Ambient ultrafine particles: classification, chemical characterization, and quantification of ubiquitous PAHs via DTD-GC×GC-TOFMS

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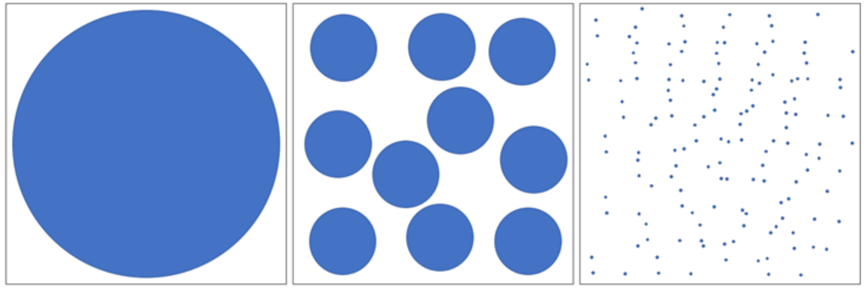
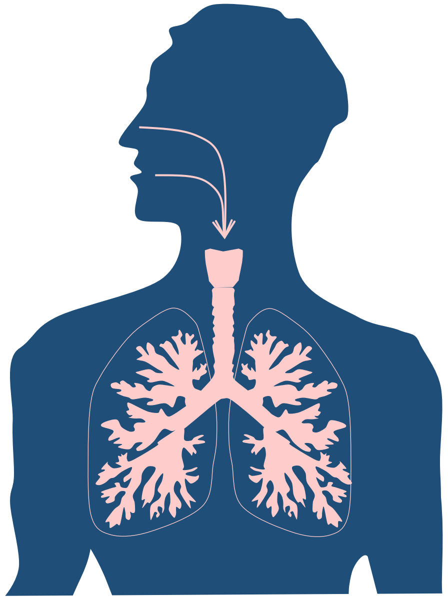
Ultrafine Particles (UFP)



	10 µm (Coarse)	2.5 µm (Fine)	0.1 µm (Ultrafine)
Total mass	1	1	1
Particle number	1	64	1,000,000
Surface area per particle	1	0.0625	0.0001
Total surface area per mass	1	4	100

Adapted from: Kwon, HS., Ryu, M.H. & Carlsten, C. Ultrafine particles: unique physicochemical properties relevant to health and disease. *Exp Mol Med* 52, 318–328 (2020).

- Due to their small size and mass sampling and analysis is challenging
- Due to their high surface area they can act as carrier of chemical compounds



A. Das, J. Pantzke, S. Jeong, […], R. Zimmermann, Generation, characterization, and toxicological assessment of reference ultrafine soot particles with different organic content for inhalation toxicological studies, Science of The Total Environment, **2024**.

- While exposure limits for PM2.5 and PM10 have recently been updated by the WHO, still no limits for UFP exist
- urge for further studies on their chemical composition, potential sources and impact on the environment and human health

Sampling Setup

Urban

Augsburg, Germany

March and September 2023

Sampling time 24 h

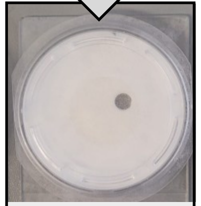
Sampling flow 30 L/min

PM10 inlet head

three-stage cascade impactor

PM2.5
PM1
PM0.1

Cut-off diameters



Ambient UFP

PM<100nm

E. Eckenberger, A. Mittereder, N. Gawlitta, J. Schnelle-Kreis, M. Sklorz, D. Brüggemann, R. Zimmermann, A. C. Nölscher, Performance evaluation of four cascade impactors for airborne ultrafine-particle (UFP) collection: the influence of particle type, concentration, mass, and chemical nature, Aerosol Research, **2025**, https://doi.org/10.5194/ar-3-45-2025.

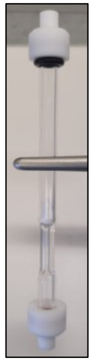
Chemical Analysis

Sample

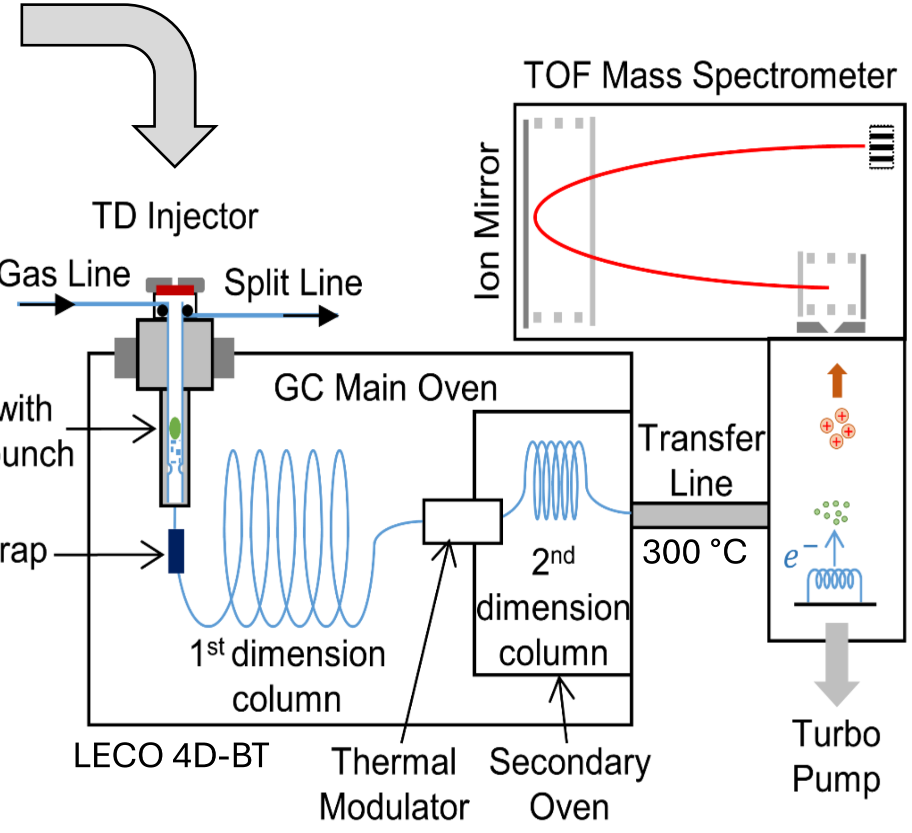
Ambient UFP

Filterpunch (Ø 7 mm)

1µL Internal Standard



Direct Thermal Desorption (DTD) –
Comprehensive two-dimensional Gas Chromatography –
Time of Flight Mass Spectrometry (GC×GC-TOFMS)



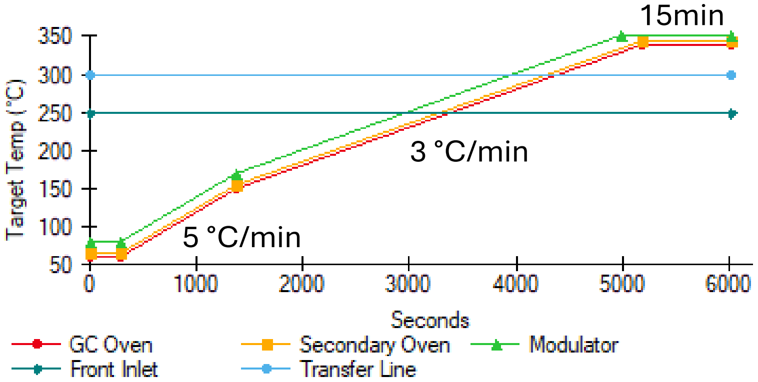
LECO Pegasus BT4D

Detector
29-600 Da
100 spectra/s

70 eV

Ion Source (EI)
250 °C

"Normal" configuration: non-polar (BPX5, 60m, 0.25mm, 0.25µm) - polar (BPX50, 2m, 0.1mm, 0.1µm)

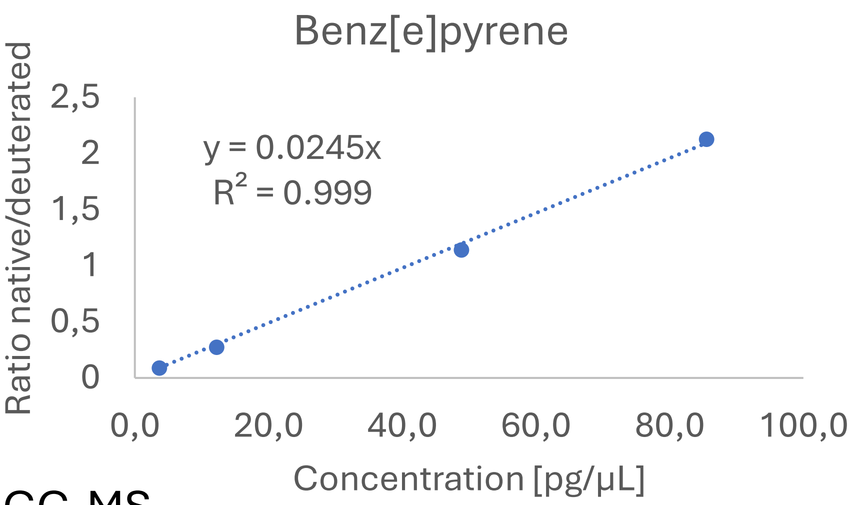


<u>Internal Standard</u>
Fluoranthene-d10
Pyrene-d10
Benz[a]anthracene-d12
Chrysene-d12
Benz[e]pyrene-d12
Benz[a]pyrene-d12
Perylene-d12
Indeno[1,2,3-cd]pyrene-d12
Dibenz[ah]anthracene-d14
Benzo[ghi]perylene-d12

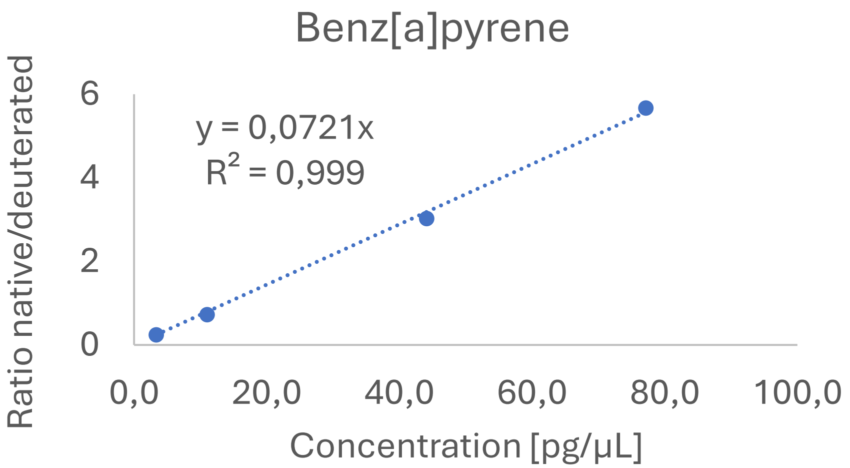
Adapted from: Hartner E., Paul A., Käfer U., et al. *ACS Earth and Space Chemistry* **2022** *6* (5), 1358-1374

PAH-Quantification – Method Validation

External Calibration of PAHs corrected with equivalent internal deuterated standard

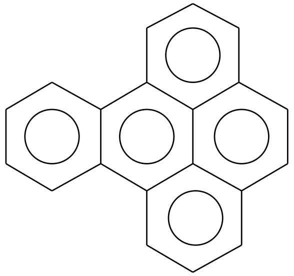


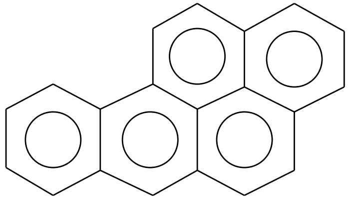
GC×GC-MS

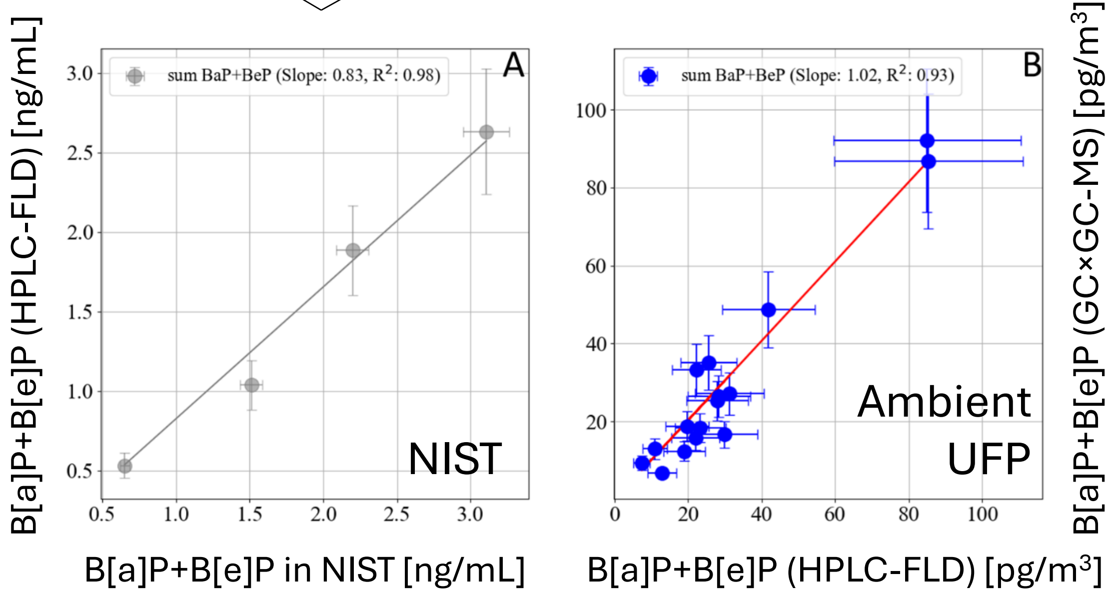


Quantification ion (**m/z**)

Benz[e]pyrene	**252**	Benz[a]pyrene	**252**
Benz[e]pyrene-d12	**264**	Benz[a]pyrene-d12	**264**



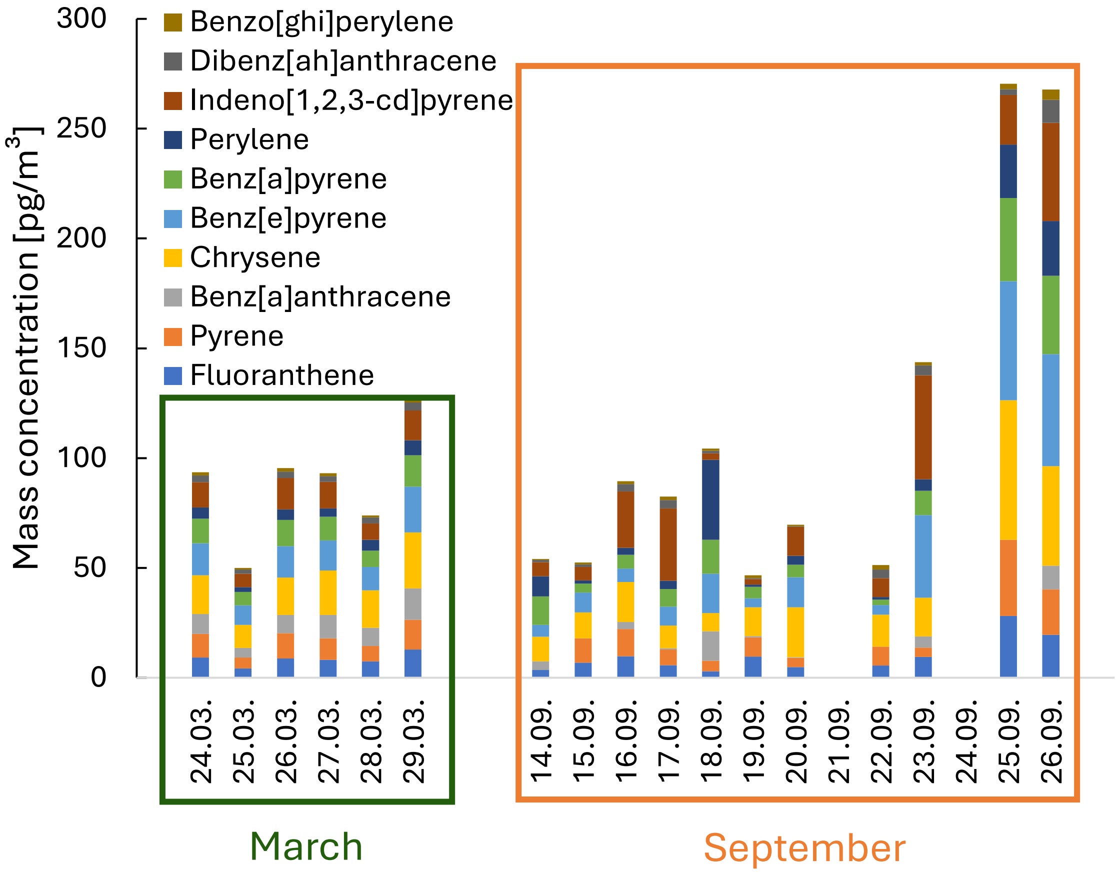




2-Step-Method-Validation with HPLC-FLD and NIST standard material

PAH-Quantification in atmospheric UFP

Preliminary data



- Concentration of the 10 monitored particle-bound PAHs are relatively constant in March compared to September
- The last two sampling days of September (25./26.09.) show higher PAH concentrations
- Benz(a)pyrene 37 pg/m^3 , [2.4 -15.4 pg/m^3]
  Chrysene 54 pg/m^3, [10.5-22.8 pg/m^3]
  Pyrene 28 pg/m^3, [4.2-12.3 pg/m^3]

Correlation to physico-chemical data?

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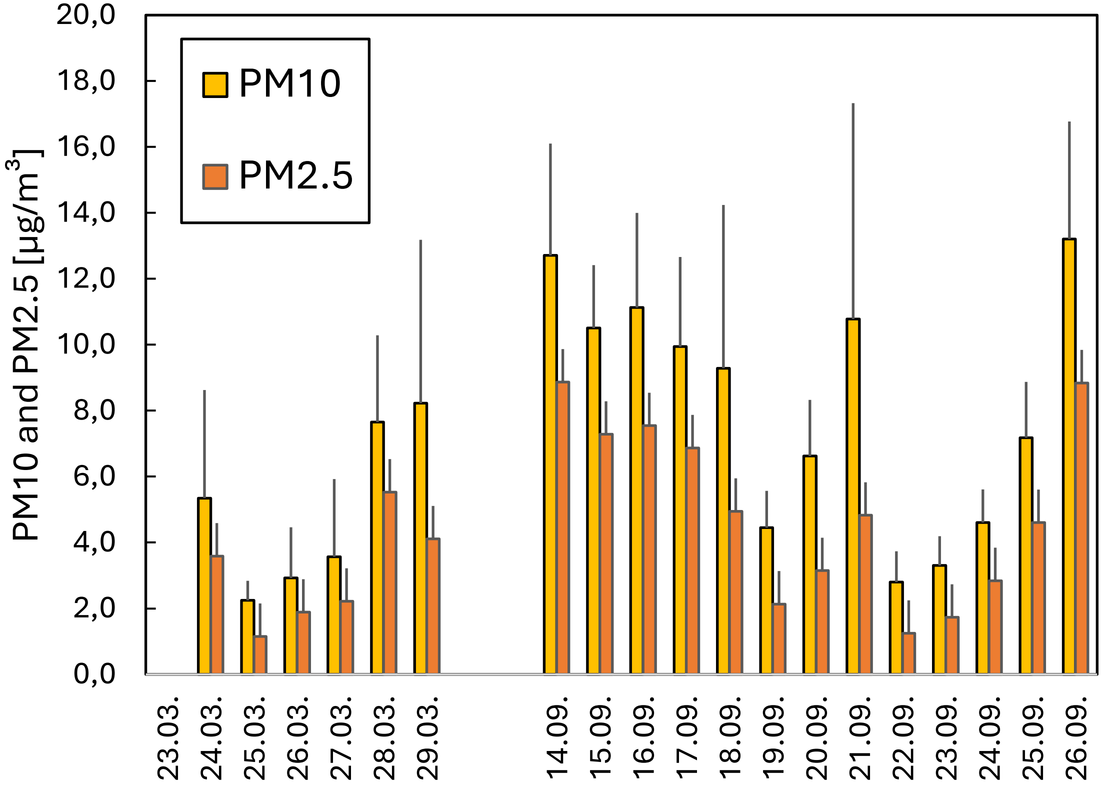
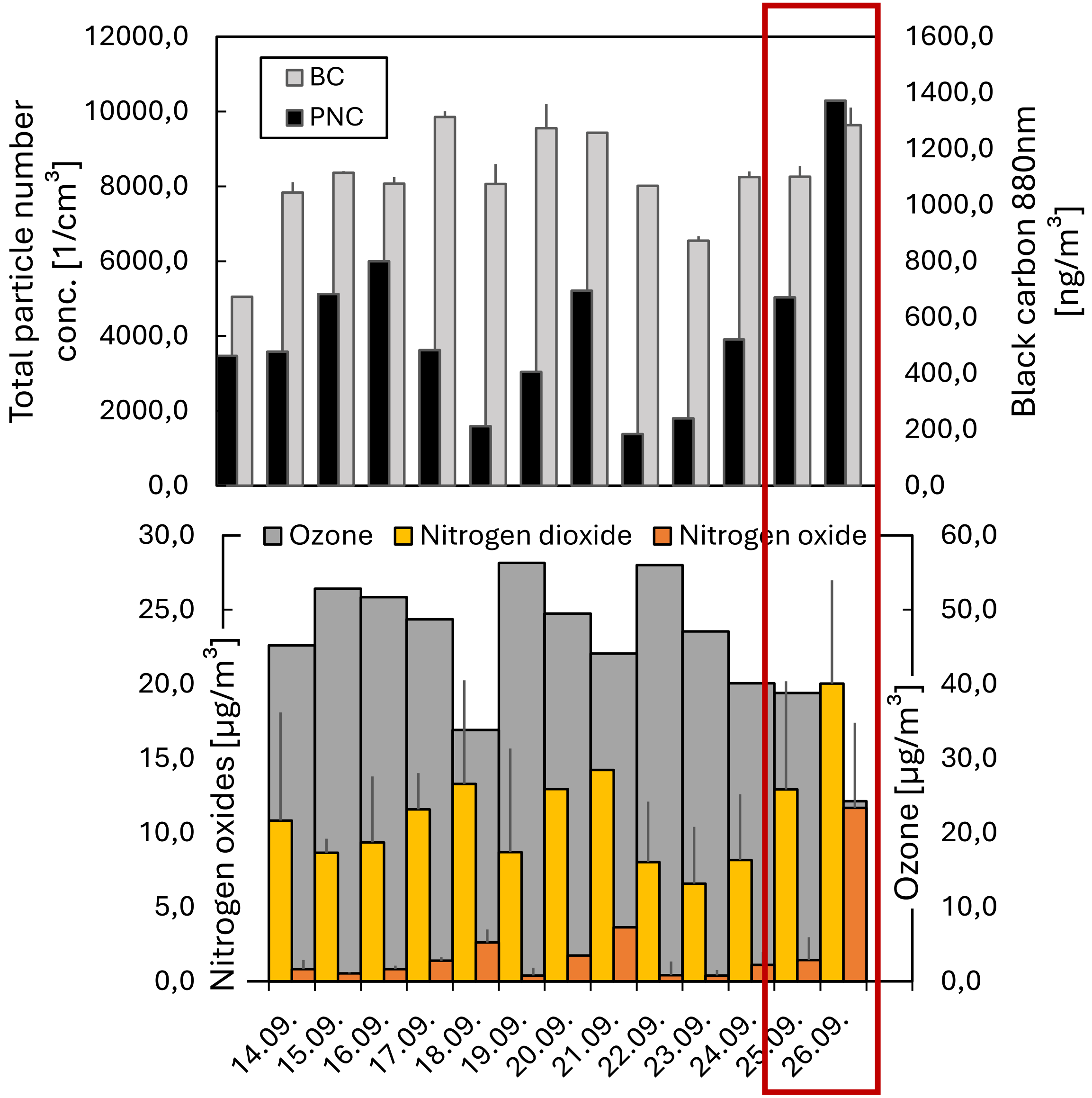
Correlation with physico-chemical data

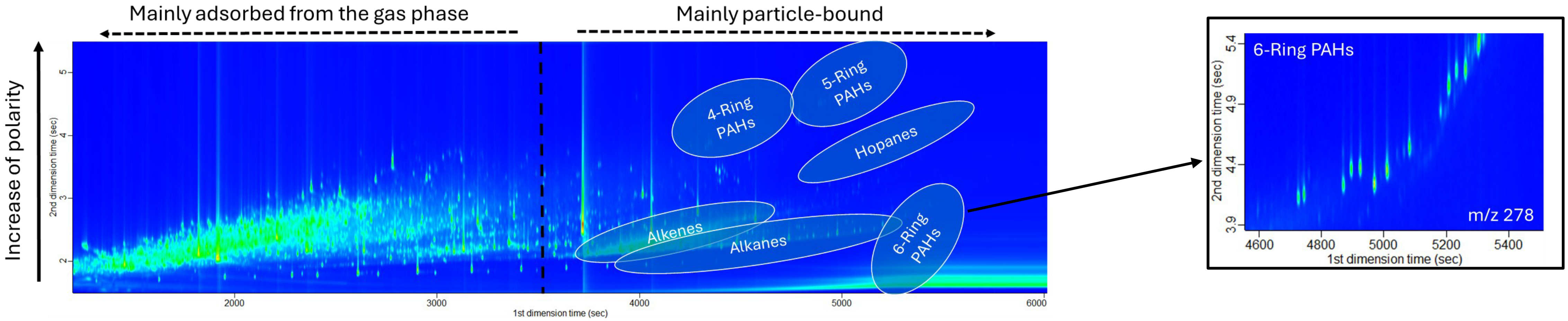
Outline | Introduction | Methods | Results | Summary | Outlook

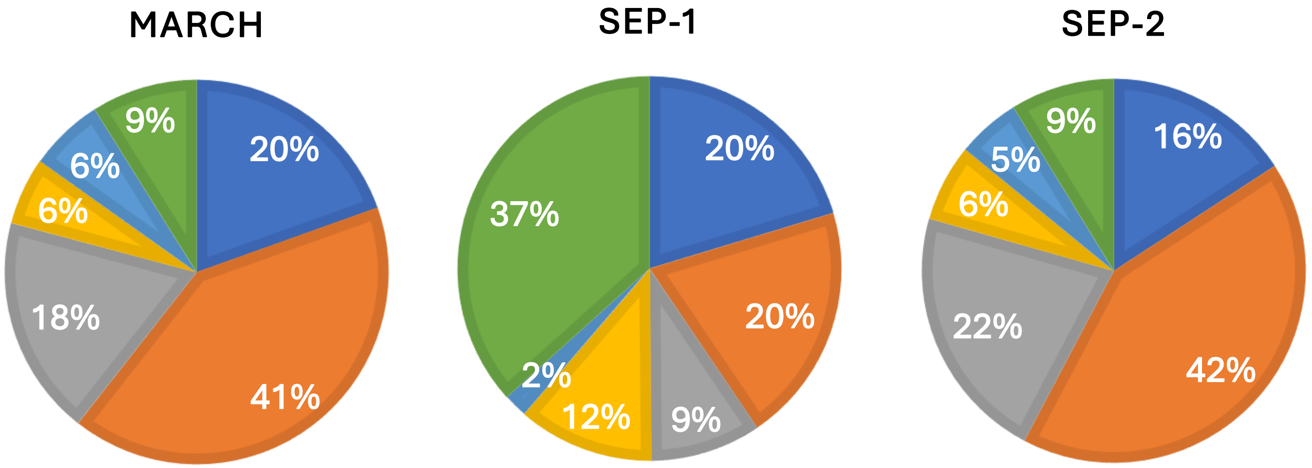


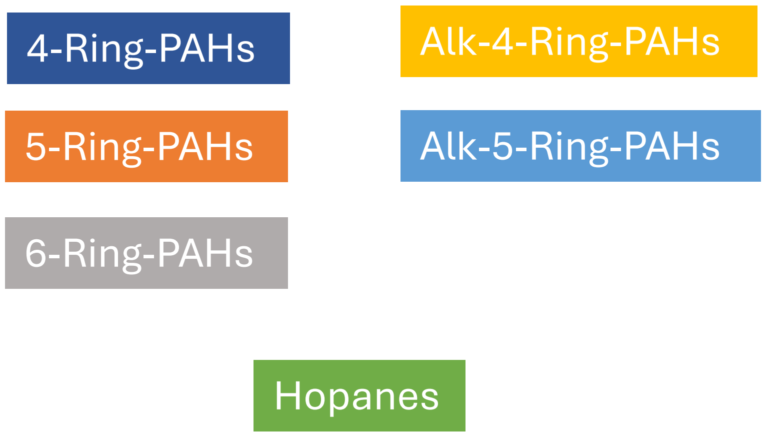


- ➢ No correlation to PM2.5, PM10, BC and Ozone
- ➢ Slight correlation with PNC and NOx

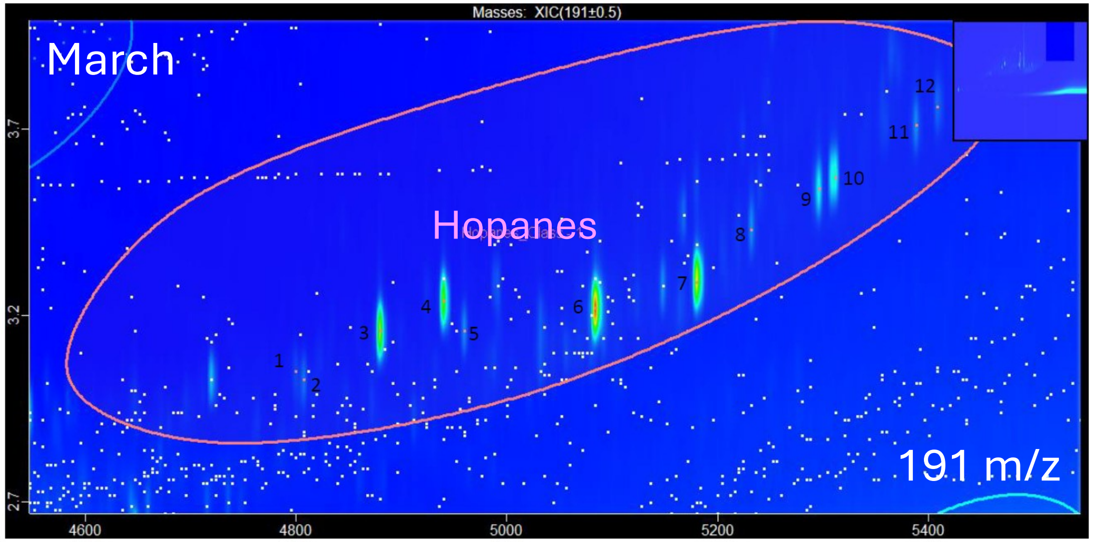
Classification



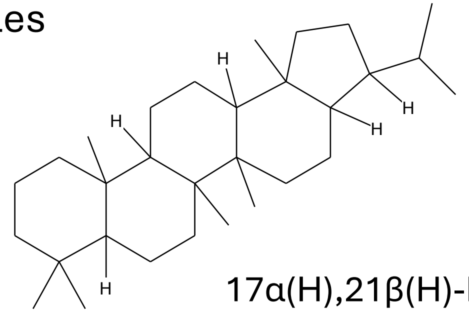




Hopane pattern



- constituents of all mineral-oil- or coal-based fuels and lubricants
- identified in emissions from coal burning, heating oil burning, and vehicles



17α(H),21β(H)-hopane

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

	Ts/Tm	**30ab/(30ab+30ba)**	**31abS/(31abs-31abR)**
March	0.92 – 1.17	0.81 – 0.89	0.18 – 0.39
September	0.89 – 1.60	0.91 – 0.99	0.44 – 0.60
	higher Ts/Tm ratios	hopane index > 0.9	homohopane index ~ 0.6

Mineral-oil derived emission sources

Semi Volatile Organic Compounds in Ambient $PM_{2.5}$. Seasonal Trends and Daily Resolved Source Contributions, Jürgen Schnelle-Kreis, Martin Sklorz, Jürgen Orasche, Matthias Stölzel, Annette Peters, and Ralf Zimmermann. *Environmental Science & Technology* **2007** *41* (11), 3821-3828.

Mineral-oil derived emissions in September and potentially additional coal combustion emissions in March

- Target analysis of particle-bound PAHs revealed large differences in concentration based on seasonal but also daily variation
- High PAH concentrations in UFP fraction difficult to explain by mass-based physico-chemical parameters (e.g., PM2.5, PM10)
- Alkylated and other unsubstituted PAHs showed a similar trend as the target PAHs
- Hopane pattern indicates different UFP sources based on seasonal variations

→ Daily monitoring of UFP and physico-chemical parameters (e.g. PNC) needed to gain further insights regarding their sources and impact on the environment and human health

Acknowledgements

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Thank you for your attention!

Questions?

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