAHs using
452 DTD-GC $\times$ GC-TOFMS. Our quantification approach was validated with HPLC-FLD and NIST
453 standard reference material. The mass concentrations of the 10 quantified PAHs varied
454 between 76 and 307 pg/m^3 in March and September 2023. Using a suspect screening
455 approach, we compared the composition of other PAH classes and hopanes between the
456 different sampling periods. We found only slight differences in PAH and hopane intensities
457 between spring and autumn, but high variability within autumn (Sep-1 and Sep-2). Therefore,
458 our study confirmed a low effect of seasonality on traffic-related emissions for UFP as
459 previously demonstrated for $\text{PM}_{0.36}$ at the same sampling site. Although we identified the
460 contribution of residential heating as source of hopanes in spring, their intensities stayed
461 comparably low, suggests the main contribution of hopanes in the UFP-fraction results from
462 traffic emissions. The comparison of chemical composition and physico-chemical properties
463 revealed no significant correlation of $\text{PM}_{2.5}$, PM_{10} and BC and only weak correlations of NO_x ,
464 PNC and particle size distribution with PAH concentrations. Moreover, the effects of
465 meteorological conditions such as O_3 , temperature and solar radiation seem to have negligible

466 effects on PAH concentrations in the UFP fraction. In contrast, low altitude and low velocity
467 winds from northeast direction seem to strongly impact the composition of UFP by
468 accumulating near-ground emitted pollutants, e.g. PAHs, from local sources.

469 To our knowledge, this is the first time, ambient UFP are representatively sampled daily and
470 comprehensively characterized over a period of more than two weeks. Moreover, the link to
471 weather conditions and air quality parameters provided novel insights on the composition and
472 pattern of airborne UFP, mirroring the interplay of sources, atmospheric mixing and transport
473 process, driving their potential impact on human health and the environment. Future studies
474 should focus on sampling and analysis of UFP for longer timeframes and at different urban and
475 rural environments as the local signature can be highly variable. Therefore, general
476 assumptions regarding the health and environmental impact of UFP cannot be made without
477 extensive field studies and comprehensive chemical characterization.

478

479 **Limitations**

480 Due to the limited number of samples for only two different seasons general conclusions based
481 on seasonal influences are hampered. Nevertheless, the comparison of our study to literature
482 confirms previously identified trends for PM_{0.36}. To gain further insights into the seasonal
483 impact on UFP composition longer sampling periods during all seasons are required. Although
484 10 high molecular weight PAHs were targeted and the list of suspects was expanded to other
485 (alkylated) PAHs and hopanes, the use of derivatization for GC-MS or the use of HPLC for other
486 atmospheric marker compounds including more polar species could expand the possibility to
487 identify contributions of other sources. The classification of hopanes based on their base ion
488 (191 m/z) lead to an underestimation compared to PAHs due to their stronger fragmentation
489 pattern. Therefore, the relative contributions of hopanes compared to PAH within one
490 sampling day should be considered with care.

491

492 **Funding**

493 This project was financed by the Bavarian State Ministry of the Environment and Consumer
494 Protection.

495

496 **Author contributions**

497 Nadine Gawlitta: UFP sampling, GC×GC-MS analysis, data analysis and curation,
498 conceptualization, writing – original draft, writing (review and editing)

499 Elisabeth Eckenberger: development and deployment of the automated UFP sampling device,
500 HPLC-FLD measurements, writing (draft, review and editing)

501 Martin Sklorz: Conceptualization, writing (review and editing)

502 Jürgen Schnelle-Kreis: Supervision, conceptualization, data curation (HYSPLIT modeling),
503 writing (review and editing)

504 Josef Cyrus: Data analysis (MPSS), writing (review and editing)

505 Anke C. Nölscher: Resources, Funding Acquisition, Project administration, Conceptualization,
506 data curation, writing – original draft, writing (review and editing)

507 Ralf Zimmermann: Resources, Funding Acquisition, Project administration, Conceptualization,
508 writing (review and editing)

509

510 **Conflicts of interest**

511 The authors declare that they have no known competing financial interests or personal
512 relationships that could have inappropriately influenced this work.

513

514 **Data availability**

515 Data will be made available on reasonable request.

516

517 **Acknowledgments**

518 The authors would like to acknowledge Sandra Piel and Thomas Gröger for the support of the
519 GC×GC-MS analysis and Ramona Brejcha for her support during the sampling campaign. We
520 would also like to greatly acknowledge the Bavarian Environment Agency, in particular Dr.-Ing.
521 Adam Mühlbauer, for providing physico-chemical data. We would further like to thank Susanne
522 Sues and Simonas Kecorius for the collection of MPSS data. We would also like to acknowledge
523 the DWD for providing meteorological data.

524

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653

Supplementary Material

Sampling and Chemical Characterization of Ambient Ultrafine Particles using Direct Thermal Desorption GC×GC-MS: A Case Study in Augsburg, Germany

Nadine Gawlitta^{1,2*}, Elisabeth Eckenberger³, Martin Sklorz⁵, Jürgen Schnelle-Kreis¹, Josef Cyrus⁶, Anke C. Nölscher^{3,4}, Ralf Zimmermann^{1,5,7*}

*Co-corresponding authors: Nadine Gawlitta (nga@plen.ku.dk), Ralf Zimmermann (ralf.zimmermann@uni-rostock.de)

¹Joint Mass Spectrometry Centre (JMSC) at Comprehensive Molecular Analytics, Helmholtz Zentrum München, Neuherberg, Germany

²Now at: Analytical Chemistry Group, Department of Plant and Environmental Science, Faculty of Science, University of Copenhagen, Frederiksberg C, Denmark

³Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Germany

⁴Now at: Institute of Climate and Energy Systems, ICE-3: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany and Institute of Geophysics and Meteorology, University of Cologne, Cologne, Germany

⁵Joint Mass Spectrometry Centre (JMSC) at Chair of Analytical Chemistry, Institute of Chemistry, University of Rostock, Rostock, Germany

⁶Institute of Epidemiology, Helmholtz Zentrum München, Neuherberg, Germany

⁷Department of Chemistry and Sustainable Technology, Faculty of Science, Forestry and Technology, University of Eastern Finland, Finland

For thermal desorption, QFFs were cut by defined punches (7 mm Ø) and placed into glass inserts for the direct thermal desorption unit for analysis. These glass inserts were deactivated with trimethylchlorosilane (TMCS, Fisher Scientific, Germany) prior use. The reader is referred to Gawlitta et al. (2023) for more detailed information on thermal desorption. The chromatographic column setup is summarized in Table S1.

Table S1: Details on the column setup.

	<i>Phase</i>	<i>Length (m)</i>	<i>Inner Diameter (μm)</i>	<i>Film Thickness (μm)</i>	<i>Company</i>
<i>Pre-column</i>	BPX5	1.3	250	0.25	SGE, Australia
<i>GC Oven</i>	BPX5	60.0	250	0.25	SGE, Australia
<i>Secondary Oven</i>	BPX50	1.6	100	0.1	SGE, Australia
<i>Transfer line</i>	Deactivated	0.6	100	0.1	SGE, Australia

The modulation time for the second-dimension separation was 4 s with a hot pulse time of 1.2 s and a cold pulse time of 0.8 s. The second-dimension oven temperature was ramped according to the GC oven temperature program with a relative offset of 5 °C. The modulator temperature was ramped accordingly but with an offset of 15 °C relative to the second-dimension oven temperature. The temperature program of the first, second and modulator oven were kept to a maximum of 340 °C.

Table S2: Summary of the quantifier ions selected for the quantification of target PAHs. Every native target was “corrected” by its respective deuterated internal standard.

	<i>Quantifier (m/z)</i>
<i>Fluoranthene</i>	202
<i>Fluoranthene-d10</i>	212
<i>Pyrene</i>	202
<i>Pyrene-d10</i>	212
<i>Benz[a]anthracene</i>	228
<i>Benz[a]anthracene-d12</i>	240
<i>Chrysene</i>	228
<i>Chrysene-d12</i>	240
<i>Benz[e]pyrene</i>	252
<i>Benz[e]pyrene-d12</i>	264
<i>Benz[a]pyrene</i>	252
<i>Benz[a]pyrene-d12</i>	264
<i>Perylene</i>	252
<i>Perylene-d12</i>	264
<i>Indeno[1,2,3-cd]pyrene</i>	276
<i>Indeno[1,2,3-cd]pyrene-d12</i>	288
<i>Dibenz[ah]anthracene</i>	278
<i>Dibenz[ah]anthracene-d14</i>	292
<i>Benzo[ghi]perylene</i>	276
<i>Benzo[ghi]perylene-d12</i>	288

For the external calibration, 1 µL of standard solution of native PAHs and 1 µL of deuterated PAHs summarized in Table S2 were applied to desorbed QFF in four concentration ranges. The concentration range in pg/m³ can be found in Table S3. Native standard responses were corrected by their equivalent deuterated standard response. Every concentration step was measured in triplicates. The four concentration steps and the applied calibration curve including its linearity expressed as R² are summarized in Table S3. The quantification of each target PAH was based on their respective quantifier ion and corrected by the quantifier ion of the corresponding standard as summarized in Table S2.

Table S3: Concentration range in pg/m³ of calibration curve for quantification of target PAHs by external calibration.

<i>PAH</i>	<i>Concentration range of calibration curve [pg/m³]</i>				<i>Response, R2</i>
<i>Fluoranthene</i>	2.5	8.2	33	57	y=0.0568x, 0.999
<i>Pyrene</i>	2.5	8.3	33	58	y=0.0379x, 0.999
<i>Benz[a]anthracene</i>	2.4	7.8	31	55	y=0.0254x, 0.982
<i>Chrysene</i>	2.5	8.4	33	59	y=0.0273x, 0.997
<i>Benz[e]pyrene</i>	2.8	9.4	38	66	y=0.0245x, 0.999
<i>Benz[a]pyrene</i>	2.5	8.5	34	59	y=0.0721x, 0.999
<i>Perylene</i>	2.5	8.1	32	57	y=0.0237x, 0.999
<i>Indeno[1,2,3-cd]pyrene</i>	2.4	7.9	32	55	y=0.0446x, 0.998
<i>Dibenz[ah]anthracene</i>	2.3	7.7	31	54	y=0.026x, 0.999
<i>Benzo[ghi]perylene</i>	1.6	5.4	21	38	y=0.2054x, 0.997

Table S4: Summary of compound classes, the applied mass filter and the quantifier ion for the chosen compounds based on these mass filters within a distinct chromatographic space. The abundance of each compound class was normalized to the internal standard BeP-d12 within every measurement.

Compound class	Mass filter based on ion abundance	“Quantifier ion” (m/z)
$\Sigma\text{PAH}_{\text{Alk4}}$	m/z 230.2 $\pm$ 0.2 Da > m/z 115.1 $\pm$ 0.2 Da AND m/z 230.2 $\pm$ 0.2 Da > 950	230
	m/z 242.2 $\pm$ 0.2 Da > m/z 121.1 $\pm$ 0.2 Da AND m/z 242.2 $\pm$ 0.1 Da > 950 OR m/z 254.1 $\pm$ 0.1 Da > 950	242
$\Sigma\text{PAH}_{\text{Alk5}}$	m/z 266.1 $\pm$ 0.2 Da > m/z 133.1 $\pm$ 0.2 Da AND m/z 266.1 $\pm$ 0.2 Da > 950	266
ΣPAH_4	m/z 228.1 $\pm$ 0.2 Da > m/z 114.1 $\pm$ 0.2 Da OR m/z 228.1 $\pm$ 0.2 Da > m/z 113.1 $\pm$ 0.2 Da AND m/z 228.1 $\pm$ 0.2 Da > 950 AND m/z 240.1 $\pm$ 0.2 Da < m/z 228.1 $\pm$ 0.2 Da AND m/z 227.1 $\pm$ 0.2 Da < m/z 228.1 $\pm$ 0.2 Da	228
ΣPAH_5	m/z 252.1 $\pm$ 0.2 Da > m/z 264.1 $\pm$ 0.2 Da AND m/z 252.1 $\pm$ 0.2 Da > m/z 126.1 $\pm$ 0.2 Da AND m/z 252.1 $\pm$ 0.2 Da > 950	252
ΣPAH_{5+6}	m/z 276.1 $\pm$ 0.2 Da > 950 OR m/z 278.1 $\pm$ 0.2 Da > 950	278
ΣHop	m/z 191.2 $\pm$ 0.2 Da > m/z 95.1 $\pm$ 0.2 Da AND m/z 95.1 $\pm$ 0.2 Da > m/z 55.1 $\pm$ 0.2 Da AND m/z 191.2 $\pm$ 0.2 Da > 950	191

Sample preparation for HPLC-FLD analysis

For the HPLC-FLD analysis, we extracted the marker components from the filters using a refined solvent-based protocol

1. **Filter Division:** The particle-laden filter was divided into two equal halves. One half was designated for extraction, while the other served as a backup.
2. **Internal Standard Addition:** The half intended for extraction was spiked with 50 μL of internal standards—3-Methylcholanthrene (3-MC, 0.4 μM) and Nicotinic acid (NA, 10 μM). This filter was then cut into small pieces.
3. **Solvent Addition:** The filter pieces were placed into a glass container with a screw cap, followed by the addition of 2 mL of extraction solvent, such as analytical-grade Dichloromethane (DCM, Fisher Chemical, 99.8%) and Methanol (MeOH, Carl Roth, $\geq 99.9\%$).
4. **Extraction Process:** The samples were subjected to agitation for 15 minutes using a vortex shaker at 2000 rpm within a sealed container.
5. **Filtration:** The remaining filter residues were left in the container, and the liquid extracts were filtered through specialized glass frits (1 cm in diameter, 20 μm pore size) to remove any residual filter particles.

This extraction and filtration process (steps 3 to 5) was repeated three times, using different solvents each time: initially with pure MeOH, then with a 50:50 mixture of MeOH and DCM, and finally with pure DCM. The combined extracts were then subjected to evaporation under a gentle stream of nitrogen (N_2 , 99.99%) while being ice-cooled to prevent the loss of semi-volatile substances. A small amount of residue was retained, which was dissolved in 1 mL of a 60:40 mixture of Acetonitrile (ACN, Carl Roth, 99.95%) and Millipore water (H_2O , obtained from the Seralpur PRO 90 CN system with Supor DCF filter, Electronics Grade, 0.2 μm). This final solution was transferred to a vial for subsequent analysis.

Quality Checks

To assess the efficacy of our sample preparation and extraction process, recovery experiments were conducted in triplicate. A pre-heated quartz fiber filter (Whatman QM-H, 47 mm) was used, with one half spiked with 10 μL of a 10 μM standard solution containing BeP and BaP.

The spiked filter was then subjected to the previously described extraction procedure. Recovery rates (Rec) were determined using external standard (ESTD) calibration and calculated by comparing the measured concentration of each marker to the known spiked concentration.

The recovery formula applied was:

$$\text{Rec} = \frac{C_{\text{measured}}}{C_{\text{expected}}} \cdot 100$$

The observed recovery rates for the markers were as follows: sum BaP+BeP 85±7%. This value indicates the average systematic loss during the extraction process. Accordingly, we corrected our data using these recovery rates to ensure accuracy.

$$C_{\text{sample}_{\text{corrected}}} = C_{\text{sample}_{\text{measured}}} \cdot \left(\frac{100}{\text{Rec}} \right)$$

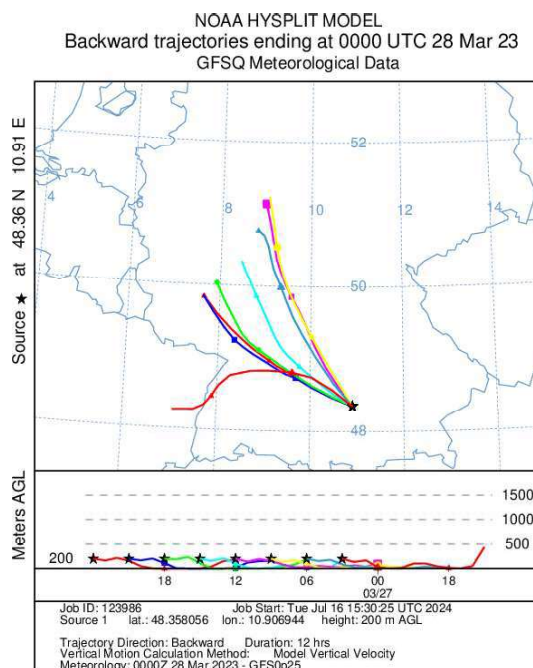
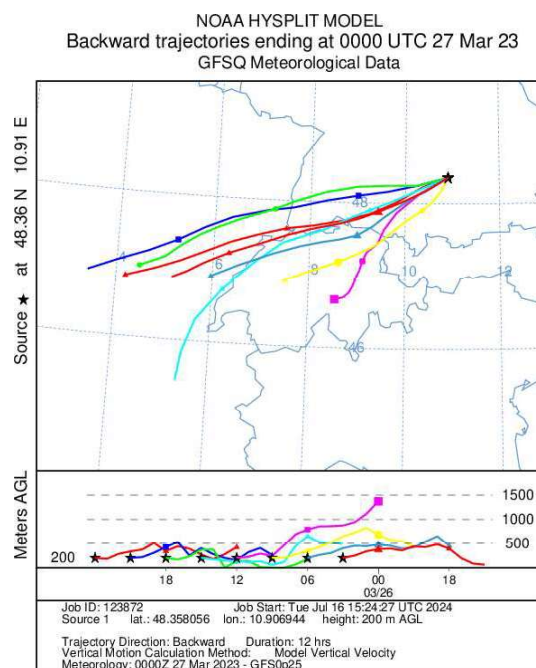
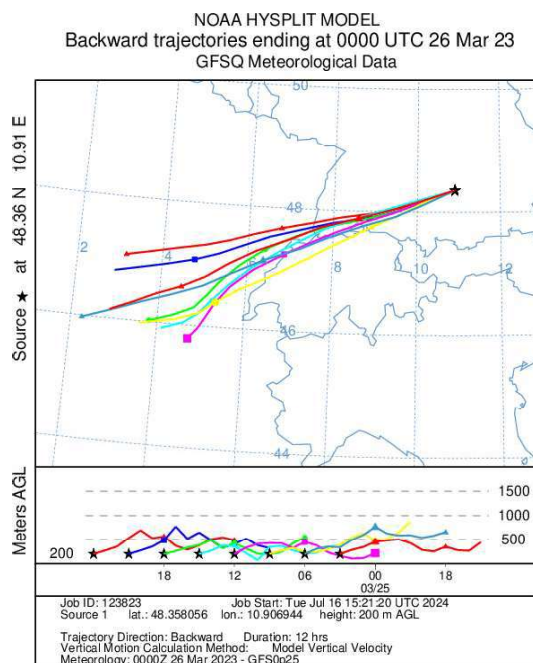
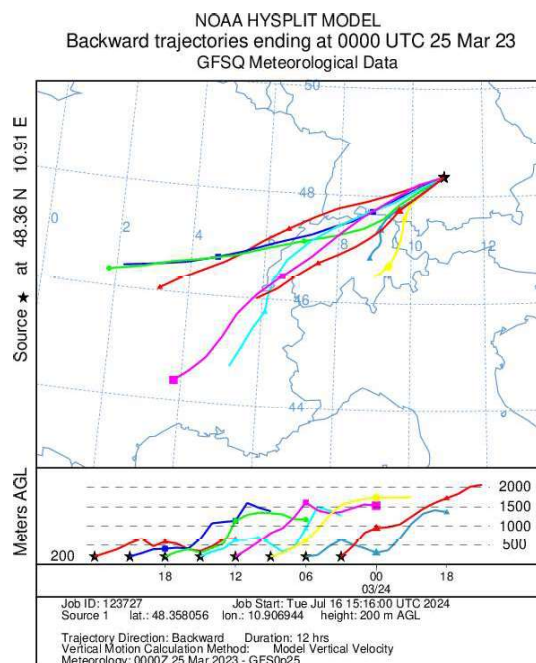
The HPLC-FLD analysis was conducted using an EC 125/4 Nucleosil 100-5 C18 HD analytical column (125 mm x 4 mm, 5 µm) maintained at a temperature of 30 °C. The injection volume was set at 25 µL, and the autosampler temperature was maintained at -5 °C. The flow rate was 1 mL/min. The gradient program for the mobile phase consisted of acetonitrile (ACN) and Milli-Q water (H₂O) with the following profile: starting at 60% ACN, increasing to 70% ACN at 5 minutes, holding at 70% ACN until 8 minutes, then increasing to 80% ACN at 12 minutes, maintaining 80% ACN until 15 minutes, increasing to 90% ACN at 19 minutes, and finally returning to 60% ACN at 22 minutes. Fluorescence detection (FLD) was employed with the following excitation (λ_{ex}) and emission (λ_{em}) wavelengths over time: at 0 minutes, λ_{ex} 259 nm and λ_{em} 386 nm; at 3.3 minutes, λ_{ex} 242 nm and λ_{em} 388 nm; at 5.8 minutes, λ_{ex} 250 nm and λ_{em} 370 nm; at 7.5 minutes, λ_{ex} 270 nm and λ_{em} 390 nm; and at 13 minutes, λ_{ex} 290 nm and λ_{em} 430 nm.

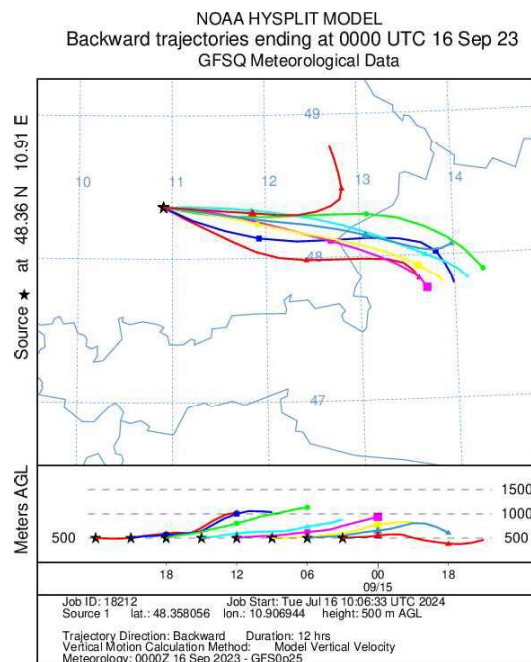
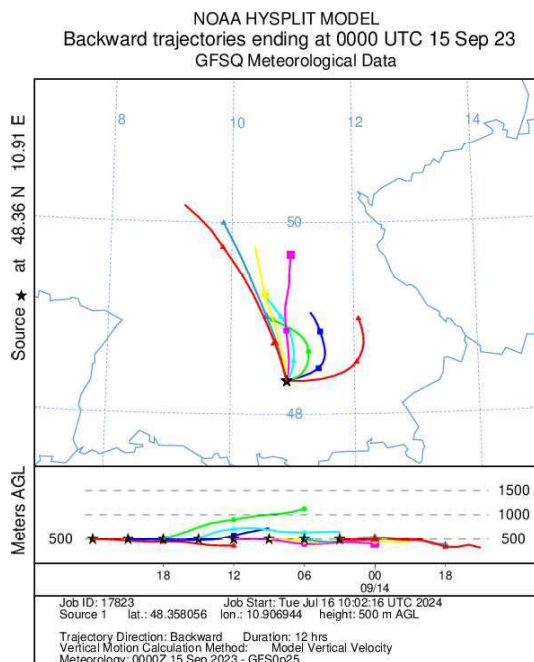
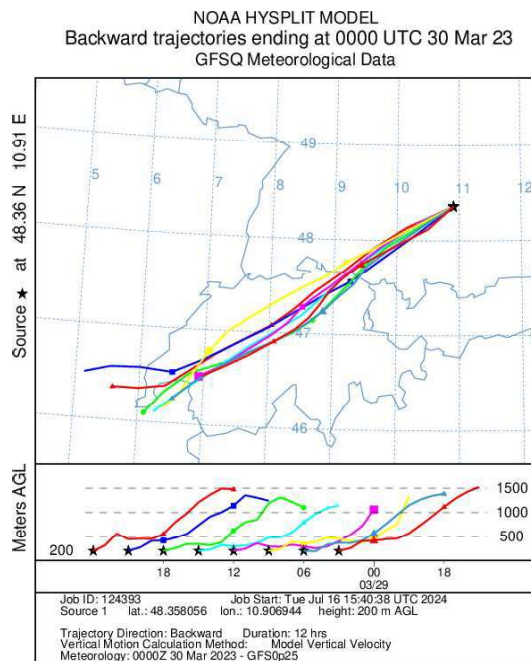
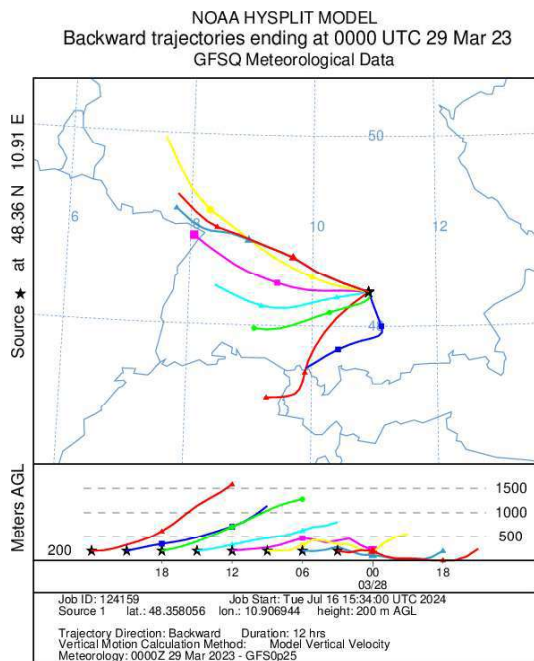
For a solid-phase dilution, we used sodium sulfate (Na₂SO₄) which was heated at 300 °C for 24 hours to ensure complete dehydration and evapoartion of other compounds. After cooling to room temperature, the Na₂SO₄ was transferred into a vial, and the NIST standard was added. The solid mixture was then shaken with a Cortex Shaker at maximum speed for 15 minutes to achieve thorough mixing. The mixture was visually inspected for any large heterogeneous

components. If necessary, it was shaken for an additional 15 minutes. The homogeneous mixture was then used for further dilutions with Na_2SO_4 , with the remainder stored in vials for future use. Subsequently, different masses of the various solid dilutions were weighed onto half of a QFF. These filters were then extracted and analyzed in triplicates with HPLC-FLD.

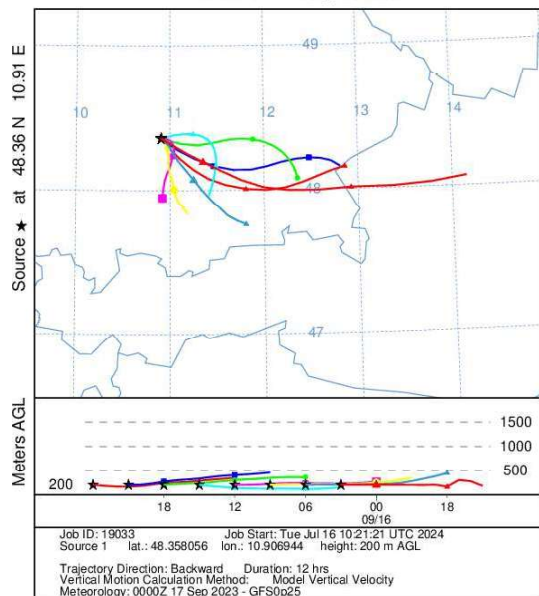
Table S5: Concentration [pg/m³] of ten particle-bound PAHs found in the ambient UFP in Augsburg during two different measurement campaigns in March (24.03.-29.03.) and September (14.09.-26.09.). The average of each target PAH in March, Sep-1 (14.09.-23.09.) and Sep-2 (25./26.09.) sampling periods are summarized. ΣPAH Targets: Sum of the target PAHs of each sampling day. On 21.09. and 24.09. no sample due to filter exchange and no valid data, respectively. Flu – Fluoranthene, Pyr – Pyrene, B[a]ant – Benz[a]anthracene, Chr – Chrysene, BeP – Benz[e]pyrene, BaP – Benz[a]pyrene, Per – Perylene, Ind[]pyr – Indeno[123-cd]pyrene, Dib[ah]ant – Dibenz[ah]anthracene, B[ghi]per – Benz[ghi]perylene.

Date	Flu	Pyr	B[a]ant	Chr	BeP	BaP	Per	Ind[]pyr	Dib[ah]ant	B[ghi]per	ΣPAH Targets
24.03.	9.4	11	9.2	18	15	11	5.2	12	3.1	1.4	96
25.03.	4.4	5.0	4.5	11	9.0	6.4	2.3	6.1	1.9	0.8	51
26.03.	9.0	12	8.6	17	15	12	5.0	15	3.1	1.6	98
27.03.	8.4	10	11	21	14	11	3.9	12	2.6	1.4	96
28.03.	7.7	7.2	8.5	18	11	8	5.2	7.7	2.8	0.9	76
29.03.	13	14	15	26	21	15	7.0	14	3.7	1.7	130
March	8.7	9.8	9.3	18	14	11	4.8	11	2.9	1.3	91
14.09.	3.6	3.5	1.6	12	5.5	13	9.4	0.7	1.1	0.3	51
15.09.	7.1	11	1.2	12	9.1	4.2	1.5	6.3	1.1	0.8	55
16.09.	10	13	7.3	19	6.3	6.4	3.3	26	3.5	1.3	96
17.09.	5.8	7.3	2.3	11	8.8	8.2	3.9	34	3.9	1.6	86
18.09.	3.0	4.9	0.9	8.6	18	16	1.1	2.9	1.2	1.0	58
19.09.	10	8.9	2.9	13	4.2	5.4	1.0	2.5	0.5	1.2	50
20.09.	4.9	4.4	3.5	23	14	5.9	4.2	13	0.5	0.6	75
21.09.	-	-	-	-	-	-	-	-	-	-	-
22.09.	5.8	8.7	6.9	15	4.5	2.5	1.2	8.9	4.0	2.2	60
23.09.	9.7	4.3	9.5	18	39	11	5.3	49	4.6	1.6	151
24.09.	-	-	-	-	-	-	-	-	-	-	-
25.09.	29	35	46	65	56	39	25	23	2.6	2.6	323
26.09.	20	21	27	46	52	37	26	46	11	4.8	291
Sep-1	6.7	7.3	4.0	15	12	8.1	3.4	16	2.3	1.2	76
Sep-2	24	28	37	56	54	38	25	34	6.7	3.7	307

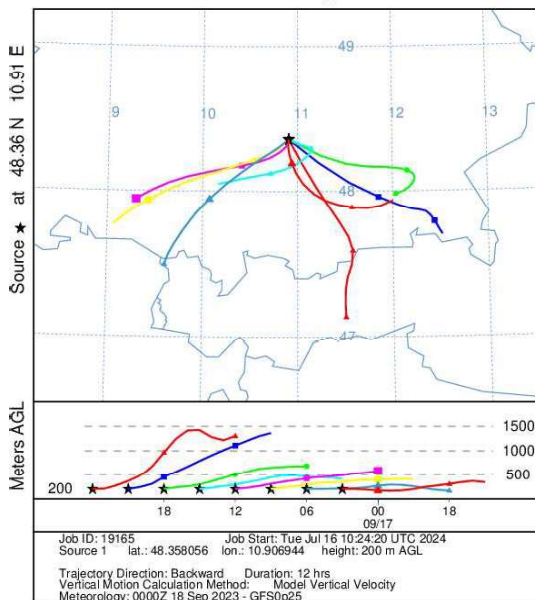




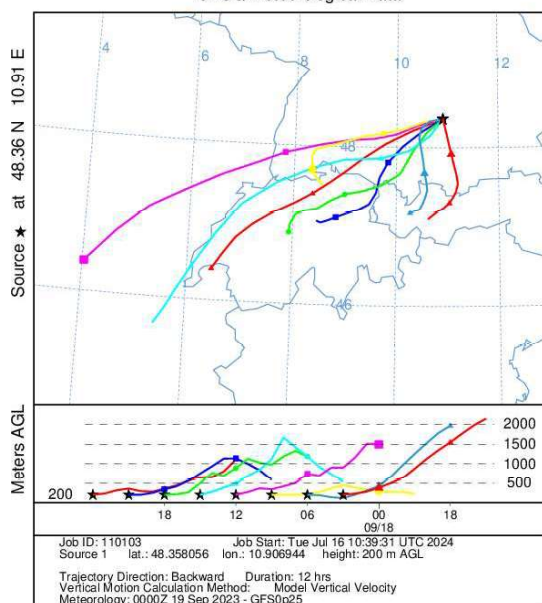
NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 17 Sep 23
GFSQ Meteorological Data



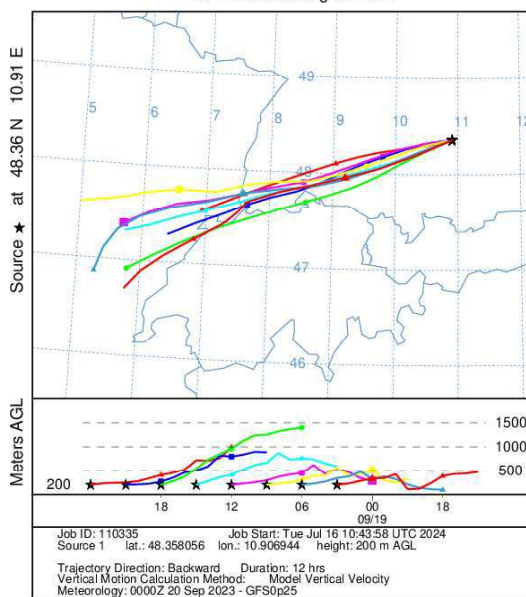
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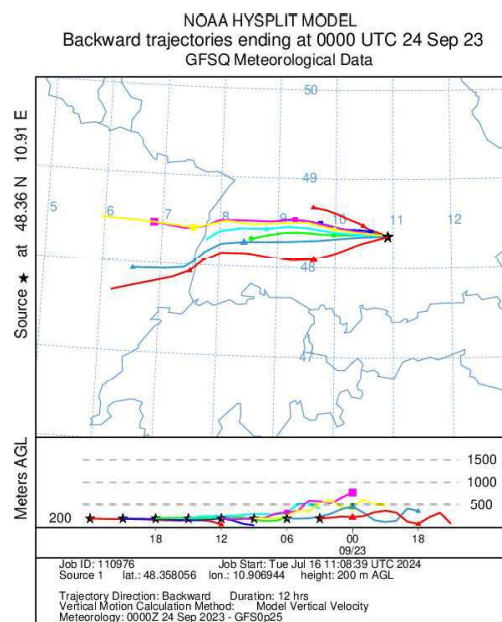
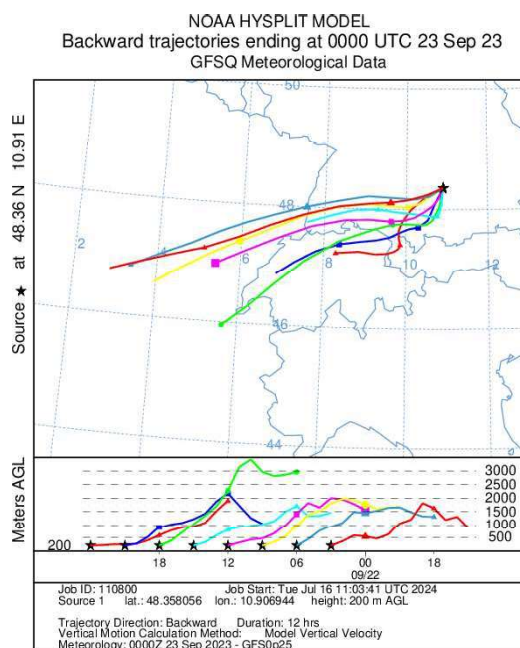
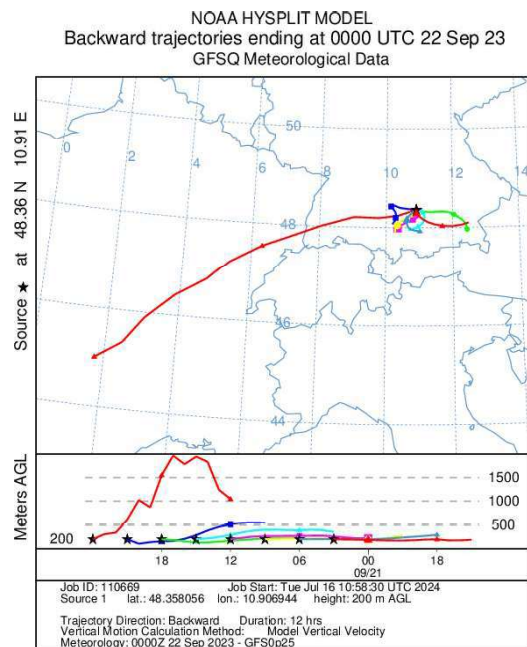
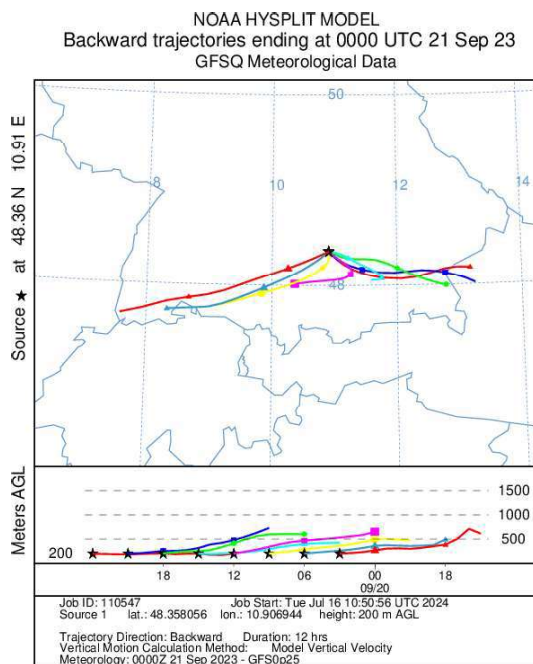


NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 19 Sep 23
GFSQ Meteorological Data



NOAA HYSPLIT MODEL
Backward trajectories ending at 0000 UTC 20 Sep 23
GFSQ Meteorological Data





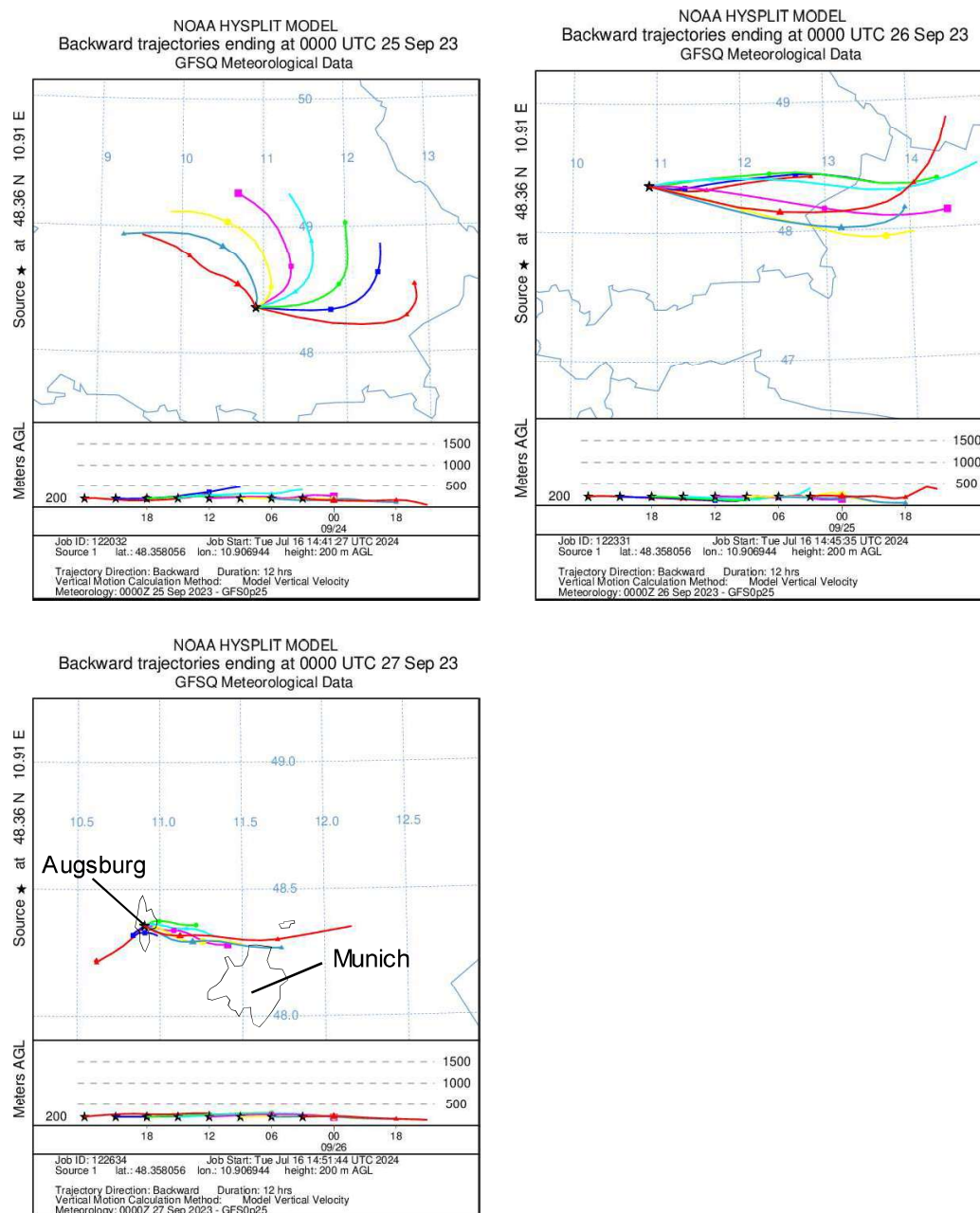


Figure S1: 12 h backward trajectories calculated during the sampling days in March and September by NOAA HYSPLIT Model ².

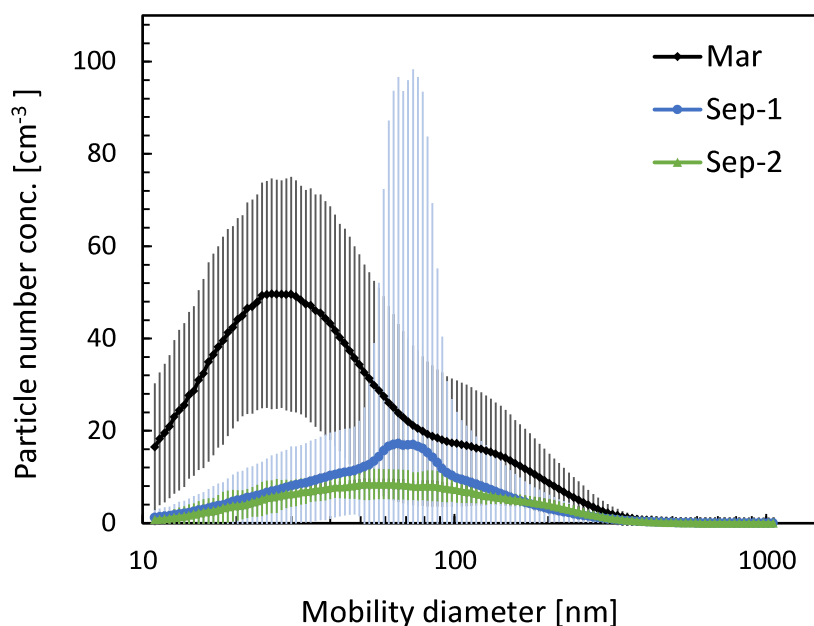


Figure S2: Particle size distribution measured by MPSS in March (Mar) and September (Sep-1, Sep-2). Thick lines show mean particle number concentration (PNC) for each size bin averaged for the three time periods March, Sep-1 and Sep-2. The error bars represent the relative standard deviation.

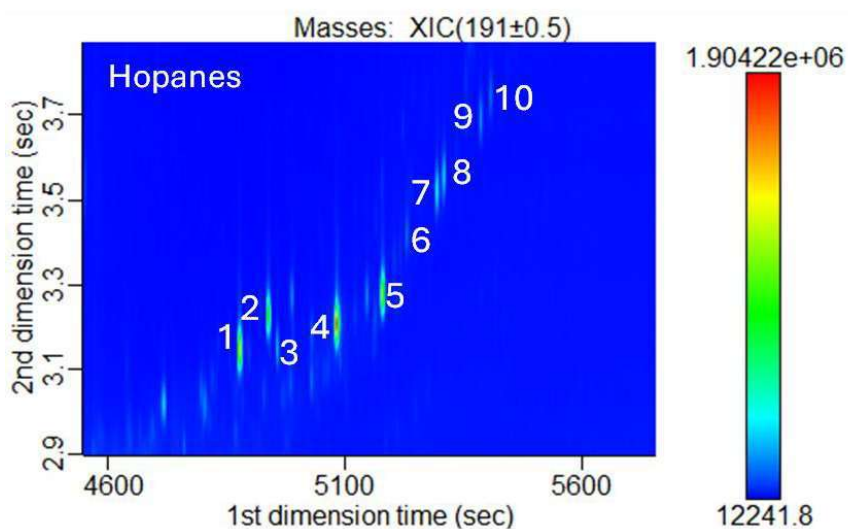


Figure S3: Two-dimensional GC×GC chromatogram of the extracted ion 191 m/z representative for hopanes. The different hopanoids are numbered from 1 to 10 corresponding to Table 1 in the main manuscript.

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Published Article IV

About the Variability of Tire and Road Wear Marker Components in Air: From Emissions to Atmospheric Deposition

About the Variability of Tire and Road Wear Marker Components in Air: From Emissions to Atmospheric Deposition

Elisabeth Eckenberger,* Myriam Younes, Tobias Mayer, Manuel Loeber, Linda Bondorf, Tobias Schripp, Sarmite Kernchen, Christian Laforsch, and Anke C. Nölscher*



Cite This: *Environ. Sci. Technol.* 2026, 60, 2023–2036



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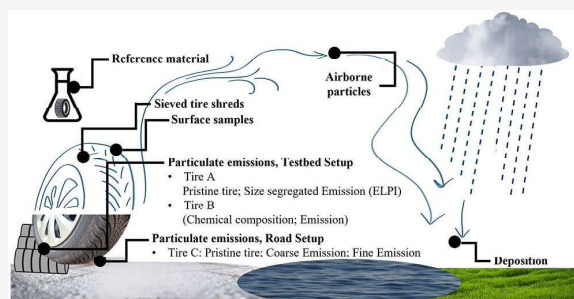
Article Recommendations



Supporting Information

ABSTRACT: Particles originating from tire wear and road interactions, tire and road wear particles (TRWP), are an emerging class of nonexhaust emissions with growing environmental concern. Yet, little is known about their atmospheric abundance and variability due to emissions, transport and transformation processes. This study addressed this gap by quantifying six tire additives that serve as markers for the indirect detection of TRWP in complex environmental samples. Using a newly developed analytical workflow based on high-performance liquid chromatography–mass spectrometry (HPLC-MS), we traced three anti-ozonants, *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD), *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD), and *N,N'*-diphenyl-*p*-phenylenediamine (DPPD), their oxidation products (6PPD quinone and IPPD quinone), and the vulcanization accelerator 1,3-diphenylguanidine (DPG) across a wide range of sample types. This single-method framework enabled us to observe marker variabilities, from pristine tire material to abrasion-related emissions from the testbed and road, airborne ultrafine particles (UFPs), and total atmospheric deposition. Marker composition varied strongly with source, emission conditions, and environmental exposure. During abrasion, 6PPD decreased by ~90%, while 6PPD quinone increased along the emission pathway. In ambient UFP from six Bavarian (Germany) sites, mean 6PPD concentrations ranged from <0.01 to 0.55 ng m⁻³. In the particulate fraction in total deposition from an urban, semi-industrial site, the ratio of oxygenated and parent PPD varied seasonally, revealing a higher degree of oxidation during summer. 6PPD dominated in the autumn and winter with an average of 6.6 ± 0.91 ng m⁻² day⁻¹, while 6PPDq was highest in spring and summer with average concentrations of 5.6 ± 5.91 ng m⁻² day⁻¹ and reaching an estimated annual deposition of 1.7 ± 0.5 μg m⁻² year⁻¹. By linking source materials to atmospheric samples, this study demonstrated the traceability of TRWP along their emission pathway for the first time and highlighted the importance of accounting for the chemical transformation of dedicated marker components in assessing their environmental fate.

KEYWORDS: tire and road wear particles, organic marker compounds, tire emission lifecycle, environmental samples, ultrafine particles, atmospheric deposition



1. INTRODUCTION

Whether tire and road wear particles (TRWP) impact air quality has been a widely debated question for many years. TRWP are now recognized as one of the largest sources of microplastic pollution worldwide.^{1–4} When transported within air, TRWP could pose a potential risk to both ecosystem integrity and human health far from roads. Their size and composition are crucial when assessing their potential health risk following inhalation or ingestion as well as when calculating the overall mass concentration in airborne aerosols or precipitation. Yet, observations of airborne TRWP, their emission, and atmospheric fate are rare and remain highly uncertain.

One reason for this uncertainty is the lack of tools for direct identification and quantification of TRWP in atmospheric samples.^{5,6} The formulation of tire rubber is complex but

broadly consists of 40–60% natural and/or synthetic elastomers and 20–25% reinforcing fillers such as carbon black or silica. Bulk fillers are neither unique nor specific in the environment, thus complicating the identification of TRWP.⁷ During production, tire wear softeners, vulcanization agents, and other additives are added in variable compositions. During driving, heat and friction can alter the chemical composition of tire surfaces and the emitted particles. As material of the road can be incorporated, these particles are defined as tire and road

Received: September 10, 2025

Revised: December 17, 2025

Accepted: December 18, 2025

Published: January 6, 2026



ACS Publications

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American Chemical Society

2023

<https://doi.org/10.1021/acs.est.5c12735>
Environ. Sci. Technol. 2026, 60, 2023–2036

wear particles, which enter the atmosphere directly upon emission or through resuspension from the surface. Their complex mixture of components includes heavy metals, polycyclic aromatic hydrocarbons (PAHs), and reactive antioxidants, which can transform into toxic products, making TRWP a potential air pollutant.^{8–10}

TRWP were first recognized as a potential air pollutant in road dust by Thompson et al.¹¹ Contrastingly, Cadle & Williams stated that tire wear products are likely not a significant air pollution problem because most of the TRWP are coarse, covered with road debris, and would have settled within 5 m distance from the road. Moreover, TRWP were likely prone to atmospheric oxidation.^{12,13} Later, TRWP were detected in airborne urban dust (PM_{2.5} and PM₁₀) in London, Los Angeles, and Tokyo with mass concentrations of up to 4.5 $\mu\text{g m}^{-3}$ and with high variability based on location and particle size.^{14–16} TRWP could contribute to around 5% of ambient PM concentrations on average, with studies reporting values between 0.2 and 22% depending on various parameters.¹⁷ In 2025, Lenssen et al. found that rubber markers were up to 5 times higher near major roads compared to the urban background. Moreover, TRWP were found in marine air in the northern Atlantic (max. 35 ng m^{-3}), suggesting effective long-range transport.^{18,19} To date, emission rates are mostly determined in the laboratory with a simulator and vary significantly between 1 and over 1000 mg km^{-1} .^{20–24} The simulator surface deviating from the real road surface properties likely causes some of the variability in these results. Studies on a road simulator highlighted that freshly emitted TRWP can have submicrometer diameters, concluding that even vehicles with zero tailpipe emissions could be a significant source of particles in the fine and ultrafine range.^{25,26}

The identification and quantification of TRWP in environmental samples remain analytically challenging. Most studies on TRWP were based on thermodegradation methods, such as via pyrolysis or thermal extraction gas chromatography–mass spectrometry (Pyr-GC-MS/TED-GC-MS). Here, specific pyrolysis products such as 4-vinylcyclohexene and dipentane were used as identifiers for detection.^{27–29} Recent advances in Py-GC/MS also apply combined pyrolysis markers to quantify and apportion tire versus polymer-modified bitumen.³⁰ However, the review by Røddland et al. highlights that current polymer- and marker-based methods for quantifying TRWP in environmental samples remain limited by scarce method validation, matrix interferences, and uncertainties in marker specificity and tread-to-TRWP conversions.³¹ Contrastingly, particle-based morphological analyses of TRWP require optical techniques. With scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), Camatini et al. documented the warped, porous nature, and S and Zn as typical elements of tire debris.³² However, as TRWP are predominantly black carbonaceous particles, they exhibit strong visible-light absorption with minimal light scattering. Their small size and similarity to other black carbonaceous particles (e.g., soot or charcoal) further complicate optical detection.^{33,34} Several other TRWP detection methods were based on Zn quantification in samples, as tire wear contains a significant amount of Zn, which can be used as a chemical marker.^{35,36} However, Zn is not tire wear-specific, and its analysis needs correction.^{29,37} Recently, organic additives were proposed as more unique tire markers within TRWP samples.

While tires contain an estimated 30–60 different organic additives, only a small subset have attracted attention, promising to be suitable as reliable TRWP markers: they are analytically detectable at low environmental concentrations, uniquely attributable to tire sources, and assumed to exhibit minimal transformation over time.³⁸ Examples are the para-substituted phenylenediamines (PPDs) and their quinones (PPDqs), 1,3-diphenylguanidine (DPG), phthalates, benzo-thiazoles, and alkylphenols.^{38,39} Among them, *N*-(1,3-dimethylbutyl)-*N'*-phenyl-1,4-benzenediamine (6PPD) and 6PPD quinone (6PPDq) have been of particular interest. 6PPD is added to the tire as an antiozonant. Upon reaction with ozone, it is turned into 6PPDq, which is a critical pollutant with an impact on ecosystems and human health.^{9,10,40–42} 6PPDq has been detected in freshwater systems with proven impact on the ecosystem's organisms.¹⁰ It was found in surface water with a large variability of concentrations over multiple orders of magnitude driven by the distance from roads and by the occurrence of storms.⁴³ Airborne 6PPDq in PM_{2.5} can range from a few to several pg m^{-3} , which was reported for several Chinese cities⁴⁴ and with large spatial and temporal heterogeneity.^{45–47}

To date, only a few studies have investigated TRWP in atmospheric samples. Yet, they reveal a substantial variability across emissions, road runoff, airborne particulate matter, deposition, and surface waters. The observed variability likely reflects various influential factors: the diverse instrumentation used, the choice of marker components, the tire wear material itself, the conditions during emission, and atmospheric processes. Therefore, we here aim to highlight the characteristics, occurrence, and potential transformation of selected organic TRWP marker components following the typical lifecycles of TRWP in the atmosphere. We hypothesize that organic TRWP marker composition varies systematically with sample type because abrasion and subsequent atmospheric processing oxidize PPDs to quinones. Therefore, we developed a comprehensive analytical workflow for the detection of six organic TRWP marker compounds (DPG, 6PPD, 6PPDq, IPPD, IPPDq, and DPPD) that works in the same manner across a range of sample types. We focus on PPDs and their quinones, as they are known components of tire formulations and demonstrated atmospheric and ecotoxicological relevance, and on DPG as a frequently reported accelerator.^{48–52} Because DPG also originates from nontire rubber and industrial uses, we treat it as an auxiliary tracer and rely on multimarker fingerprints and ratios rather than single-compound attribution.

The method combines solvent extraction with high-performance liquid chromatography coupled with mass spectrometry (HPLC-MS) and is applied to reference materials, abrasion emission from testbed and road setups, ultrafine particles (UFPs) from various Bavarian locations, and monthly resolved atmospheric deposition. We performed a comprehensive suite of tests to highlight the variability of organic markers in TRWP and discuss potential drivers determining their environmental fate.

2. MATERIALS AND METHODS

2.1. Reagents and Solvents

The six target compounds analyzed as TRWP markers were IPPD, 6PPD, DPPD, IPPDq, 6PPDq, and DPG (chemical structure: Table S1). Internal standards were 3-methylcholan-

threne (3-MC, Merck, 98% yield, 0.4 μM), nicotinic acid (NA, Merck, 99.5% yield, 10 μM), 6PPD- d_5 (ASCA-Berlin, 5 μM), and $^{13}\text{C}_5$ -6PPDq (LGC, 99% yield, 5 μM). All reagents, solvents, and standards were purchased from LGC Standards, Merck, Carl Roth, ASCA-Berlin, and Fisher Chemical with purities ranging from >95 to 99.99%. HPLC-grade acetonitrile (ACN, Carl Roth, 99.95%), methanol (MeOH, Carl Roth, 99.99%), dichloromethane (DCM, Fisher Chemical, 99.8%), water (H_2O , Seralpur PRO 90 CN system, electronics grade, 0.2 μm), and formic acid (HCOOH , Carl Roth, $\geq 98\%$) were used in the mobile phase. High-purity nitrogen (N_2 , 99.999%) was used for solvent evaporation.

2.2. HPLC-MS Analysis

We identified and quantified selected TRWP markers with HPLC-MS (Agilent 1100 series/single quadrupole Agilent 6130). Chromatographic separation was performed on a C18 column (Gemini Su C18 110A, 150 $\times$ 4.6 mm, 5 μm) with a pre-column (Nucleosil 100-5 C18, 4 $\times$ 3 mm), held at 30 $^\circ\text{C}$. A mobile phase gradient consisting of (a) 4 mM formic acid:80% methanol (MeOH) and (b) 4 mM formic acid:80% acetonitrile (ACN) was used to achieve optimal separation of analytes (Table S2 and Figure S1). The mass spectrometer was operated in positive electrospray ionization mode (ESI^+) with the following settings: a capillary voltage of 4000 V, a drying gas temperature of 350 $^\circ\text{C}$, a nebulizer pressure of 35 psi, and a drying gas flow of 10 L/min. Detection was performed in selected ion monitoring (SIM) mode. The monitored m/z values for each compound were as follows: DPG (m/z 212; RT_{MeOH} 3.21 min; RT_{ACN} 10.02 min), IPPD (m/z 227; RT_{MeOH} 4.51 min; RT_{ACN} 10.90 min), 6PPD (m/z 269; RT_{MeOH} 8.04 min; RT_{ACN} 11.97 min), DPPD (m/z 274; RT_{MeOH} 19.21 min; RT_{ACN} 23.59 min), IPPDq (m/z 261; RT_{MeOH} 13.48 min; RT_{ACN} 16.22 min), and 6PPDq (m/z 299; RT_{MeOH} 18.62 min; RT_{ACN} 22.82 min). The internal standards were monitored at NA (m/z = 124; RT_{MeOH} 6.08 min; RT_{ACN} 6.19 min), 6PPD- d_5 (m/z = 274; RT_{MeOH} 7.89 min; RT_{ACN} 11.78 min), and $^{13}\text{C}_5$ -6PPDq (m/z = 305; RT_{MeOH} 18.71 min; RT_{ACN} 22.86 min). DPPD and 6PPD- d_5 , both monitored at m/z = 274, were baseline-resolved chromatographically and integrated within compound-specific retention time (RT) windows. All data were processed using MassHunter Qualitative and Quantitative Analysis software (Agilent Technologies).

2.3. Sample Preparation

The sample preparation was designed to be applicable to different sample types in the same way. The marker compounds were extracted from tire reference material, unworn tire material, used tire surface samples, emission samples, and particulate matter collected on filters or from total atmospheric deposition. The sample preparation was optimized to maximize the recovery and repeatability for the selected marker components. First, the sample was transferred into a screw-cap glass vial. Depending on the sample type, this included pure tire wear material (reference, shredded material, and emissions), alumina filters (size-resolved emissions), or quartz fiber filters (UFP and total atmospheric deposition). Filter samples for size-resolved emissions and UFP were halved, while atmospheric deposition samples were quartered, using a custom-made stainless-steel cutter with a defined contact area matching the filter diameter, ensuring precise and reproducible division. For analysis, one-half or one-fourth of the filter was used, while the remaining part was stored. In

postprocessing, the measured concentrations were scaled accordingly (by a factor of 2 or 4) to account for the subdivision under the assumption of near-uniform submicron particle deposition. Each sample was spiked with 50 μL of each internal standard (IS) 3-MC (0.4 μM), NA (10 μM), 6PPD- d_5 , and $^{13}\text{C}_5$ -6PPDq (5 μM) prior to solvent extraction.

The samples underwent extraction through vortex shaking within a closed flask at a speed of about 400 rpm for a duration of 15 min. Following the extraction, the resultant extracts were subjected to filtration using glass frit filters with a diameter of 1 cm and a pore size of 20 μm (custom-made by a glass blower) to eliminate potential sample residue. This extraction process was repeated three times, each time employing 2 mL of a different extraction solvent. The solvents were (1) pure MeOH, (2) a 50/50 mixture of MeOH and DCM, and (3) pure DCM. Subsequently, the solvent from the combined extracts was evaporated under a gentle flow of N_2 while maintaining the glass container ice-cooled. The resulting residual droplet was dissolved in 1 mL of an ACN/ H_2O solution in a 60/40 ratio and then transferred into a vial for subsequent analysis (yielding nominal final IS concentrations of 5.4 ng (3-MC), 61.6 ng (NA), 68.3 ng (6PPD- d_5), and 75.1 ng ($^{13}\text{C}_5$ -6PPDq)). Throughout the entire sample preparation process, the samples were stored ice-cooled to avoid losses due to evaporation.^{53,54} We chose shaking over ultrasonication to limit the sonochemical transformation of analytes during extraction.⁵⁵ All samples were processed according to the same protocol for the internal standard addition, extraction, evaporation, and preparation for injection.

2.4. Method Validation

We evaluated the newly developed analytical methods and sample preparation in terms of sensitivity, repeatability, linearity, and extraction efficiency. For calibrations, we prepared standard solutions of all markers in ACN in the concentration range 0.1 to 4 μM . These were stored at -10 $^\circ\text{C}$. The sensitivity was determined with both internal and external standard methods. The instrumental uncertainty was determined as the relative standard deviation of repeated injections (n = 4) of a mixed standard solution at 0.9 μM concentration and was on average 5% across all target analytes. The variability is reported as the relative standard deviation for each marker component. We assessed the limit of detection (LOD) by diluting the standard solution to a level that resulted in peak matching in height three times the level of noise of the baseline. Additionally, we calculated the LOD_{Air} for the markers detected in atmospheric samples (e.g., UFPs collected on a filter) by dividing the LOD by the total sampled volume of air (Table S4, range: 0.0146–0.0542 ng m^{-3}). LOD_{Air} is calculated from the calibration-based laboratory LOD that is blank corrected.

$$\text{LOD}_{\text{Air}} [\text{ng m}^{-3}] = \frac{\text{LOD} [\text{ng mL}^{-1}] \times V_{\text{Extraction}} [\text{mL}]}{43.2 \text{ m}^3}$$

All samples were analyzed using both ACN- and MeOH-based HPLC-MS methods. As both methods yielded comparable results with minor differences in sensitivity depending on the target compound (Table S3), concentrations were averaged across both methods for each marker to increase robustness and data coverage. To determine the efficiency of the extraction, recovery rates were determined in quadruplicate (Table S5). We spiked one-half of a quartz fiber filter (QFF, 47 mm Whatmann) with 10 μL standard solution containing all

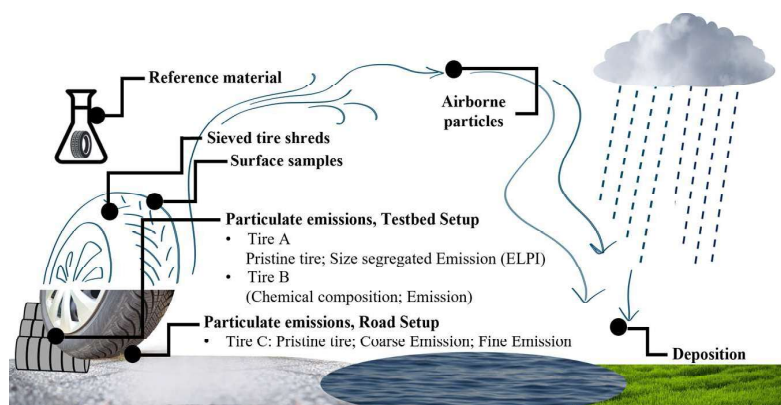


Figure 1. Schematic representation of the tire-related samples analyzed in this study, including reference material, sieved tire shreds, surface samples, testbed, and road emissions, as well as atmospheric particles and deposition samples.

markers. Afterward, the spiked filter underwent the extraction procedure described above. The recoveries were calculated by dividing the measured concentration of each marker by the expected (spiked) concentration.

Blanks were regularly collected from instrument, filter materials, laboratory, and field and processed alongside samples. They underwent the exact same sample preparation as the samples. Instrument blanks were measured between runs using the pure solvent. Filter blanks were prepared by placing clean filters into holders without air sampling and by removing them again. For atmospheric deposition samples, field blanks were taken monthly following the exact same preparation and collection protocol as original samples but with prefiltered water and solvents only. Additionally, extraction blanks were prepared regularly by running empty vials through the full extraction protocol.

Blank signals were generally low. Each sample batch included at least two instrument/solvent blanks and additionally matrix-matched blanks (UFP: two field/filter blanks per batch; deposition: one field/filter blank per sample; other sample types: two procedural (no-filter) blanks). Blank magnitudes were of the same order within each blank category and typically were well below sample signals. We subtracted the batch-matched blank peak area from the sample peak area. The subtraction rules and blank values are provided in the SI (Table S6 and Text S1). If blank values varied strongly within a batch or exceeded the expected background levels, affected samples were excluded from further analysis.

We report both field replicates and technical replicates for each data set (Table S7). Unless noted otherwise, each field sample was analyzed twice by using two chromatographic methods (ACN and MeOH mobile phases). Error bars represent SD across field replicates unless stated otherwise (categories without field replication report analytical SD across technical replicates).

2.5. Tire Wear Samples

An overview of all analyzed tire samples is provided in Figure 1 and Table S8 of the SI.

2.5.1. Reference Material Samples with a Known Amount of DPG and 6PPD. To evaluate the quality of the newly developed analytical and sample preparation methods in relation to TRWP markers, we conducted the extraction and

analysis of reference samples. Specifically, we examined tire material (Evonik) with known contents of DPG and 6PPD.

2.5.2. Shredded Tire Wear Material Mix. In a subsequent step, we aimed to test whether our method is repeatable and independent of the particle size. Therefore, we used a mixture of shredded old truck tires that are composed of elastic fine rubber powder with a defined grain spectrum, derived from vulcanized natural rubber (NR) and styrene–butadiene rubber (SBR) mixtures (MRH, Gummimehl Type K0002, obtained from the manufacturer already processed by cryogenic grinding). Here, the entire tire was shredded, resulting in most of the material not being exposed to actual environmental conditions, as the fraction of bulk relative to surface material is high. In order to assess whether the extraction efficiencies are dependent on the particle size, we sieved the test material into three size ranges (20–50, 50–75, and 50–200 μm), extracted, and analyzed them accordingly.

2.5.3. Used Tire Surface Samples. We analyzed tire treads that have been exposed to environmental conditions to obtain a broader spectrum of marker compositions under real conditions. Therefore, we meticulously extracted sections from the tread surfaces of used passenger-car summer tires. The specification as the manufacturer, the year of manufacturing, and the tire model can be found in Table S9 in the SI. Prior to analysis, these sections were further reduced in size using a scalpel to achieve dimensions of approximately 3–5 mm. Subsequently, they underwent the process of sample preparation and analysis.

2.5.4. Teststand Particles. First, we sampled the particulate emissions from a BMW i3 (new tires (Bridgestone Ecopia EP 500, 155/70 R 19 84 Q), testbed tire A) under controlled conditions on a ventilated all-wheel drive chassis dynamometer at the DLR Institute of Vehicle Concepts in Stuttgart, Germany.⁵⁶ Tire and brake wear emissions were separated by enclosing the brake and tire in individual housings on the chassis dynamometer with an offset plate physically isolating the two components. We placed an electric low-pressure impactor (ELPI+, Dekati) directly in the tire sampler outlet to determine the size distribution of the freshly emitted particles. Particles were collected on aluminum filters in the size range of 0.094–3.6 μm .⁵⁷ Second, passenger tires with a known amount of 6PPD and DPG, provided by Continental (testbed tire B), were collected immediately after generation during the dynamometer test and analyzed as a bulk to link the

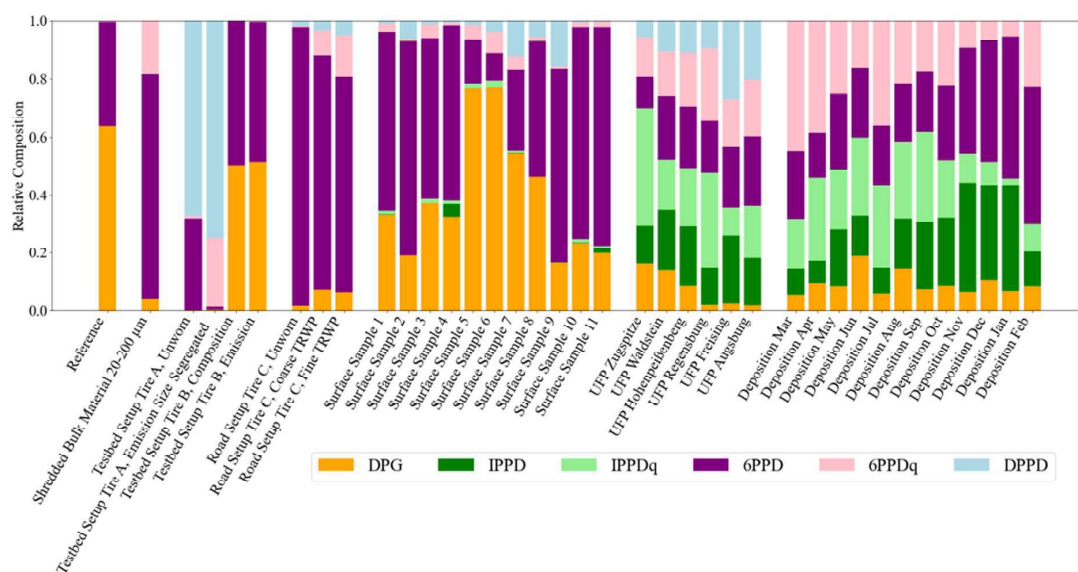


Figure 2. Relative mass composition of six selected TRWP markers DPG (orange), IPPD (green), IPPDq (light green), 6PPD (purple), 6PPDq (pink), and DPPD (light blue) in various samples, including reference tire material, shredded tire bulk material, direct (particulate) emissions from tires driven on the testbed and the road, tire surface samples, and atmospheric ultrafine particles and deposition samples.

observed TRWP marker composition in emissions to the original pristine tire wear material.

2.5.5. Road Emission Samples. To bridge the tire material to real-world TRWP emissions, we analyzed samples collected from a tire (tire C) during driving on the road. For this, the ZEDU-1 demonstrator vehicle was used.^{26,58} Around the tire of this vehicle, air is directed and extracted in front of it, cleaned by a filter system, and discharged through openings in the bonnet. The system comprises a central housing, coarse and fine filters, multiple fans, and collection containers for larger particles and smaller road dust. We collected TRWP during the ZEDU-1 test ride on the Bosch test track in Boxberg, Germany, including various driving dynamics surfaces, incline hills, handling tracks, a high-speed oval, and spanning driving profiles spanning 0–120 km h⁻¹. Aerosol was drawn upstream of the fan/filter system, with the sampling flow increasing with vehicle speed to a maximum of 250 L s⁻¹.²⁶ The composition of the road emission samples was compared to their pristine counterpart.²⁶

2.5.6. Airborne Particulate Matter. Atmospheric UFPs were collected from six sites in Bavaria, Germany, which represented mixed environmental settings as well as anthropogenic activities. These sites included (1) the high-altitude background station Zugspitze located in the Bavarian Alps, (2) the forested rural site Waldstein, (3) the rural observation site Hohenpeißenberg, (4) the urban Freising site with car and air traffic, (5) the urban Regensburg site characterized by dense road traffic and mixed residential and commercial land use, and (6) the metropolitan city of Augsburg, representing a densely populated urban location. We sampled UFP at these sites to span an urban, suburban, and rural gradient and a range of traffic influences (near-road vs urban background). Site metadata (coordinates, land use, distance to major roads) are provided in Table S10. The campaigns covered typical regional meteorology in summer 2023 (Source: German Weather Service (Deutscher Wetterdienst (DWD))); Table S11). For each site, the first three samples collected after each of two

weekly maintenance intervals were selected, resulting in six samples per location. For sampling, air was drawn first with a flow rate of 30 LPM through an inlet with a PM10 preseparator to cut off the coarsest particles and an ozone denuder consisting of honeycomb ceramic bodies coated with potassium thiosulfate (≥95%, Merck). The ozone denuder was designed to scrub ozone from the sampled air, thereby preventing oxidation reactions of already collected particles on the filter when ozone-rich air continues to flow through the filters (Eckenberger et al. in preparation). Then, particles with aerodynamic diameters smaller than 100 nm were separated by a three-stage Micro-Orifice Uniform Deposit Impactor (ultra-MOUDI).⁵⁹ The impactor plates were all coated with vacuum grease to prevent the re-entrance of larger particles into the sampling stream, which could lead to an erroneous mass-based chemical analysis of organic marker components indicative of tire wear. Finally, below the lowest cutoff stage of the impactor, preheated quartz fiber filters (0.40 µm, Whatman, 300 °C, 24 h) were placed. An automated low-volume filter changer (DIGITEL) was programmed in intervals to switch the filters in a 24 h sampling period, collecting a total volume of 43.2 m³ of air per sample (Gawlitta et al. in preparation).

2.5.7. Total Atmospheric Deposition Samples. At an urban environment of a semi-industrial area in the city of Bayreuth, Germany (49.96033° N, 11.59597° E), we also collected atmospheric total deposition (TD) once per month over the course of one year. The atmospheric deposition was collected in a stainless-steel funnel (Ø = 25.7 cm, Sartorius) and an amber glass bottle placed at the bottom of the funnels inside an aluminum frame.⁶⁰ At the end of each month and before the bottle with the sample was collected, the funnel was rinsed with 500 mL of prefiltered water to include all particulate matter adhering to the funnel surface. Blanks, consisting of prefiltered water in amber glass bottles, were taken during most of the months of field sampling. After sampling, insects and plant residues were removed using precleaned stainless-steel tweezers and rinsed above the funnel

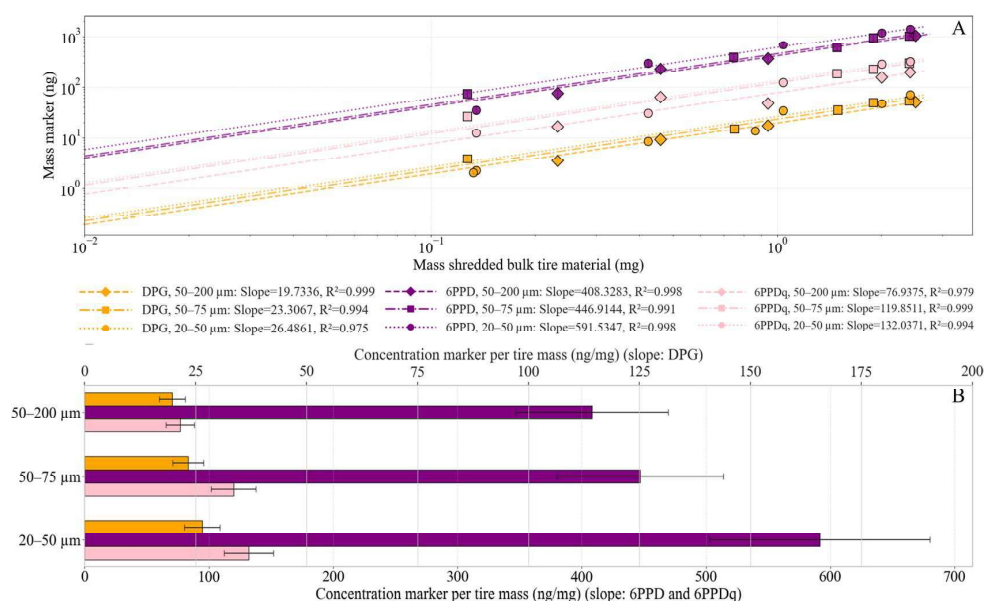


Figure 4. Extracted concentrations of DPG, 6PPD, and 6PPDq from shredded bulk tire wear particles as a function of the tire material mass across three particle size fractions (ng mg^{−1}). (A) Marker identities are indicated by the color: DPG (orange), 6PPD (purple), and 6PPDq (pink). Particle size fractions are represented by marker shapes: circles for 20–50 μm, squares for 50–75 μm, and diamonds for 50–200 μm. Linear regression models were fitted through the origin for each marker-size combination, and log–log scaling is applied to both axes. Points are individual field samples ($n = 4$ per size fraction); each sample was analyzed twice using ACN and MeOH mobile phases, and duplicate analyses were averaged within the sample. Both axes are log–log scaled for visualization only to accommodate the wide range. The fitted lines represent the results of a linear regression forced through the origin. (B) Absolute marker concentrations per analyzed tire mass (ng/mg), derived from the regression slopes in panel A. Bars show slope-derived concentrations; error bars represent the standard error (SE) of the regression slope propagated to ng mg^{−1}.

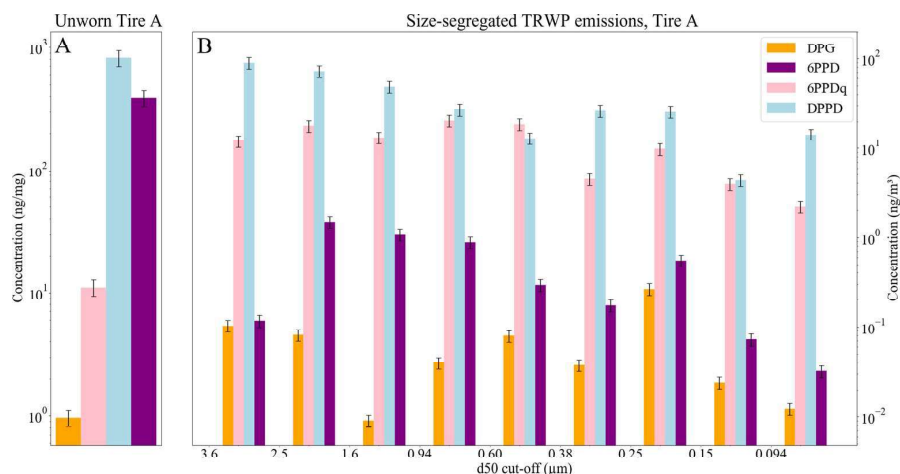


Figure 5. Mass concentrations per analyzed tire mass (ng/mg) of four tire-derived markers in unworn tire A of the testbed setup (panel A) and corresponding size-resolved concentrations normalized to the sampled air volume (ng/m³) in airborne particles collected with an ELPI (panel B). The markers shown are DPG (orange), 6PPDq (pink), DPPD (light blue), and 6PPD (purple). Panel A: $n = 4$ independent replicates; each replicate was analyzed twice using ACN and MeOH mobile phases, and duplicate analyses were averaged within the replicate; error bars = SD across replicates. Panel B: one filter per size bin; each bin analyzed 3X per solvent (ACN and MeOH; 6 analyses total) and averaged; error bars = SD (analytical).

fraction is consumed or immobilized during tire manufacture and vulcanization and is therefore no longer extractable as the parent DPG.

3.2. Particle Size Dependency of Marker Extraction

To investigate whether particle size influences the marker extraction from TRWP, we analyzed three fractions of

shredded bulk tire material with different size distributions: 20–50, 50–75, and 50–200 μm. While the tested markers did not show statistically significant differences between these size groups (DPG: $p = 0.2807$; 6PPD: $p = 0.1897$; 6PPDq: $p = 0.0771$, ANOVA test), we could observe size-dependent trends in our extraction efficiency. For all markers, the extracted mass

per tire wear mass increased when the particle size distribution was shifted toward smaller sizes. 6PPD concentrations increased from $439.3 \pm 65.9 \text{ ng mg}^{-1}$ ($50\text{--}200 \mu\text{m}$) to $591.5 \pm 88.7 \text{ ng mg}^{-1}$ ($20\text{--}50 \mu\text{m}$), while DPG increased from 19.8 ± 3.0 to $26.5 \pm 4.0 \text{ ng mg}^{-1}$, and 6PPDq from 77.0 ± 11.6 to $132.0 \pm 19.8 \text{ ng mg}^{-1}$ over the same size range (Figure 4). 6PPDq exhibited the largest relative increase with a decreasing particle size. As an oxidation product, 6PPDq is likely influenced the most strongly by the higher surface-to-mass ratio, as the oxidation reactions on the surface of the tire material particles become relatively more important.^{38,61,62} Surface reactions might thus also affect the state of the TRWP markers detected in airborne samples.

3.3. Size-Distribution of Fresh Particulate Tire Emissions

We analyzed samples collected with an ELPI from a controlled testbed setup with the testbed tire A. The ELPI classified the emitted particles over an aerodynamic diameter range of 0.094 to $3.6 \mu\text{m}$ in 9 size categories, as can be seen in Figure 5. Note that this range covers the lower part of typical atmospheric particle size distributions. It is much smaller than the size groups used for the extraction characterization, which covers coarser particles more representative of TRWP found in deposition, suspended in surface water, or road runoff. Based on our previous observations with shredded bulk tire material, we expect a more efficient organic marker extraction and assume that it is variability in extraction within this particle size range is minor compared to other effects occurring during driving processes. Among the tested markers, DPPD had the highest concentration in both the pristine, unworn tire material ($821 \pm 123 \text{ ng mg}^{-1}$) and the emitted particulate matter, from $14.2 \pm 2.13 \text{ ng m}^{-3}$ in the finest particle fraction ($<0.094 \mu\text{m}$) to a maximum of $89.4 \pm 13.4 \text{ ng/m}^3$ in the largest particle fraction (2.5 to $3.6 \mu\text{m}$). Similarly, 6PPDq concentrations in the emitted TRWP peaked in the accumulation mode, reaching a maximum of $20.5 \pm 3.08 \text{ ng m}^{-3}$ in the $0.94 \mu\text{m}$ size fraction while showing the lowest concentration in the smallest particle size fraction ($2.19 \pm 0.33 \text{ ng m}^{-3}$).

In the pristine tire material, 6PPD was the second most abundant marker ($389 \pm 58.4 \text{ ng mg}^{-1}$) but decreased in the emissions more drastically than DPPD so that its relative mass fraction dropped from 47.4 to 0.68% (averaged over all sizes). DPG showed a bimodal distribution with high concentrations in the fractions $0.15\text{--}0.25 \mu\text{m}$ ($0.27 \pm 0.04 \text{ ng m}^{-3}$) and $2.5\text{--}3.6 \mu\text{m}$ ($0.09 \pm 0.01 \text{ ng m}^{-3}$). The observed differences in the size distribution of DPPD and 6PPD, which both belong to the same class of antioxidants, may be partially explained by differences in their physicochemical properties. 6PPD has a higher vapor pressure ($2.51 \times 10^{-8} \text{ atm}$) than DPPD ($6.31 \times 10^{-9} \text{ atm}$) (median of predicted range; EPA CompTox Dashboard). A higher vapor pressure could favor volatilization, potentially contributing to its lower abundance in the emitted tire wear particles. Furthermore, its high reactivity might rapidly transform 6PPD into 6PPDq,^{63–66} explaining also the swap in relative abundance of this precursor-product marker couple when comparing unworn and emitted tire material. It is also noteworthy that the tested tire A was new. Passenger-car treads commonly employ a cap-base construction, and rubber contacts exhibit a transient run-in phase during the first kilometers that can affect early performance and emissions.^{67,68} However, we interpret the testbed emission marker profiles relative to the composition of the corresponding unworn tread

material of the same tire A, as changes relative to the source rather than absolute emission signatures.

3.4. Tire Wear and Surface Interaction Influence on Markers

To investigate how the composition of TRWP markers evolves during the wear process, we analyzed the marker content in both testbed-generated and real-world road-derived particles and compared them to the original composition of the unworn reference tire. Figure 6a contrasts the known composition of

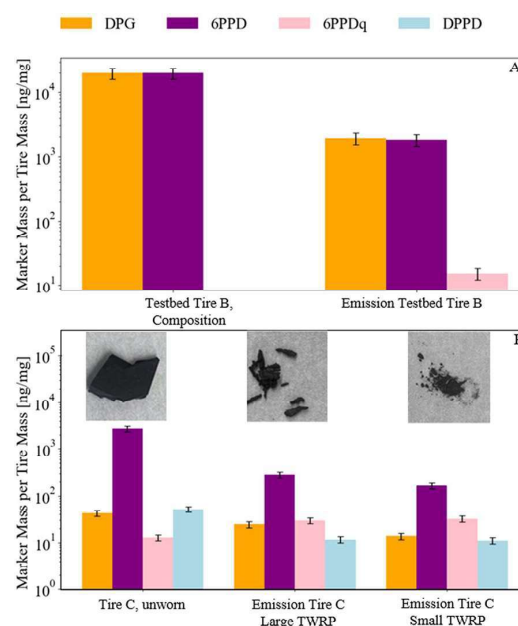


Figure 6. Marker mass concentrations per analyzed tire mass (ng mg^{-1}) of four TRWP markers generated under testbed (A) and road conditions (B). (A) Known composition of an unworn reference tire B and accordingly the measured TRWP marker in emitted particles while driving the tire on a testbed. (B) Marker mass concentration measured in pristine, unworn tire C and freshly emitted material from road interaction in coarse and fine TRWP fractions. Bars represent DPG (orange), 6PPD (purple), 6PPDq (pink), and DPPD (light blue) derived from the results of a linear regression analysis of the extracted and analyzed tire material. All values are normalized to the analyzed tire mass and displayed on a logarithmic scale. $n = 4$ independent samples per condition; each sample was analyzed twice using ACN and MeOH mobile phases, and duplicate analyses were averaged within the sample; error bars = SD across samples.

unworn testbed tire B with the measured marker concentrations in the emitted particles. Both DPG and 6PPD showed a decline from their initial levels of $20,000$ to 1920 ± 384 and $1811 \pm 362 \text{ ng mg}^{-1}$, respectively. In contrast, 6PPDq, which was not present in the tire material, appeared in the emissions at $15.2 \pm 3.0 \text{ ng mg}^{-1}$.

Accordingly, we again analyzed freshly emitted particles, yet now while driving on the road, and compared the unworn tire material C to large particulate matter (in the millimeter range) and small particulate matter (in the micrometer range). Figure 6b presents images of these samples from real road-tire interactions and points out their different natures. Likely the emitted TRWP have been exposed to different forces and heat during the driving processes.^{26,58} The concentration of 6PPD

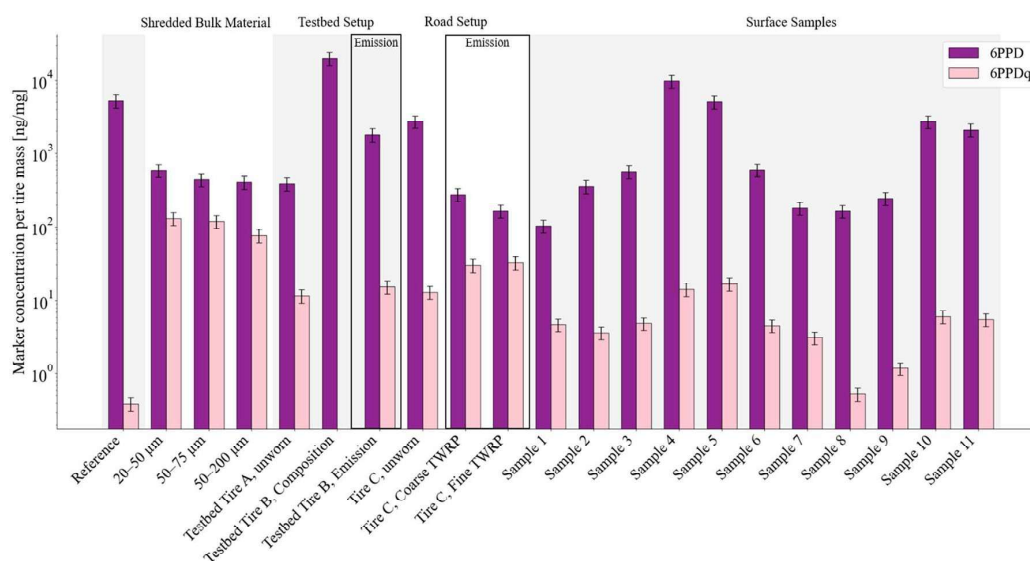


Figure 7. Comparison of mass fractions of TRWP markers per analyzed tire mass (ng/mg) for 6PPD (purple) and its transformation product 6PPDq (pink) across categorized sample types. Shown are reference tire material, shredded bulk tire particles in three size fractions (20–50, 50–75, and 50–200 μm), testbed tire materials, including the tire from a BMW i3 (testbed tire A, unworn), a synthetically composed tire with known composition (testbed tire B, composition; composition refers to the synthesis, not to the measured content), and its emitted wear particles (emission testbed tire B); as well as street emissions represented by abrasion samples (unworn tire, coarse TRWP, and fine TRWP); and surface residues collected from used tires (surface samples 1–11). Sample sizes (field n): reference = 4; shredded = 4 per size fraction; testbed tire A (unworn) = 4; testbed tire B (composition) = 4; testbed tire B (emission) = 4; road (unworn, coarse TRWP, fine TRWP) = 4 per fraction; surfaces = 1 (analytical replication only). Each field sample was analyzed twice using ACN and MeOH mobile phases; duplicate analyses were averaged within the sample. Error bars represent SD across field samples where field replication exists; for categories without field replication (surfaces), error bars represent the analytical SD across repeated analyses.

was highest in the unworn tire material, averaging 2749 ± 412 ng mg^{-1} , compared to the emitted TRWP for which we determined more than a factor of 10 lower concentrations (282 ± 42 ng mg^{-1} in large TRWP and 167 ± 25 ng mg^{-1} in small TRWP). Although the concentration of 6PPDq increased from unworn tire to emissions, particularly in the small TRWP fraction (32 ± 5 ng mg^{-1}), it could not account for the overall 6PPD loss, as it only accounts for about 1.2% of the original 6PPD concentration. This suggests that a significant fraction of 6PPD is lost or oxidized to other products than 6PPDq during the abrasion process. DPG had slightly decreasing concentrations from 43 ± 6 ng mg^{-1} in the unworn tire sample to 24 ± 4 ng mg^{-1} in the large sample and 14 ± 2 ng mg^{-1} in the small fraction. Similarly, DPPD concentrations decreased from 52 ± 8 ng mg^{-1} in pristine tire material to 12 ± 2 ng mg^{-1} in large particles and 11 ± 2 ng mg^{-1} in small particles.

Tire particle emission from both the testbed and road decreased substantially in terms of marker mass concentrations (about a factor of 10 for the example of 6PPD), which suggests that the chemical composition of emitted particles is influenced by shear forces and thermal stress that particles undergo from abrasion. It is conceivable that smaller particles were formed under conditions that mitigated mechanical and thermal forces, while larger fractions were formed under friction-enhanced situations augmented by localized heat, as presented by.⁶⁹ Since this trend was observed in both the controlled testbed setup and driving on road emissions, it likely reflects intrinsic loss or transformation of marker substances during the abrasion process itself. Yet, road-emitted TRWP may comprise variable fractions of brake wear, road dust, or

other materials. As a result, nontire material, especially in the fine fraction, can dilute and confound marker-to-PM ratios.

3.5. Tire-to-Tire Marker Variability

Whenever it was possible for our samples, we calculated the mass fraction of the selected TRWP markers per tire wear mass. This was done for the reference tire material, the shredded tires, the test vehicle tire from the emission samples, and 11 surface samples of used tires. Figure 7 highlights the variability and range of the TRWP marker content per analyzed mass, for the example of 6PPD and 6PPDq. First, the screening of used tire surfaces revealed large differences in 6PPD (ranging from 104.2 ± 20.8 to 9782.6 ± 1956.5 ng mg^{-1}) and 6PPDq concentrations (ranging from 0.52 ± 0.10 to 16.68 ± 3.34 ng mg^{-1}). Our reference materials and unworn tire samples fall as well within this range. Second, we observed a loss of 6PPD from tire material to particles emitted by an order of magnitude, as explored already in the previous paragraph.

This information is relevant for attempts that aim to scale the TRWP marker mass concentrations found in environmental samples to estimate the mass of the tire wear material. We attribute the observed wide variability to three aspects: (1) the differences in manufacturing (see also Figures 5 and 6), (2) the complex processes generating TRWP during abrasion itself and tire–road interactions (see also Figure 6), and (3) a potentially enhanced surface reactivity of finer particles. However, our experiments with shredded bulk tire material of different size fractions suggest that the impact of the latter is comparatively minor compared with the variability introduced by manufacturing and abrasion processes.

3.6. The More Urban a Location, the More TRWP Markers Can Be Found in UFPs

We determined the mass concentration of 6PPD in UFPs that were sampled in summertime in Bavaria across six characteristic locations. We focused on 6PPD since it showed the highest concentrations among all parent antioxidant markers, allowing for a more robust comparison across sites (absolute concentrations of all markers in Figure S3). Figure 8 highlights

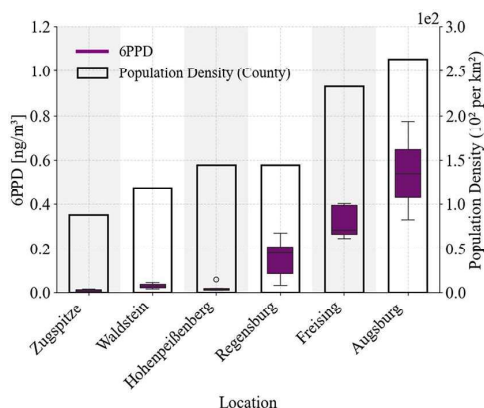


Figure 8. Comparison of 6PPD concentrations normalized to the sampled air volume (purple boxplots) and population density (black-outlined bars) across different locations, sorted by increasing population density. The left y-axis represents 6PPD concentrations [ng m^{-3}], while the right y-axis indicates the population density (10^2 per km^2). Per location, $n = 6$ independent field samples. Each sample was analyzed twice using ACN and MeOH mobile phases; duplicate analyses were averaged within the sample.

that 6PPD concentrations in UFP generally increased with population density, which can be linked to the density of roads

and mobility. At the Zugspitze, which is an alpine background station ($88 \text{ inhabitants/km}^2$), the mean 6PPD concentrations were the lowest with an average of $0.01 \pm 0.005 \text{ ng m}^{-3}$ (range: $0.004\text{--}0.014 \text{ ng m}^{-3}$). Higher concentrations of 6PPD were found in UFP from the more densely populated counties of Augsburg and Freising (264 and $233 \text{ inhabitants per km}^2$, respectively). The highest 6PPD mass concentration was observed in samples from Augsburg, with $0.55 \pm 0.18 \text{ ng m}^{-3}$ (range: $0.33\text{--}0.78 \text{ ng m}^{-3}$), and from Freising with $0.32 \pm 0.05 \text{ ng m}^{-3}$ (range: $0.27\text{--}0.37 \text{ ng m}^{-3}$). Interestingly, although Regensburg and Hohenpeißenberg have comparable population densities, Regensburg's UFP samples contained significantly more 6PPD, on average $0.16 \pm 0.10 \text{ ng m}^{-3}$ (range: $0.06\text{--}0.25 \text{ ng m}^{-3}$). This likely reflects the denser city structure and close distance of the sampling location to urban traffic in Regensburg, while the sampling at Hohenpeißenberg took place on a background station based on an elevation. Other factors, such as local emissions, infrastructure, weather conditions, wind patterns, and topography, potentially have considerable effects on 6PPD concentrations in UFP as well. This example data set presents the TRWP marker variability in airborne UFP across an urban-to-background gradient and highlights the need for more studies adding statistically relevant data sets.

3.7. TRWP Markers in Atmospheric Deposition Are Dominated by Oxygenated Products

We identified the selected TRWP markers in the particulate fraction ($0.4\text{--}10 \mu\text{m}$) of monthly atmospheric deposition samples. Figure 9 highlights that 6PPD had the highest annual mean deposition rate ($5.2 \pm 1.96 \text{ ng m}^{-2} \text{ day}^{-1}$) and increased during the winter months, reaching an average of $6.6 \pm 0.91 \text{ ng m}^{-2} \text{ day}^{-1}$ across the autumn and winter seasons. This coincides with mean lower air temperatures ($7.1 \pm 5.6 \text{ }^\circ\text{C}$) and higher relative humidity ($85.1 \pm 3.5\%$) from September to February (source: German Weather Service (DWD); Figure

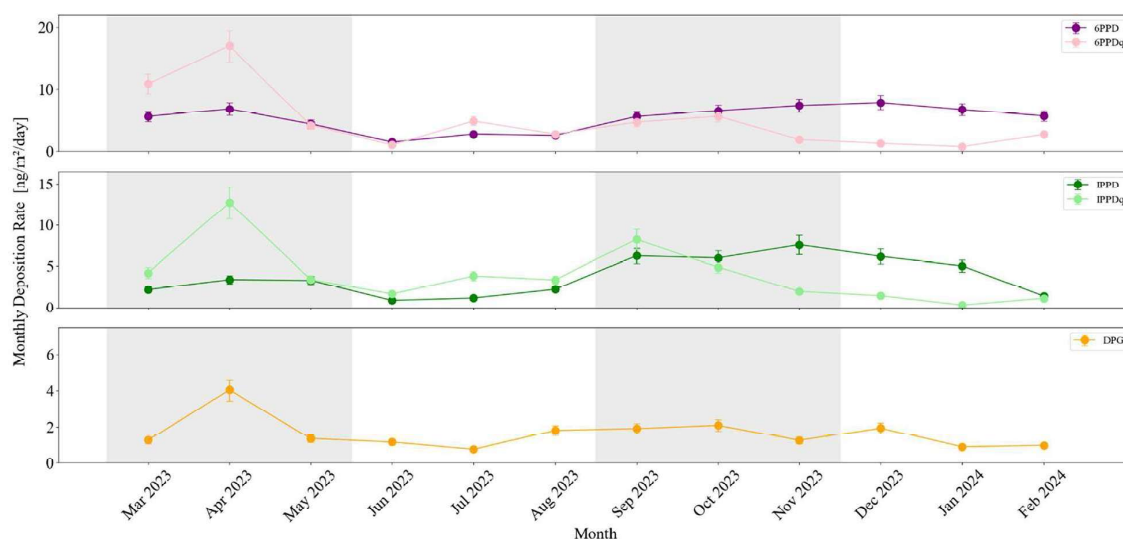


Figure 9. Monthly deposition rates normalized to sampled surface area and collection time ($\text{ng/m}^2/\text{day}$) of five TRWP marker compounds across one year. The top panel shows 6PPD (purple) and its transformation product 6PPDq (pink); the middle panel presents IPPD (green) and IPPDq (light green), and the bottom panel displays DPG (orange). Shaded background areas represent meteorological seasons: spring, summer, autumn, and winter. Per month, $n = 1$ sample; each month was analyzed 3X per solvent (ACN and MeOH; 6 analyses total) and averaged; error bars = SD (analytical).

S4). Its product, 6PPDq, reached a slightly lower annual mean of $4.8 \pm 4.1 \text{ ng m}^{-2} \text{ day}^{-1}$ but fluctuated more strongly throughout the year. Contrasting its precursor, 6PPDq had higher deposition rates in spring and summer ($5.6 \pm 5.91 \text{ ng m}^{-2} \text{ day}^{-1}$) than in autumn and winter ($3.2 \pm 2.05 \text{ ng m}^{-2} \text{ day}^{-1}$). Spring and summer were characterized by higher mean temperatures ($13.5 \pm 5.9 \text{ }^{\circ}\text{C}$) and lower relative humidity ($73.5 \pm 6.2\%$) (Figure S4) compared to autumn and winter. This likely reflects the enhanced photochemical transformation of 6PPD to 6PPDq under spring and summertime conditions. IPPD and IPPDq showed the same seasonal variation as indicated by their respective Pearson correlation coefficients, $r = 0.76$ (6PPD vs IPPD) and $r = 0.85$ (6PPDq vs IPPDq). The markers IPPD and IPPDq showed deposition rates with annual means of 3.9 ± 3.7 and $3.8 \pm 2.6 \text{ ng m}^{-2} \text{ day}^{-1}$, respectively, placing them in the same order of magnitude as the 6PPD-derived markers. Furthermore, IPPD deposition showed a pronounced peak in the autumn/early winter, averaging $6.26 \pm 1.28 \text{ ng m}^{-2} \text{ day}^{-1}$ across November, December, and January, with its highest monthly rate observed in November. DPG, which is structurally distinct from the antioxidants and serves primarily as a vulcanization agent in tire manufacturing, was consistently present but at lower concentrations with an annual average of $1.6 \pm 0.87 \text{ ng/m}^2/\text{day}$. DPPD remained below the detection limit throughout the year.

The seasonality can also be seen in the relative contributions of the detected TRWP markers: In spring and summer, 6PPD accounted for 20.4%, 6PPDq for 32.6%, IPPDq for 26.0%, IPPD for 12.3%, and DPG for 9.1%. Combined, quinones 6PPDq and IPPDq made up more than half of the total analyzed TRWP marker mass in the summer (58.6%). In winter, it was only 24.1%. Our case study reveals a seasonal shift in marker composition, from quinone-dominated in the warm season to parent-compound-dominated in the cold season. This appears to be primarily driven by local meteorology, mirroring the transition from a warm, oxidative atmosphere to cold, and humid conditions that enhance deposition. Throughout the study period, winds were predominantly from the west-southwest ($264.7^{\circ} \pm 4.9^{\circ}$; Figure S4), indicating relatively stable source regions. Thus, the observed seasonality is likely governed by atmospheric photooxidation and deposition, while local or regional sources could be relatively steady in time.

3.8. Degree of Marker Oxidation

PPDs are added to tire wear material as antioxidants. The unsaturated nature of the PPDs makes them reactive toward atmospheric oxidants, which makes them effective ozone scavengers protecting the tire wear from weathering. Particularly, the transformation of 6PPD to 6PPDq is crucial, as the latter can be a significant environmental burden.^{10,70–74} Furthermore, it complicates the use of the marker as it potentially transforms during production of TRWP and during transport in the atmosphere (e.g., Cao et al., 2022; Helm et al., 2024). Thus, in Figure 10, we compared the degree of oxidation as indicated by the relative fraction of 6PPD and 6PPDq with respect to the total mass of both markers.

The relative ratio of 6PPD and 6PPDq varied across all samples from the reference material (1% 6PPDq of 6PPD + 6PPDq) and shredded tires (15%), to surface material (10%), to emission samples collected during driving (26%), and to UFP in rural (46%) and urban (51%) air. Seasonal differences were observed in deposition samples collected at an urban

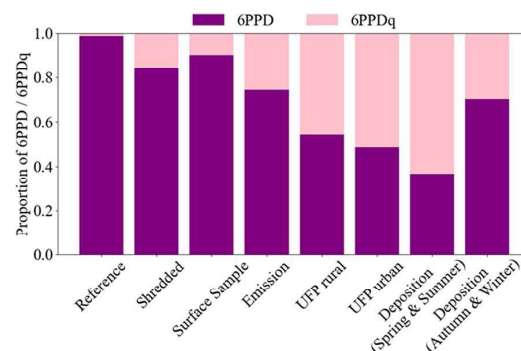


Figure 10. Degree of oxidation presented a relative fraction of 6PPD and 6PPDq with respect to the total mass of both compounds across different samples. The chart shows the mean proportions of 6PPD (purple) and 6PPDq (pink) for each sample type.

location in spring and summer (63%) and autumn and winter (30%). The elevated relative abundance of 6PPDq in environmental samples suggests that atmospheric oxidative processes continue considerably beyond the point of emission. This indicates ongoing degradation of precursor PPDs during atmospheric transport, aging, and scavenging. While this observation is essential for understanding the atmospheric fate of the TRWP marker, it also has direct ecological consequences, as these compounds enter terrestrial and aquatic ecosystems via atmospheric deposition, causing environmental damage. This has been documented for 6PPDq for surface water, soils, and vegetation.^{15,42,75–80} Based on our results from the deposition analysis, we can calculate the mass of 6PPDq, which entered the ground over the course of one year as $1.7 \pm 0.5 \mu\text{g m}^{-2} \text{ year}^{-1}$. For comparison, storms near roads can be followed by concentration peaks of up to 200 ng L^{-1} in a city creek.⁸¹ Yet the deposition is only one pathway adding to surface waters, such as lakes and rivers. Here, ecosystem impact is currently discussed, e.g., in studies testing the acute toxicity of 6PPDq on sensitive salmonids and other organisms with concentrations in water from 0.04 to 1 to more than $12 \mu\text{g L}^{-1}$.^{52,81–83}

3.9. Possible Implications of the Observed Variability in TRWP Markers

Our results reveal substantial variability in both absolute TRWP marker concentrations and their relative mass composition. Influencing factors are the tire material origin and history, tire–road interactions during TRWP production, and the degree of environmental exposure and atmospheric aging. We highlighted the presence of TRWP markers in airborne UFP and total deposition. TRWP markers in UFP were mostly driven by their sources and increased with urbanization. We noticed a great potential for oxidation in all atmospheric samples, which was highest in summertime atmospheric deposition. Interestingly, in none of the deposition samples could we find the marker DPPD, despite its presence in most of the tested tires, emissions, and airborne UFP.

Concluding, we can make three final statements: First, the usage of markers for tracing, identifying, and quantifying TRWP is a valuable approach for highlighting their presence in the environment, which however needs to be well characterized and understood. Second, the marker's transformation could be a potential treasure for characterizing their history

and fate, particularly if the products could be studied in even more detail. Third, determining the variability in TRWP markers will certainly increase knowledge about the fate of the often unfortunately toxic products in the environment.

■ ASSOCIATED CONTENT

Data Availability Statement

Data will be made available upon request.

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.5c12735>.

Detailed chemical structures and IUPAC names; full HPLC–MS method parameters and representative chromatograms; statistical validation of size effects (ANOVA); calibration, LOD/LOQ data, spike recoveries, and blank subtraction details; replicate design and metadata for analyzed samples, including tire surface specifications and UFP site descriptions; relative composition data across sample types; regression fits, ambient concentration boxplots, and meteorological summaries (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Elisabeth Eckenberger — Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, 95447 Bayreuth, Germany; orcid.org/0009-0006-7590-3257; Email: Elisabeth.eckenberger@uni-bayreuth.de

Anke C. Nölscher — Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, 95447 Bayreuth, Germany; Present Address: Institute of Climate and Energy Systems, ICE-3: Troposphere, Forschungszentrum Jülich GmbH, 52428 Jülich, Germany and Institute of Geophysics and Meteorology, University of Cologne, 50969 Cologne, Germany; Email: a.noelscher@fz-juelich.de

Authors

Myriam Younes — Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, 95447 Bayreuth, Germany

Tobias Mayer — Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, 95447 Bayreuth, Germany

Manuel Loeber — Department of Chemical Kinetics and Analytics, Institute of Combustion Technology, German Aerospace Center (DLR), 70569 Stuttgart, Germany; orcid.org/0000-0002-4492-952X

Linda Bondorf — Department of Chemical Kinetics and Analytics, Institute of Combustion Technology, German Aerospace Center (DLR), 70569 Stuttgart, Germany

Tobias Schripp — Department of Chemical Kinetics and Analytics, Institute of Combustion Technology, German Aerospace Center (DLR), 70569 Stuttgart, Germany

Sarmite Kernchen — Department of Animal Ecology I and BayCEER, University of Bayreuth, 95447 Bayreuth, Germany; orcid.org/0000-0003-2082-7307

Christian Laforsch — Department of Animal Ecology I and BayCEER, University of Bayreuth, 95447 Bayreuth, Germany

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.est.5c12735>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the Landesanstalt für Umwelt Baden-Württemberg (LUBW), Karlsruhe, and Dr. Harald Creutzmacher and Dipl.-Ing. Anke Veith for providing support, analytical standards, and the Evonik Industries tire reference material. We also thank André Wehmeier and Prof. Dr. Menzel (Evonik Industries) for producing the tire reference material used in this study. We further acknowledge Dr. Till Rehm (Umweltforschungsstation Schneefernerhaus), Dr. Werner Thomas (DWD), Dr. Adam Mühlbauer (Bayerisches Landesamt für Umwelt (LfU)), and Julius Seidler (University of Bayreuth) for their support and for facilitating access to the respective UFP sampling sites. For support and supply of reference material, we acknowledge Daniel Wagner, Seema Agrawal (Z01), and Continental Reifen Deutschland GmbH. We thank the German Weather Service (DWD) for the provision of meteorological data. This project is financed by the Bavarian State Ministry of the Environment and Consumer Protection and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) SFB 1357 - project no. 391977956. The article processing charges for this open-access publication were covered by the Forschungszentrum Jülich.

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Supporting Information

About the variability of tire wear marker components in air: from emissions to atmospheric samples

Elisabeth Eckenberger¹, Myriam Younes¹, Tobias Mayer¹, Manuel Loeber², Linda Bondorf², Tobias Schripp², Sarmite Kernchen³, Christian Laforsch³, Anke C. Nölscher¹, §,*

¹ Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, 95447 Bayreuth, Germany

² Department of Chemical Kinetics and Analytics, Institute of Combustion Technology, German Aerospace Center (DLR) 70569 Stuttgart, Germany

³ Department of Animal Ecology I and BayCEER, University of Bayreuth, 95447 Bayreuth, Germany

§ now at: Institute of Climate and Energy Systems, ICE-3: Troposphere, Forschungszentrum Jülich GmbH, 52428 Jülich, Germany, and Institute of Geophysics and Meteorology, University of Cologne, 50969 Cologne, Germany
Correspondence to: Elisabeth Eckenberger (Elisabeth.eckenberger@uni-bayreuth.de), Anke C. Nölscher (a.noelscher@fz-juelich.de)

Chemical & methods

- **Table S1:** Chemical structures & IUPAC names of DPG, IPPD, IPPDq, 6PPD, 6PPDq, DPPD.
- **Table S2:** HPLC–MS methods (ACN vs. MeOH): column, gradients, monitored SIM ions (ESI+), dwell times, detector settings.
- **Figure S1:** SIM TICs for the six markers (MeOH top, ACN bottom).

Statistics & validation

- **Table S3:** One-way ANOVA for size effects in shredded bulk fractions (per marker; F, df, p, ω^2 ; BH–FDR).
- **Table S4:** Calibration & limits (slope; R^2 ; LOD/LOQ (ng), LOD_{col}/LOQ_{col} (ng on-column), LOD_{Air} (ng m⁻³), LOD_{Dep} (ng m⁻² d⁻¹)).
- **Table S5:** Spike recoveries by compound and method (mean ± SD).
- **Table S6:** Blank on-column masses by blank type (HPLC/solvent, procedural, field/filter; mean ± SD, pg).
- **Text S1:** Blank subtraction.
- **Table S7:** Replicate design by dataset (field vs. technical; error bars used).

Datasets & metadata

- **Table S8:** Description of analyzed sample types (origin, purpose, key findings).
- **Table S9:** Specifications of 11 tire surface samples (make, year, model).
- **Table S10:** UFP site overview (coordinates, sampling period, land use, altitude, road proximity).
- **Table S11:** Meteorological summary for UFP sampling periods (DWD daily records; proxy stations noted).
- **Table S12:** Relative composition (% of total marker mass) across sample types.

Additional figures

- **Figure S2:** Regression of extracted marker mass vs. reference material mass (MeOH/ACN; through-origin fits).
- **Figure S3:** Boxplots of ambient marker concentrations at six sites.
- **Figure S4:** Monthly meteorology near the deposition site (Mar 2023–Feb 2024).

Table S1 Chemical structures of the six analyzed tire-associated marker compounds: DPG, IPPD, IPPDq, 6PPD, 6PPDq, and DPPD.

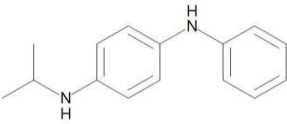
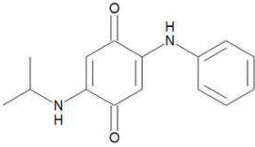
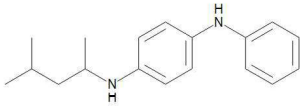
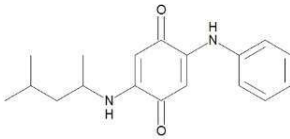
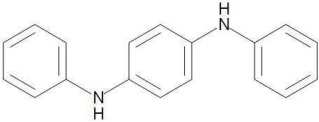
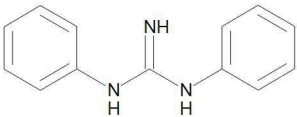
Name	Structure
IPPD N-isopropyl-N'-phenyl-p-phenylenediamine	
IPDDq IPPD-quinone	
6PPD N-(1,3-dimethylbutyl)-N'-p-phenylenediamine	
6PPDq 6PPD-quinone	
DPPD N,N'-diphenyl-p-phenylenediamine	
DPG N,N'-Diphenylguanidine	

Table S2 Overview of the HPLC-MS methods used for the quantification of marker compounds in all TWP samples, including gradient settings, mobile phase composition (MeOH and ACN), monitored ions, and detection conditions.

Parameter	ACN method HPLC-MS pos	MeOH method HPLC-MS pos
Analytical column	Gemini 5u C18 110A (150 mm x 4.6 mm, 5 µm) S/NO 354356-8	Gemini 5u C18 110A (150 mm x 4.6 mm, 5 µm) S/NO 354356-8
Column temperature	30 °C	30 °C
Autosampler temperature	23 °C	23 °C
Injection volume	20 µL	20 µL
Flow rate	0.3-0.5 mL/min	0.3-0.5 mL/min
Gradient	A) 80% ACN, B) 4 mM HCOOH 0 min 5% A 2 min 10% A 7 min 75% A 15 min 100% A 20 min 50% A 23 min 5% A	A) 80% MeOH, B) 4 mM HCOOH 0 min 50% A 3 min 80% A 12 min 100% A 18 min 90% A 20 min 50% A 25 min 75% A
Detector	MSD	MSD
	Time ESI(+)-m/z-ions Dwell times 0 min 124 (NA) 56 212 (DPG) 56 227 (IPPD) 56 269 (6PPD) 56 56 257 (IPPDq) 14 min 261 (DPPD) 71 299 (6PPDq) 71 71	Time ESI(+)-m/z-ions Dwell times 0 min 124 (NA) 56 212 (DPG) 56 227 (IPPD) 56 269 (6PPD) 56 56 257 (IPPDq) 12 min 261 (DPPD) 71 299 (6PPDq) 71 71

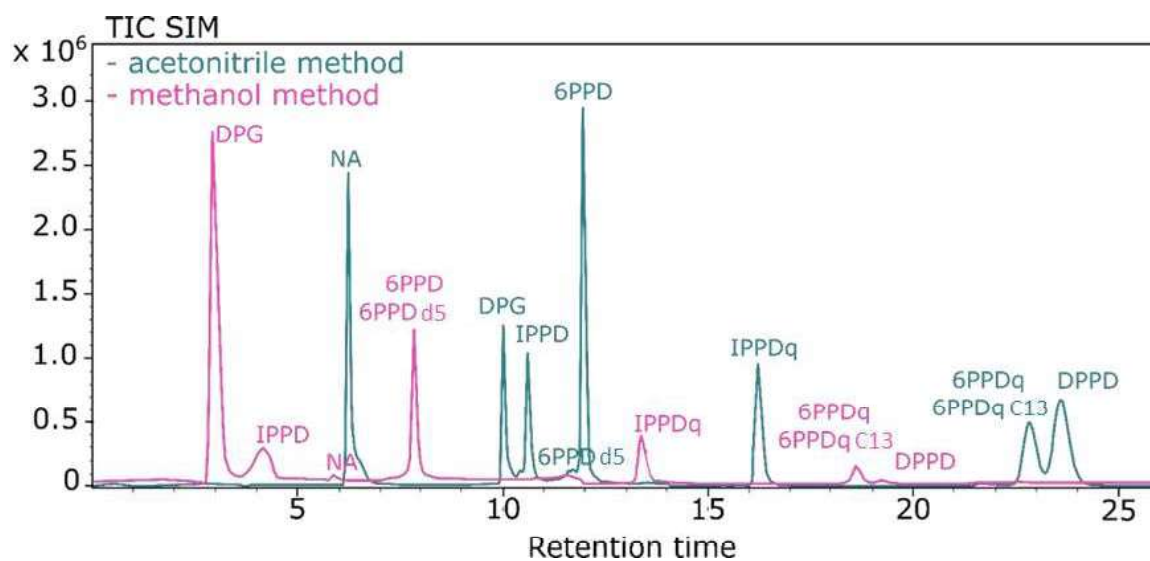


Figure S1 Total ion chromatograms (TIC) in SIM mode of the six marker compounds obtained using MeOH (top) and ACN (bottom) as eluents, plotted as a function of retention time.

Table S3. One-way ANOVA results for size effects in shredded bulk tire fractions.

Marker	Size groups (n)	Primary test	Transform	F	df1	df2	p	Effect size (ω^2)	Multiple comparisons
DPG	20–50 (5); 50–75 (5); 75–200 (4)	One-way ANOVA	none	1.403	2	13	0.2807	0.048	BH-FDR across markers
6PPD	20–50 (5); 50–75 (5); 75–200 (4)	One-way ANOVA	none	1.941	2	11	0.1897	0.118	BH-FDR across markers
6PPDq	20–50 (5); 50–75 (4); 75–200 (5)	One-way ANOVA	none	3.263	2	11	0.0771	0.244	BH-FDR across markers

Table S4 Calibration parameters, limits of detection (LOD), limits of quantification (LOQ) and corresponding LODs in air and deposition samples for six TWP marker compounds using two HPLC-MS methods (MeOH and ACN as mobile phase). Slopes and R² values are based on linear regression through the origin.

Meth od	Comp ound	Slope	R ²	LO D [ng]	LO Q [ng]	LOD _c ot [ng]	LOQ _c ot [ng]	LOD _{Air} [ng m ⁻³]	LOD _{Dep} [ng m ⁻² d ⁻¹]
ACN	6PPD	42078.19	0.9786	1.85	6.17	0.0370	0.123	0.0428	1.21
ACN	6PPD _q	16403.71	0.9943	1.98	6.60	0.0396	0.132	0.0458	1.30
ACN	DPG	40687.45	0.9981	1.17	3.90	0.0234	0.0780	0.0271	0.769
ACN	DPPD	26362.30	0.9604	1.15	3.83	0.0230	0.0767	0.0266	0.756
ACN	IPPD	18577.08	0.9535	1.99	6.63	0.0398	0.132	0.0461	1.31
ACN	IPPD _q	20112.79	0.9925	2.08	6.93	0.0416	0.139	0.0481	1.37
MeO H	6PPD	21767.08	0.9891	2.02	6.73	0.0404	0.1347	0.0468	1.33
MeO H	6PPD _q	3452.12	0.9920	2.12	7.07	0.0424	0.141	0.0491	1.39
MeO H	DPG	101074.7 5	0.9958	0.63	2.10	0.0126	0.0420	0.0146	0.414
MeO H	DPPD	1856.74	0.9379	2.34	7.80	0.0468	0.156	0.0542	1.54
MeO H	IPPD	24012.96	0.9664	2.01	6.70	0.0402	0.134	0.0465	1.32
MeO H	IPPD _q	10228.34	0.9930	2.10	7.00	0.0420	0.140	0.0486	1.38

Table S5 Filter spike recoveries by compound and method (mean ± SD).

Method	Compound	Recovery
ACN	6PPD	69±8%
ACN	6PPD _q	73±5%
ACN	DPG	99±7%
ACN	DPPD	83±6%
ACN	IPPD	77±7%
ACN	IPPD _q	70±4%
MeOH	6PPD	75±7%
MeOH	6PPD _q	81±7%
MeOH	DPG	102±6%
MeOH	DPPD	78±6%
MeOH	IPPD	67±7%
MeOH	IPPD _q	71±5%

Table S6 Blank on-column masses by compound and blank type. Values are mean $\pm$ SD for HPLC/solvent, procedural (extraction), and field/filter blanks; no matrix normalization is applied in this table.

Compound	HPLC/Solvent blank [pg]	Procedural blank [pg]	Field/Filter blank [pg]
6PPD	1.13 $\pm$ 0.7	3.82 $\pm$ 1.3	5.18 $\pm$ 2.2
6PPDq	2.88 $\pm$ 1.1	4.73 $\pm$ 1.6	8.04 $\pm$ 2.8
DPG	0	0.201 $\pm$ 0.04	0.140 $\pm$ 0.03
DPPD	6.33 $\pm$ 1.9	7.98 $\pm$ 2.1	6.15 $\pm$ 1.9
IPPD	5.24 $\pm$ 1.7	5.72 $\pm$ 2.2	4.01 $\pm$ 1.7
IPPDq	6.25 $\pm$ 0.8	7.02 $\pm$ 1.8	8.04 $\pm$ 3.4

Text S1 Blank subtraction and reporting rules

Blank types and matching. For each batch we analyzed instrument/solvent blanks (HPLC mobile phase), procedural/extraction blanks, and field/filter blanks for every compound and method (ACN/MeOH).

Subtraction rule

Quantification used net peak areas after subtraction of the batch-matched procedural blank:

- Filter-based matrices (air, deposition): the batch-matched field/filter blank peak area was subtracted from each sample:

$$A_{net}^{Air/Dep} = A_{Sample} - \bar{A}_{field/filter\ blank, \text{ batch}}$$

- Raw material (bulk rubber/tread) extracts: the batch-matched procedural blank (no filter) was subtracted:

$$A_{net}^{sample} = A_{Sample} - \bar{A}_{procedural\ blank, \text{ batch}}$$

Instrument/solvent blanks served to verify carry-over/background and were not subtracted. If a field/filter blank was unavailable for a given batch, we used the procedural blank as fallback for filter-based samples.

Table S7 Replicate design by dataset.

Dataset	Field replicates (n)	Technical replicates per field sample	Error bars to plot
Reference	4	2 (duplicate analyses: ACN & MeOH mobile phases)	Mean $\pm$ SD (field)
Shredded (bulk)	4	2 (MeOH & ACN)	Mean $\pm$ SD (field)
Testbed Tire A unworn	4	2 (MeOH & ACN)	Mean $\pm$ SD (field)
Testbed Tire A size-segregated (ELPI)	1 filter per size bin	3 analyses per mobile phases $\rightarrow$ 6 per bin	Mean $\pm$ SD (analytical) per bin
Testbed Tire B Composition	4	2 (MeOH & ACN)	Mean $\pm$ SD (field)
Testbed Tire B Emission	4	2 (MeOH & ACN)	Mean $\pm$ SD (field)
Road setup Tire C	4	2 (MeOH & ACN)	Mean $\pm$ SD (field)
Surface	1 per surface	3 analyses per mobile phases $\rightarrow$ 6 per surface	Mean $\pm$ SD (analytical)
UFP	6	2 (MeOH & ACN)	Mean $\pm$ SD (field)
Deposition (monthly)	1 sample per month (12 months)	3 analyses per mobile phases $\rightarrow$ 6 per month	Mean $\pm$ SD (analytical) per month

Table S8 Description of all analyzed sample types, including sample origin, analytical purpose, and key findings.

Tire wear samples type		Tire type/ origin	Purpose of analysis	Key findings/ Data
1	Reference material (Evonik)	Lab reference material with known DPG and 6PPD content	Evaluate extraction and analytical method performance with known composition	Extraction efficiencies: 6PPD ~64.2%, DPG ~44.8%
2	Shredded bulk tire (MRH Gummihohl Type K0002)	Shredded truck tires from vulcanized NR/SBR blends 1) 20-50 µm 2) 50-75 µm 3) 50-200 µm	Test method reproducibility and particle-size effects on marker extraction	6PPD: 439.3–591.5 ng/mg, 6PPDq: 77.0–132.0 ng/mg, DPG: 19.8–26.5 ng/mg (No significant differences between sizes, trend: increasing extraction efficiency with decreasing size)
3	Used tire surface samples	Used tire tread of passenger car tires with environmental exposure	Assess real-world surface-exposed marker variability	Large variability across tires, no clear link to tire type/age
4	Tests and particles	Testbed tire A: particulate emissions from a BMW i3 Testbed tire B: particulate emissions from Continental tire	Link observed primary particle emissions to the original pristine tire wear material	Emission vs. pristine tire: 6PPD loss ~90% 6PPDq increase
5	Road emission samples	ZEDU-1 (tire C): Vehicle driving on Bosch test track under real-world conditions	Bridge between tire composition and road emissions under real conditions	6PPD: 2749→282→167 ng/mg (unworn→coarse→fine), 6PPDq ↑ in fine PM, DPG and DPPD decreased
6	Airborne particulate matter (UFP)	Six environmental sites across Bavaria (urban, rural, alpine)	Assess ambient levels and spatial trends of TRWP-markers in UFP	6PPD range: 0.01–0.55 ng/m ³ (increasing with urbanity), site-specific marker composition observed
7	Total atmospheric deposition samples	Urban semi-industrial site in Bayreuth, monthly collection over the course of a year	Evaluate seasonal deposition and atmospheric transformation of TRWP markers	6PPD mean: 5.2 ng/m ² /day, 6PPDq mean: 4.8 ng/m ² /day; Quinones dominated in spring/summer (>50%)

Table S9 Specifications of the 11 tire surface samples, including manufacturer, production year, and model.

Surface Sample	Year of tire production	Manufacturer	Tire model
1	2019	Michelin	Green
2	2012	Continental	Eco Contact
3	2022	Michelin	Green Primacy 3
4	2021	Michelin	Primacy 4
5	2021	Pirelli	Scorpion
6	2017	Hankook	Kinergy
7	2012	Continental	Conti Sport Contact 3
8	2022	Goodyear	Eagle F1
9	2021	Continental	EcoContact 6
10	2022	Michelin	Pilot Sport 4 SUV
11	2022	Michelin	Pilot Sport 4 SUV

Table S10 Overview of the six UFP sampling sites in Bavaria (2023). Coordinates sampling windows, qualitative land use, site altitude (m a.s.l.), and qualitative proximity to major roads are listed for each site. Sites were selected to span an urban–background gradient.

Site (short name)	Coordinates	Sampling window (2023)	Land use (qualitative)	Site altitude (m a.s.l.)	Proximity to major roads (qualitative)
Zugspitze	47.41645 N, 10.97940 E	Jun 02–20	Alpine high-mountain terrain	2 650	No major road within several km (remote alpine terrain)
Waldstein	50.14333 N, 11.86381 E	Jul 04–16	Mature spruce forest	875	Forest interior; distant from primary roads
Hohenpeißenberg	47.80143 N, 11.00951 E	Jul 17–31	Rural hilltop; forests & meadows	977	Limited local traffic; no primary roads adjacent
Freising	48.38244 N, 11.75177 E	May 20–Jun 01	Compact urban fabric, mixed residential/traffic	448	Within the A92 corridor that serves Munich Airport; near airport feeder routes
Regensburg	49.00040 N, 12.09801 E	Aug 08–22	University of Regensburg campus	337	Campus block bordered by major roads
Augsburg	48.35801 N, 10.90699 E	Sep 27–Oct 11	Dense city centre around Königsplatz	494	Surrounded by multiple high-traffic arterials

Table S11 Meteorological summary for the UFP sampling periods at six Bavarian sites. Data source: German Weather Service (Deutscher Wetterdienst, DWD). Values are computed from daily data over the site-specific sampling days: precipitation and sunshine are period totals (mm, h), while temperature, wind speed, and relative humidity are reported as mean $\pm$ SD of daily values. The DWD station in Hof is used to represent synoptic conditions for Waldstein, and in Munich Airport is used to represent synoptic conditions for Freising.

Site	Total precipitation (mm)	Total sunshine duration (h)	Mean temperature, daily mean (°C)	Daily maximum temperature (°C)	Daily minimum temperature (°C)	Mean wind speed (m s ⁻¹)	Mean relative humidity (%)
Zugspitze	6.3	56.9	2.15 $\pm$ 0.84	6.25 $\pm$ 1.33	0.13 $\pm$ 0.74	2.37 $\pm$ 0.31	82.00 $\pm$ 4.43
Waldstein (Hof)	2.6	63.4	19.48 $\pm$ 3.18	24.92 $\pm$ 3.89	13.87 $\pm$ 3.05	3.37 $\pm$ 0.92	54.33 $\pm$ 4.63
Hohenpeißenberg	44.1	36.1	16.48 $\pm$ 4.66	21.40 $\pm$ 4.99	12.70 $\pm$ 3.94	4.37 $\pm$ 1.27	76.33 $\pm$ 12.16
Regensburg	52.1	45.0	19.18 $\pm$ 4.11	26.48 $\pm$ 5.58	13.93 $\pm$ 3.94	1.77 $\pm$ 0.60	76.67 $\pm$ 8.41
Augsburg	0.0	52.2	13.10 $\pm$ 3.13	21.42 $\pm$ 3.90	5.73 $\pm$ 2.54	1.82 $\pm$ 0.67	79.67 $\pm$ 3.98
Freising (Munich Airport)	0.0	77.3	16.88 $\pm$ 1.50	23.40 $\pm$ 1.98	9.10 $\pm$ 1.58	3.30 $\pm$ 1.10	63.17 $\pm$ 7.71

Table S12 Relative composition of six tire-associated chemical markers across different sample types, expressed as percentage contribution to the total quantified marker mass per sample.

Class	Sample	DPG [%]	IPPD [%]	IPPDq [%]	6PPD [%]	6PPDq [%]	DPPD [%]
Reference	0	63.69	0	0	35.83	0.48	0
Shreddered tire	20-200 μ m	3.89	0	0	77.67	18.44	0
Testbed Emission	Tire A, Unworn	0.08	0.00	0.00	31.85	0.90	67.17
Testbed Emission	Tire A, Size Segregated TRWP	0.15	0.00	0.00	1.09	23.96	74.79
Testbed Emission	Tire B Tire Composition	50.00	0.00	0.00	50.00	0.00	0.00
Testbed Emission	Tire B TWP	51.30	0.00	0.00	48.30	0.40	0.00
Road Emission	Tire C Unworn tire	1.49	0	0	96.23	0.45	1.83
Road Emission	Tire C Coarse particles	7.03	0	0	81.11	8.48	3.38
Road Emission	Tire C Fine Particles	6.15	0	0	74.55	14.33	4.97
Surface Sample	1	33.23	0.22	1.18	61.51	2.8	1.05

Surface Sample	2	18.89	0.07	0.01	73.96	0.76	6.3
Surface Sample	3	37.12	0.04	1.45	55.29	4.77	1.34
Surface Sample	4	32.55	4.35	1.07	60.44	0.89	0.7
Surface Sample	5	76.84	0.04	1.49	15.16	5.01	1.47
Surface Sample	6	77.17	0.05	2.18	9.5	7.32	3.78
Surface Sample	7	54.23	0.09	0.72	27.99	4.82	12.15
Surface Sample	8	46.2	0	0.02	46.74	1.45	5.58
Surface Sample	9	16.45	0.05	0.06	66.83	0.75	15.86
Surface Sample	10	23.53	0.19	1.13	72.97	1.65	0.53
Surface Sample	11	19.76	1.63	1.13	75.21	1.98	0.29
UFP	Zugspitze	16.08	13.18	40.85	10.66	13.46	5.76
UFP	Waldstein	13.86	21.03	17.03	22.34	15.24	10.51
UFP	Hohenpeißenberg	8.44	20.65	19.96	21.53	18.45	10.97
UFP	Regensburg	1.8	12.86	32.91	17.91	25.03	9.49
UFP	Freising	2.37	23.58	9.65	20.86	16.74	26.8
UFP	Augsburg	1.72	16.33	18.18	24.02	19.63	20.13
Deposition	Mar	5.27	9.09	17.43	23.08	45.13	0
Deposition	Apr	9.22	7.73	28.99	15.48	38.58	0
Deposition	May	8.23	19.89	20.5	26.28	25.1	0
Deposition	Jun	18.74	14.26	26.9	23.76	16.34	0
Deposition	Jul	5.72	8.83	28.78	20.52	36.15	0
Deposition	Aug	14.35	17.64	26.51	19.88	21.62	0
Deposition	Sep	7.21	23.51	30.98	20.87	17.43	0
Deposition	Oct	8.35	23.94	19.49	25.92	22.3	0
Deposition	Nov	6.3	37.85	9.84	36.63	9.38	0
Deposition	Dec	10.37	33.07	7.75	41.93	6.88	0
Deposition	Jan	6.61	36.75	2.28	48.89	5.47	0
Deposition	Feb	8.28	11.93	9.67	47.51	22.61	0

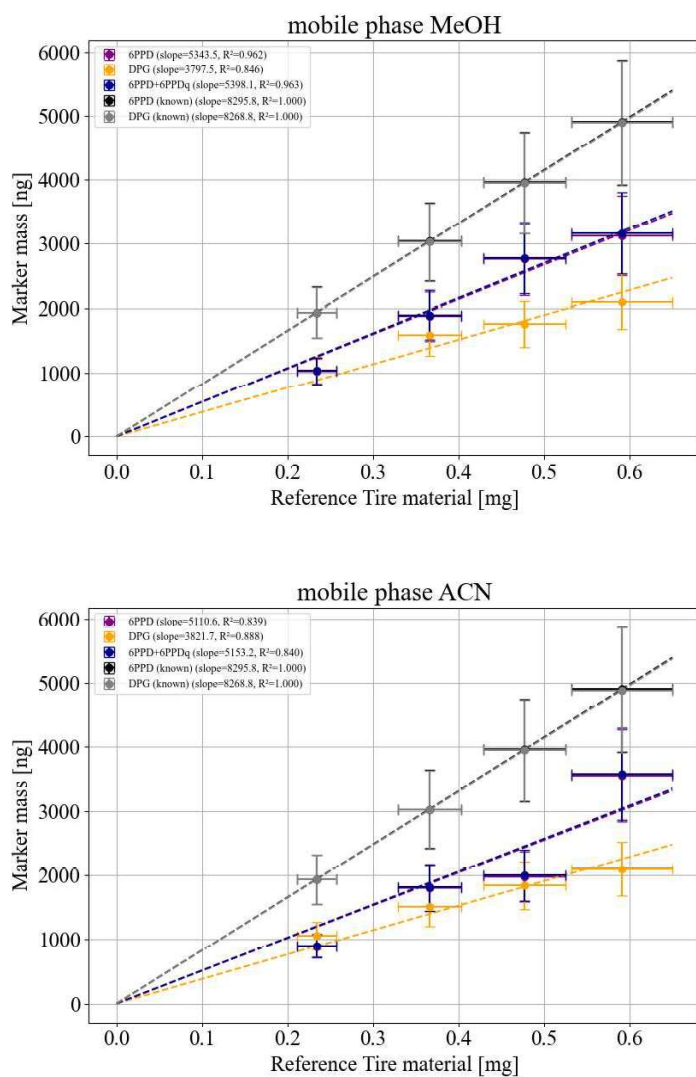


Figure S2 Regression analysis of extracted marker mass versus reference tire material mass for MeOH (top) and ACN (bottom) as extraction solvents. Marker compounds include 6PPD, DPG, and 6PPD+6PPDq, as well as their respective known spiked concentrations (known). Each marker was evaluated using a linear fit constrained through the origin.

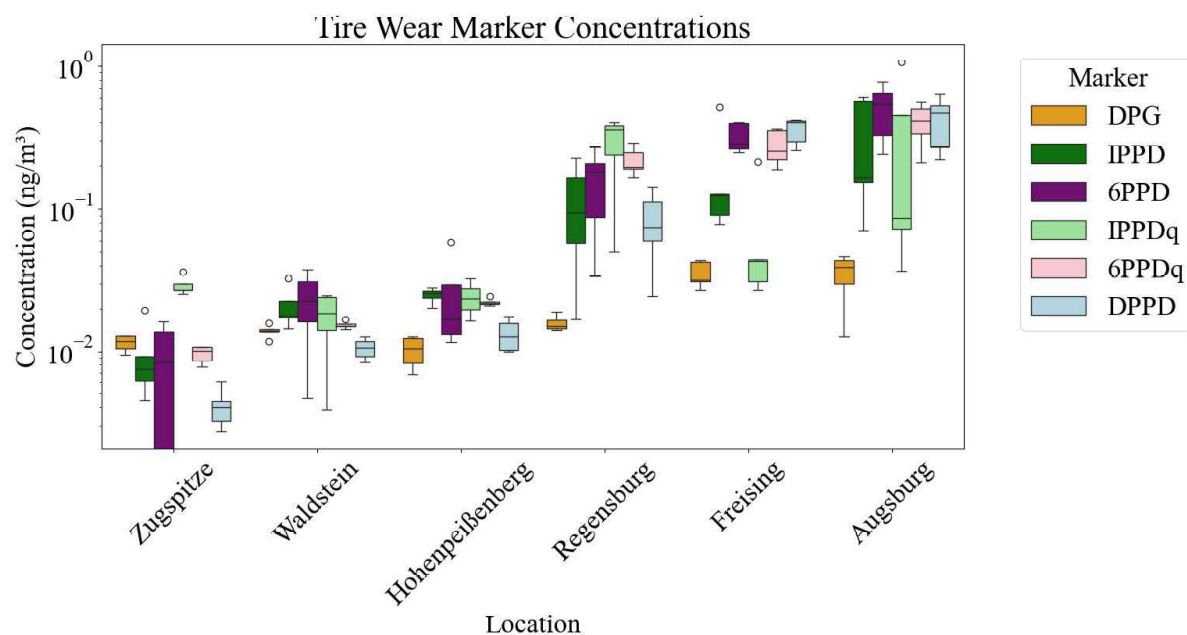


Figure S3 Boxplots of tire wear marker concentrations (DPG, IPPD, IPPDq, 6PPD, 6PPDq, and DPPD) in ambient air samples collected at six sites in Southern Germany (Zugspitze, Waldstein, Hohenpeißenberg, Regensburg, Freising, and Augsburg).

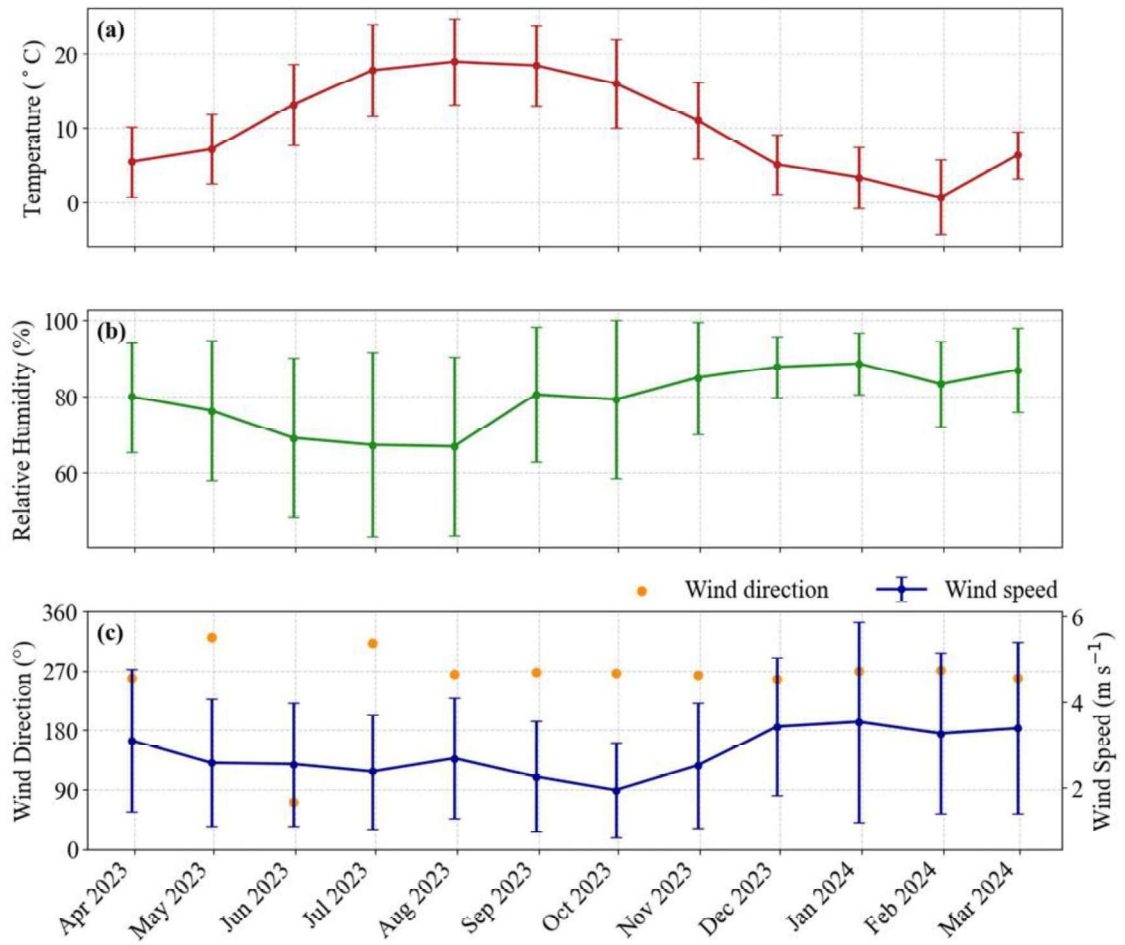


Figure S4 Monthly mean meteorological conditions used to contextualize tyre-wear particle deposition for the period March 2023–February 2024 (Data source: German Weather Service (Deutscher Wetterdienst, DWD)). Panel (a) shows monthly mean air temperature and panel (b) monthly mean relative humidity, both derived from hourly observations of the DWD at station 00320 (Heinersreuth-Vollhof). Panel (c) shows monthly mean wind direction (left y-axis) and wind speed (right y-axis) based on hourly data from the DWD at station 01357 (Fichtelberg/Oberfranken-Hüttstadt). For temperature, relative humidity, and wind speed, monthly means were calculated as the arithmetic mean of all hourly values within each calendar month; error bars represent the corresponding standard deviation (1σ) of these hourly data. Monthly mean wind direction was obtained from the hourly direction measurements by vector (circular) averaging of the unit wind vectors and converting the resulting mean vector back to degrees.

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7. Conference Contributions

2022 European Geoscience Union. Oral presentation. Title of the presentation: Catch me if you can: Evaluating sampling methods for airborne ultrafine particles' composition analysis

2022 8th UFP Conference: International Symposium on Ultrafine Particles - Air Quality and Climate Oral presentation. Title of the presentation: Tuning sampling and analysis strategies for UFP: Laboratory and field tests with selected PAH-marker components

2022 Symposium Ultrafeinstaub. Poster presentation. Title of the poster: Tuning sampling and analysis strategies for UFP Laboratory and field tests with selected anthropogenic and biogenic marker components.

2023 European Aerosol Conference. Oral presentation. Title of the presentation: UPSCALE: A novel approach to sample ultrafine particles in the atmosphere for offline chemical analysis.

2024 ACTRIS Science Conference 2024. Oral presentation. Title of the presentation: From Urban Haze to Alpine Gaze: tracing Linkages between Black Carbon and PAH in UFP

8. Acknowledgements

This work would not have been possible without the support of many people. I would like to thank everyone who has accompanied me over the past years, academically and personally.

First and foremost, I would like to thank Prof. Dr. Anke Nölscher, who made the project on which I pursued my PhD possible in the first place. I am deeply grateful for her intensive, continuous, and consistently constructive support throughout the project. In particular, I appreciate the timely impulses, the critical questions at exactly the right moments, and her support with all publications and presentations. I also sincerely value her steadiness and understanding when things did not go according to plan, and the fact that she always had an open ear, both for scientific questions and for the day-to-day challenges that inevitably come with a PhD.

My thanks also go to the entire Atmospheric Chemistry group from 2021 to 2024. Even though we were a small group and it no longer exists in that form, I remember the working atmosphere, mutual support, and team spirit very fondly. Thank you to Finja, Ines, Myriam, Andrej, Agnes, and Julius. A special thanks for always looking after everyone's wellbeing, whether it was Finja's vegan cookies, Ines's tea collection, or Agnes's home-grown vegetables. Thank you for being such great colleagues and friends.

I also want to thank the many collaborators who made this project possible, and everyone who supported me both logistically and scientifically while I carried out measurements across Bavaria.

Beyond the lab, I am incredibly lucky to have a circle of friends who kept me grounded. Sharing the highs and lows of the PhD journey with most of you made all the difference. Even though we were not at the same university, the conversations, the occasional rant when things did not work out, and the joyful evenings kept me going. Thank you to Marco, Rafi, Lucas, Kevin, Anne, Theo, Katha, and everyone else who knows they are part of this as well.

I also want to thank my Munich people, who have been part of my life for much longer and, hopefully, always will be. Thank you, Maxi, Alex, Stefan, Mik, and Felix with the newest member of the club, Louis. As well as everyone else who is just as much included. Speaking of new members of the club, a special thank you to Dr. Ferdinand Krieter. I'm curious what you will tease me about now that it can no longer be the missing "Dr." title. Thank you for proofreading, for giving me a nudge at the right moments, for your honesty, for our Mimosa-walks through the Englischer Garten, and for our talks about astrophysics on scales far larger (and sometimes far smaller) than 100 nm.

Last but definitely not least, I want to thank my parents and my brother. Thank you for everything. I could always count on your support in every way, and it means more than I can put into words.

Grammarly was used to improve language and readability.

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