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UNIVERSITY OF APPLIED SCIENCES

TECHNISCHE UNIVERSITÄT BERGAKADEMIE FREIBERG
Die Ressourcenuniversität. Seit 1765.

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Estimation of Tire Wear Contamination in Soil and Snowmelt Samples via Tire Wear-associated Markers

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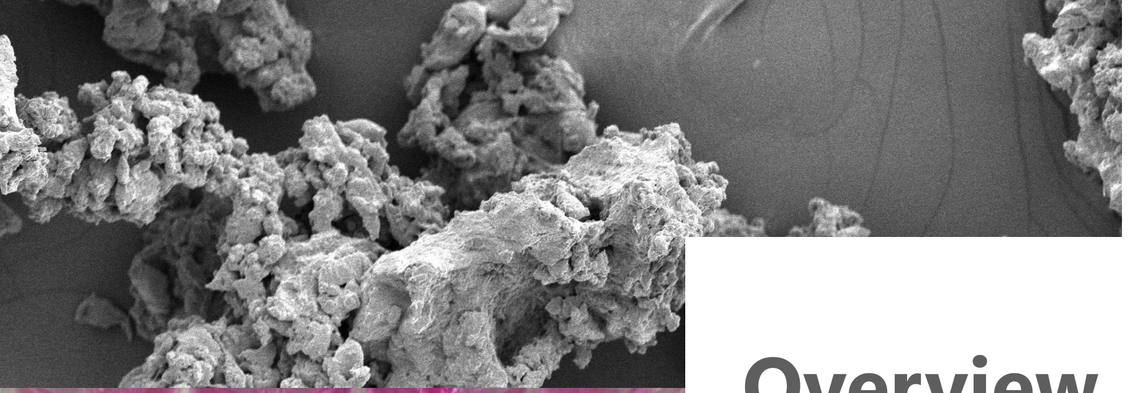
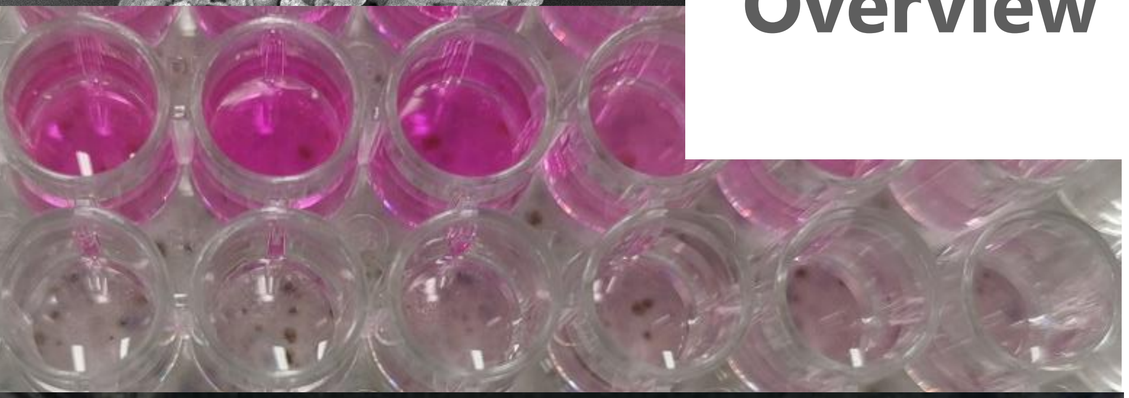
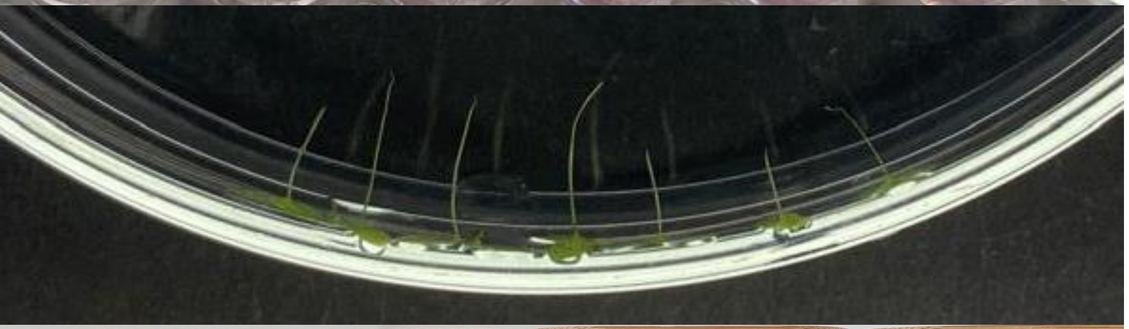
Diese Maßnahme wird mitfinanziert durch Steuermittel auf der Grundlage des vom Sächsischen Landtag beschlossenen Haushaltes.

2nd Tire Wear Workshop: 28. November 2024

M.Sc. Tomas Kleint







Overview

1. State of the Art
2. Aiming for Feasible Quantification
3. Sampling
4. Determination of Inorganic and Organic Marker Substances
5. Externally Determined Concentrations: A Compairison

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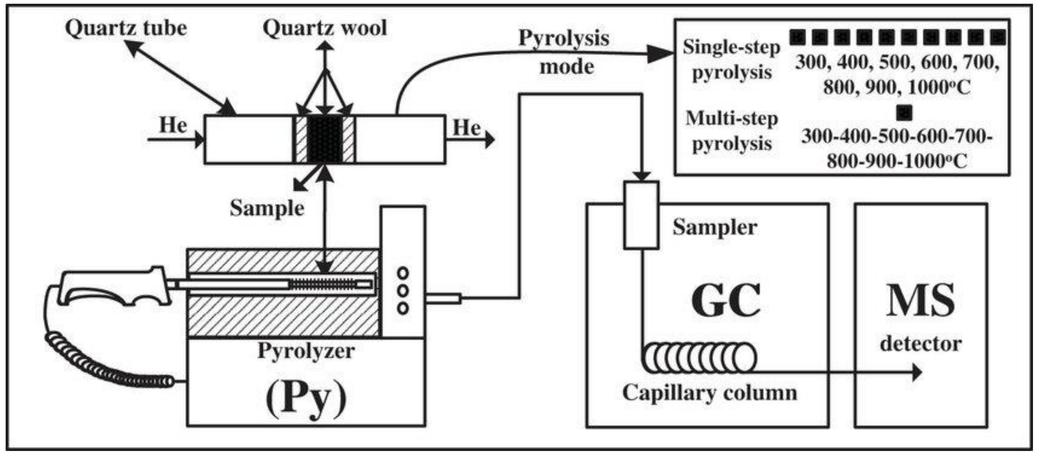
Tire Wear determination: State of the Art

Widely used methods:

- Quantification via Pyrolysis-GC/MS → identification and quantification via characteristic ions for most prevalent tire rubber types (SBR, PiB and PBR
- Rather experimental: Microscopic quantification attempts via particle shape and prevalence of certain elements



Pic.1: Schematic diagramm of Py-GC/MS [1]

Issues:

- Equipment usually very unique and cost intensive: often not available in smaller labs
- high organic content → other pyrolysis products overlay with TW peaks
- Microscopic identification via µFTIR and µRAMAN often impaired due to the black color of TW particles and a wide range of possible environmental components aggregated with the tire wear particle

[1] Xiaoping Su et al. (2023) Investigating pyrolysis characteristics of Shengdong coal through Py-GC/MS; Open Chemistry 2023; 21: 20230112

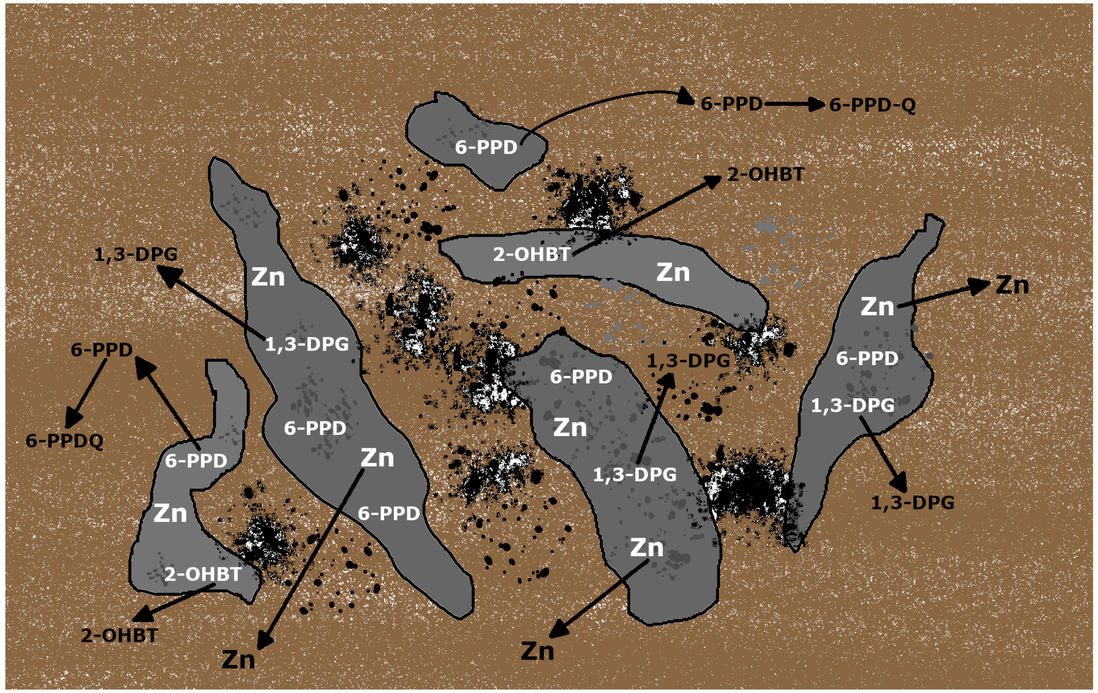
Aiming for Feasible Quantification

Our main goal:

- Find correlation between a combination of characteristic markers and actual tire wear concentration
- Organization of a correlation matrix for evaluation and comparison with externally determined tire wear concentration:
- → Which markers / marker combinations are the most useful?

Idea:

Tire wear containing several, more easily detectable organic and inorganic substances („markers substances“) → Assumption: Partial leaching from the particles into the surrounding soil (to equilibrium)



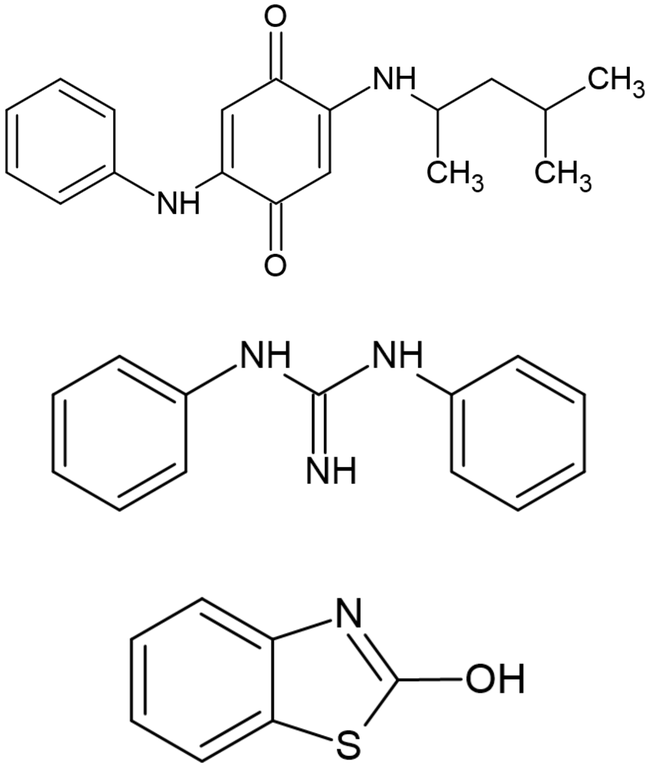
Pic.2: Markers leaching from particles into the soil

*2-OHBT: 2-Hydroxybenzothiazole / 1,3-DPG: 1,3-Diphenylguanidin

Aiming for Feasible Quantification

Approach by Indirect Methods:

- For determination / estimation: Multiple, independent parameters necessary (Specifity!)
- Organic (2-Hydroxybenzothiazole (2-OHBT)*, 6-PPD-Quinone (6-PPDQ), 1,3-Diphenylguanidine (1,3-DPG)) and inorganic analytes (Zn, Cu, Pb) tested
- Analytical Equipment:
  - AES: Zinc and other heavy metals (e.g.: Cu, Pb) (*Agilent 4210 MP-AES*)
  - UHPLC-MS/MS: organic analytes (*ExionLC system with QTOF X500R and ESI*) →in coop. Doc. Stanislavá Vrchovecka (TU Liberec)



Pic.3: 6-PPD-Quinone (top), 1,3-DPG (middle) and 2-Hydroxybenzothiazole (bottom)

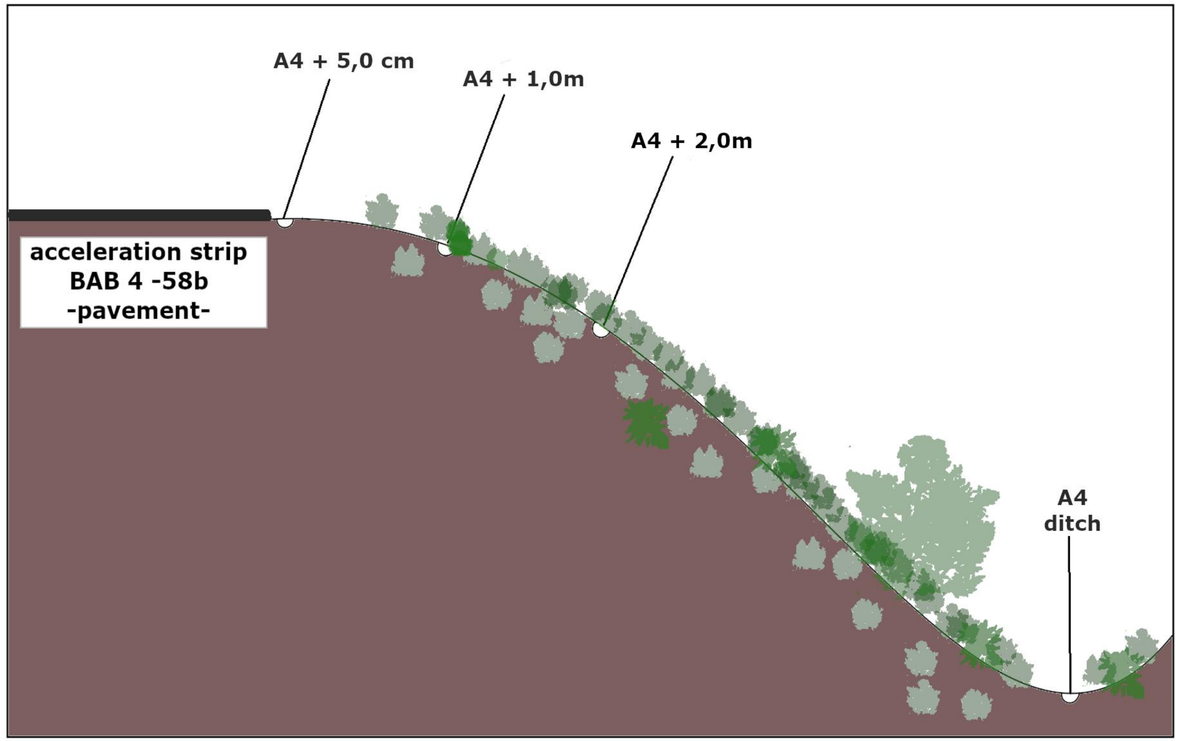
Evaluation:

Compairison to „classically“ determined concentrations:

- Particle-based methods (Snowmelt): SGS Institut FRESENIUS →Bright- and Dark-Field Microscopy, micro-FTIR, SEM/EDX
- Mass-based methods (Soil): Eurofins Ost GmbH →Pyrolysis-GC/MS

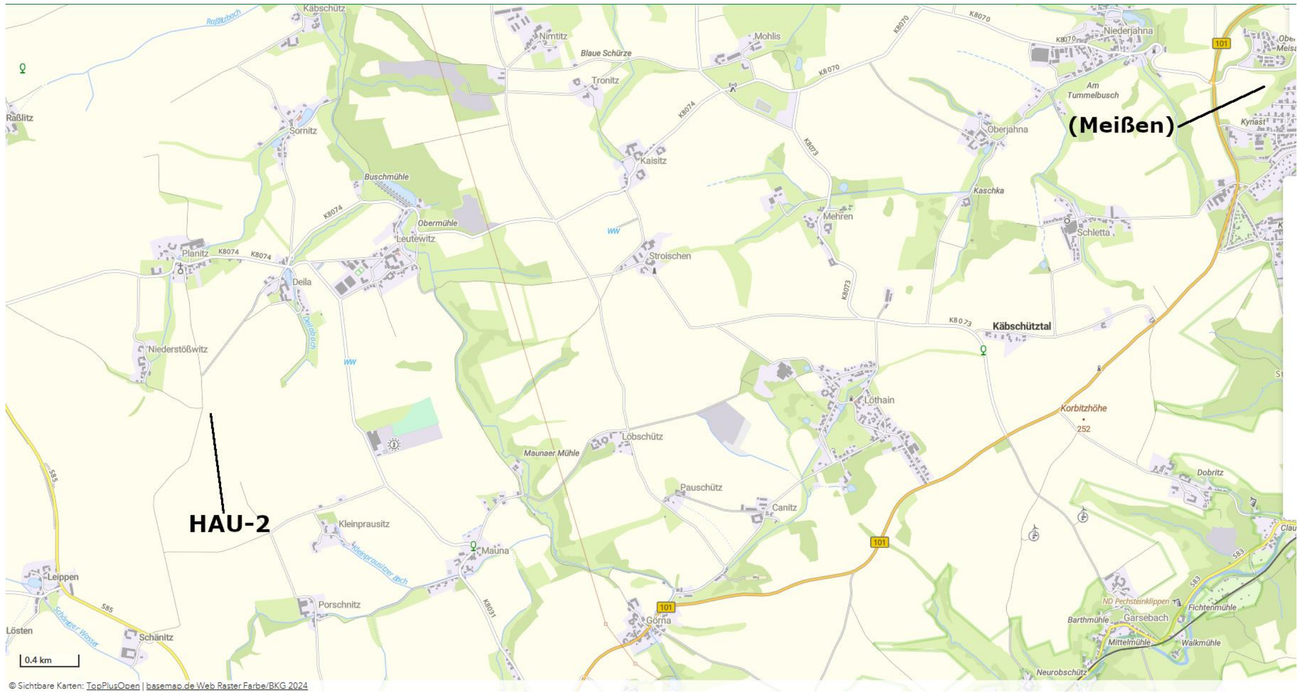
*selected example for Benzothiazoles in general

Sampling



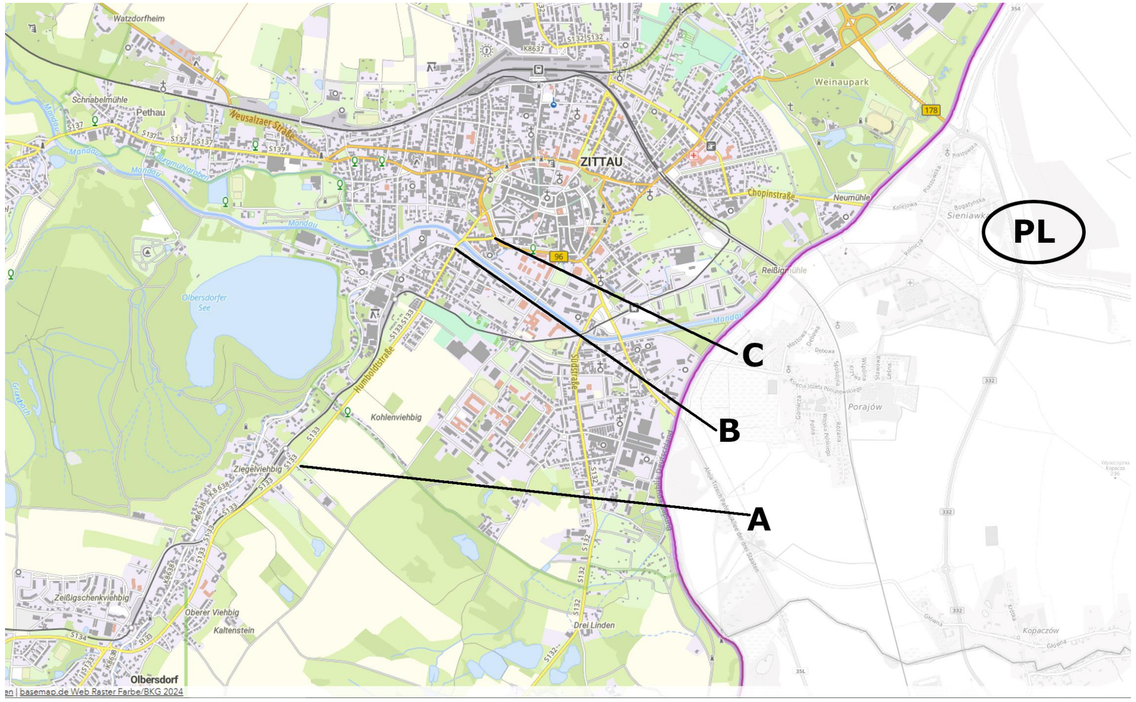
Pic. 4 and 5: Sampling Locations near Gera at BAB 4 and collection scheme

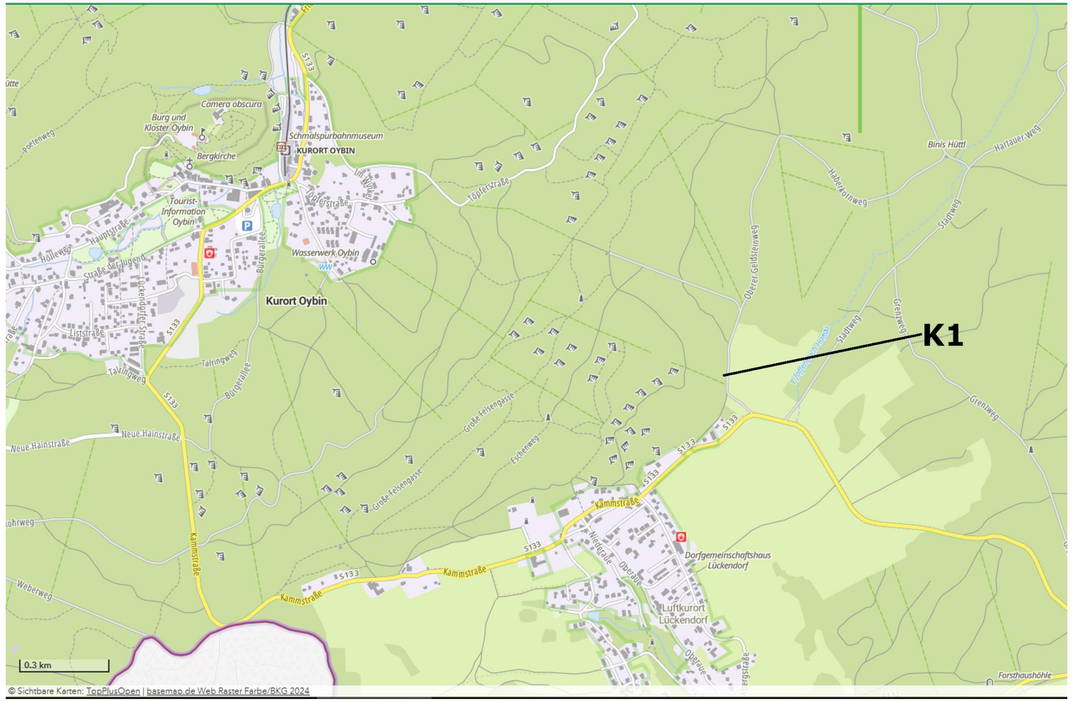
Sampling



Pic.6 and 7: Locations of lowly contaminated soil samples

Sampling



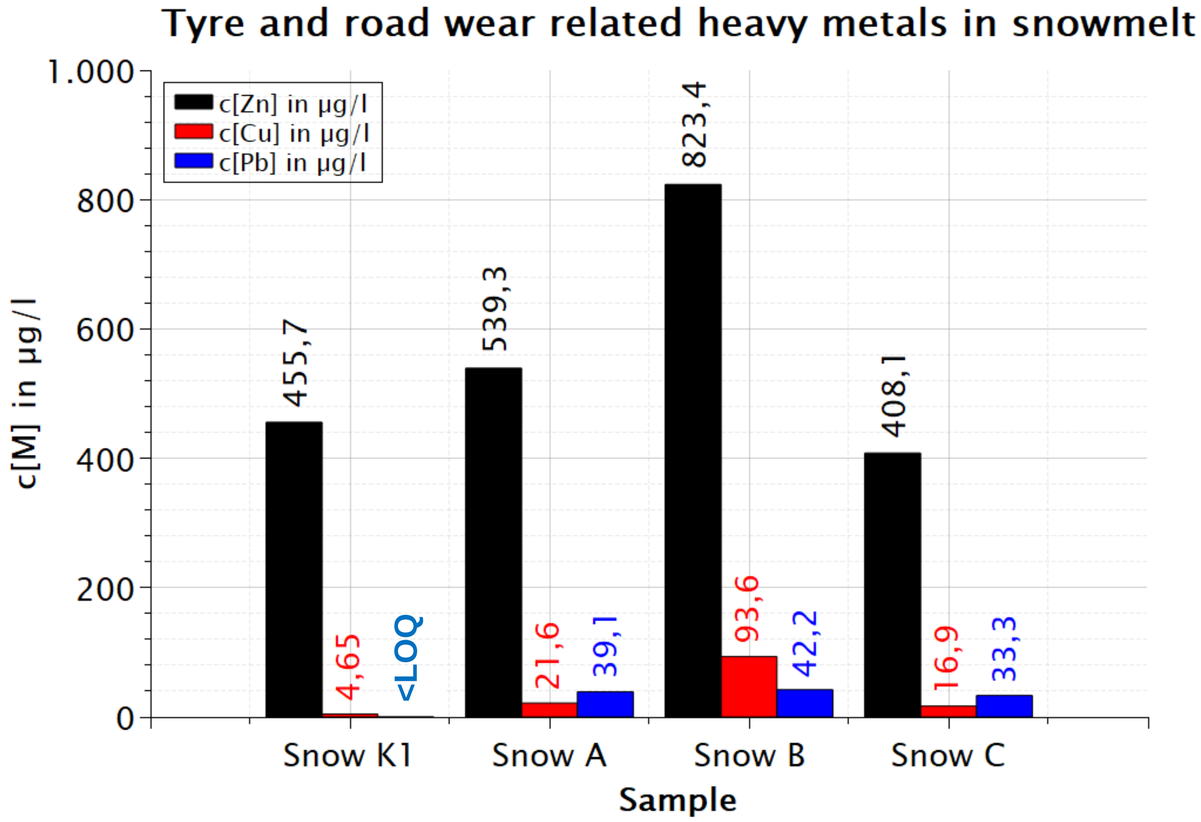


Pic. 8 and 9: Locations snow samples

Inorganic Marker Substances (1)

Sample preparation Snow / Snowmelt:

- Freezer (-18°C) for Storage
- Thawing and high pressure filtration (p=6 bar; cut-off: ≥0,45µm)
- Acidification to 0,5% HNO_3 + 2,0g/l $CsNO_3$ (Inhibition of Ionization)



Note:

Unexpected, high Zinc-Concentration in sample K1 (> Snow C!), Copper and Lead significantly lower than in A, B and C

Inorganic Marker Substances (2)

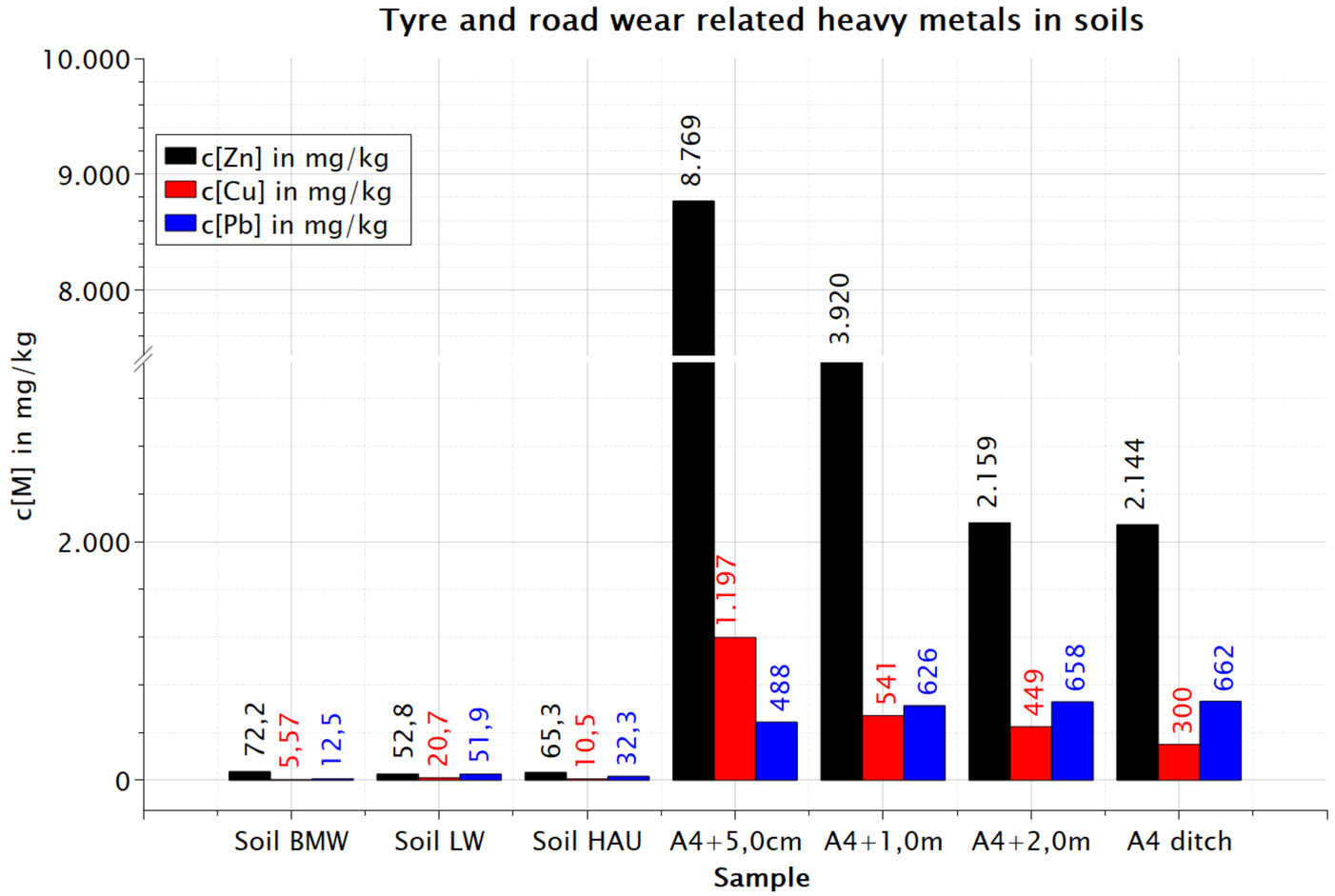
Sample preparation soils:

- Drying and sieving
- Aqua regia digestion following DIN 38414-S7 (3,0g soil + 28ml AR / 20h at RT, 3h at 130°C)
- Dilution and filtration of extracts with 0,5% HNO_3 (+ 2 g/l $CsNO_3$)

Note:

Significantly lower HM concentrations in presumably less TW-contaminated soils („BMW“, „LW“ und „HAU-2“),

Cu/Zn-ratio very similar in Autobahn soil samples



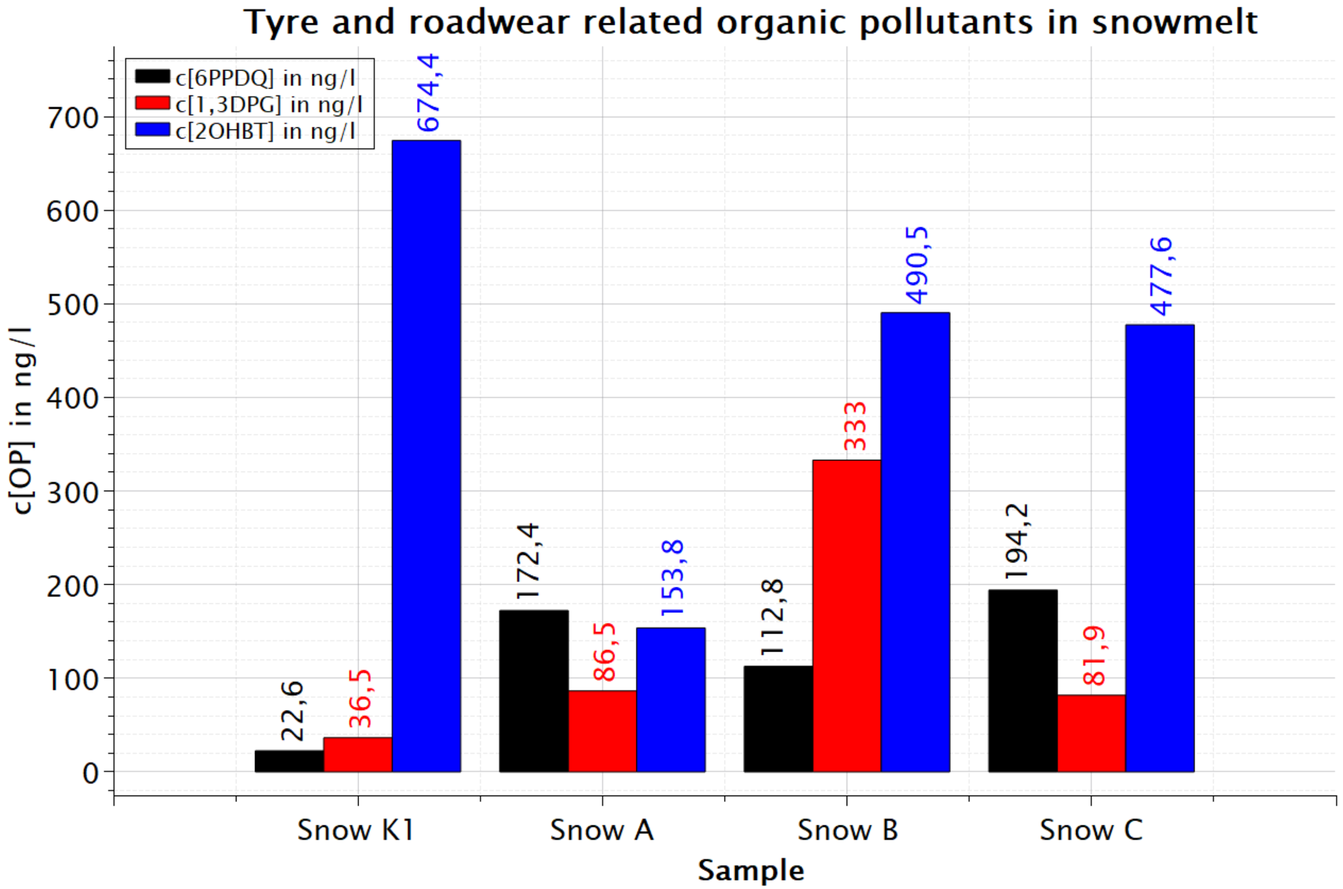
Organic Marker Substances (1)

Sample preparation snowmelt:

- Extraction with OASIS HLB-cartridges (solid phase extraction (SPE)),
- Re-Solution of analytes from solid phase: 5ml MeOH-MTBE-mixture
- Evaporation under vacuum
- Re-Suspension in 1,0 ml MeOH:H_2O (+0,1% HCOOH) – mixture; filtration

Note:

Unexpectedly high 2-OHBT concentration in K1 (> snow sample C!, similar to Zn), **6PPDQ** and 1,3-DPG as expected



Mean error of determination: ±10%

Blanks (Snowmelt/SPE):

2-OHBT	1,3-DPG	6-PPD-Q
5,38 ng/l	2,25 ng/l	22,13 ng/l

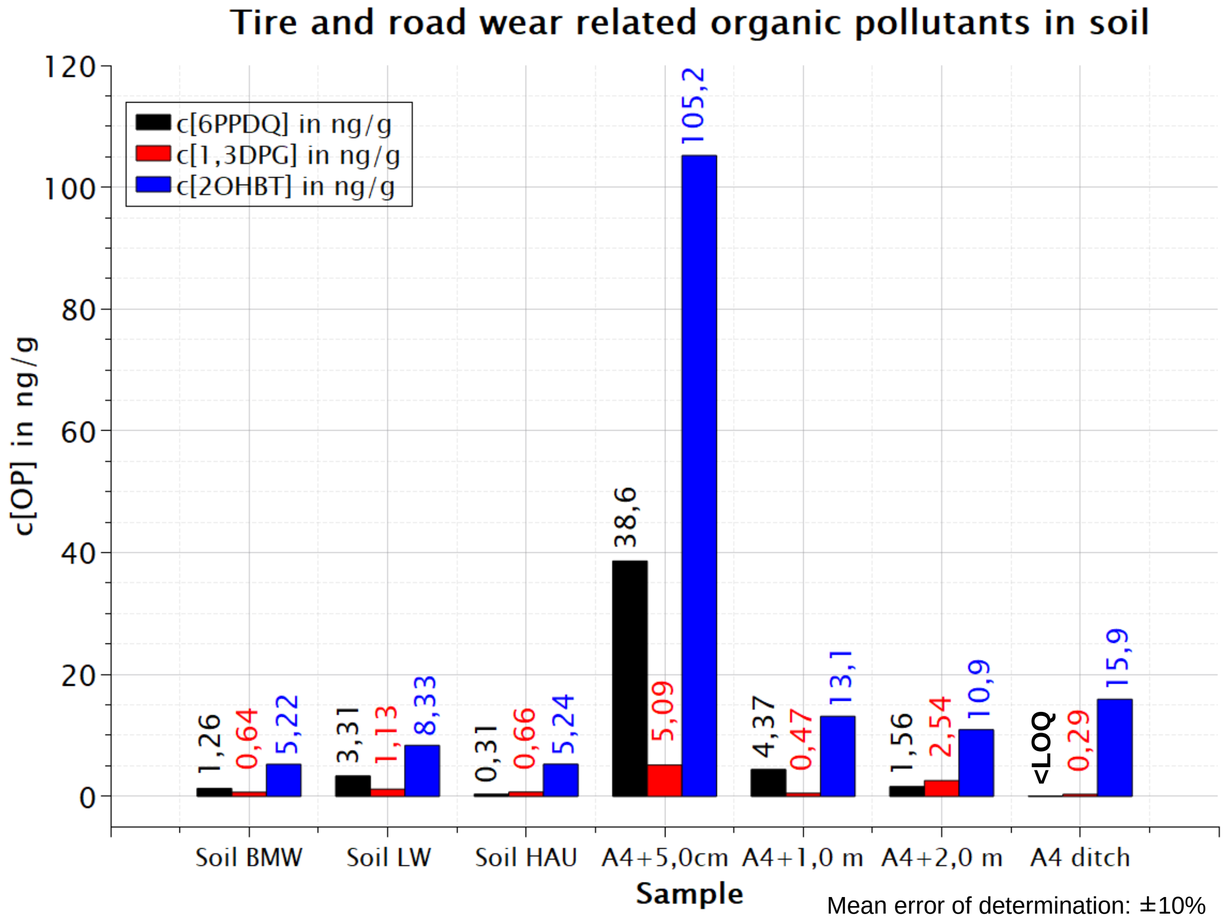
Organic Marker Substances (2)

Sample preparation soils:

- Ultrasound Extraction: 1,0g soil in 10ml Isopropyl alcohol (iPrOH); duration: 1,0h
- centrifugation, first filtration and evaporation under vacuum at room temperature
- Re-Suspension in 1,0 ml MeOH:H_2O (+0,1% HCOOH) – solution; 2nd filtration (ps: 0,22µm)

Note:

6-PPDQ seemingly correlates with the expected TW load, 2-OHBT and 1,3-DPG appear less specific: highest conc. In soil directly next to pavement but no clear trend visible in samples taken at further distance



Mean error of determination: ±10%

Blanks (Snowmelt/SPE):

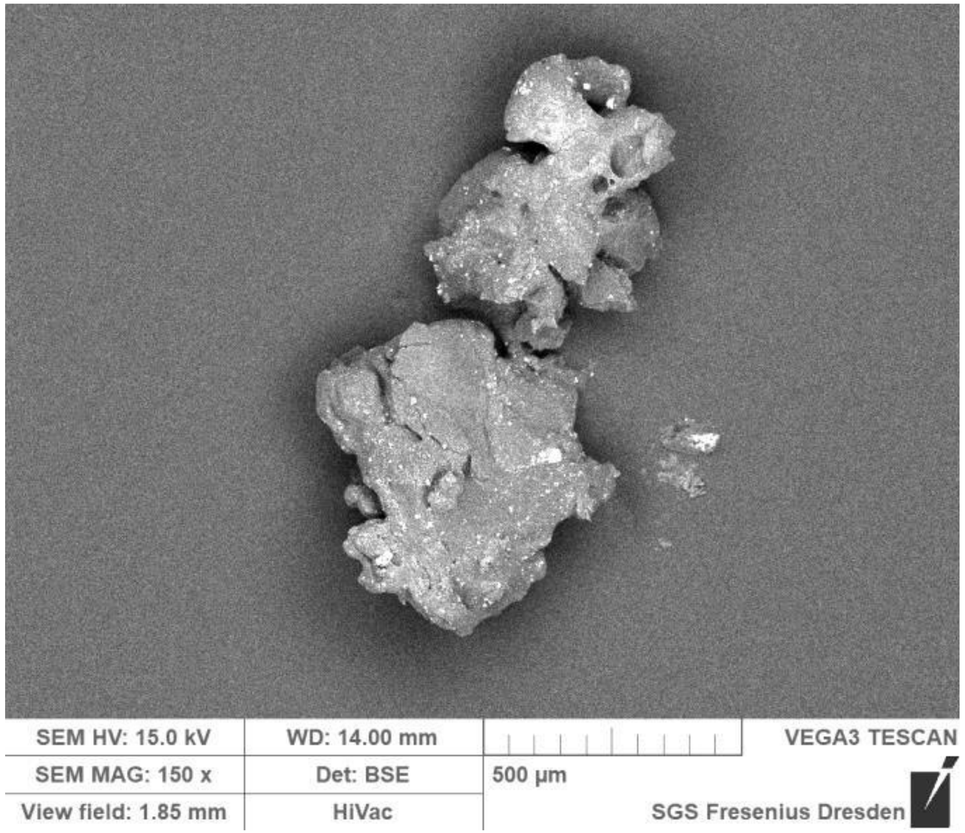
2-OHBT	1,3-DPG	6-PPD-Q
1,83 ng/g	0,19 ng/g	<LOQ

Comparison with externally determined TW concentrations

External Analytics carried out by Eurofins Ost and the SGS Institute FRESENIUS:

Particle-based analytics (snowmelt):

- Experiments concluded, results in early December 2024
- Aliquoting and purification with H_2O_2, filtration onto Si-membranes
- preview with bright and dark field microscopy → TRWP often with characteristic shape and color
- Attempted particle classification: SEM/EDX and FTIR spectra of suspected tire wear particles
- Two fractions: (1) Particles ≥500 µm and (2) Particles <500µm
- Suspicious particles (≥500µm) in A, B and C, none in K1
- Difficulty: Particles < 500µm tend to aggregate



Pic. 10: TW-suspicious particle in snow sample A

Comparison with externally determined TW concentrations

External Analytics carried out by Eurofins Ost and the Institute FRESENIUS:

Pyrolysis-GC/MS (soil)

- Determination via TW-characteristic pyrolysis products of PBR, PiP and SBR
- Unfortunately: only “**A4 + 5,0cm**” with significant tire wear concentration >LOQ
- Remaining soils: <LOQ →Issue: high amount of soil organic matter, extremely small aliquots necessary, plus: classification of pyrolysis products impaired
- Currently, no real insight in sample preparation procedures at Eurofins

Soil*	$c_{(RC)}$ [µg/kg]
A4 +5.0cm	13200
Other Soils	<20.0

* Soil extract after preparation

RC: Rubber Content; PBR: Poly-Butadiene-Rubber; PiP: Poly-Isoprene; SBR: Styrene-Butadiene-Rubber

Comparison with externally determined TW concentrations

Conclusions:

- At current state: Mainly a collection of marker concentrations
- Interpretation of tire wear concentrations in snowmelt crucial for further evaluation
- **No correlation matrix for mathematical evaluation is currently in sight due to lack of sufficient external data!**

- **Combination of individual markers seems promising, e.g.: Zinc + 6-PPD-Quinone and 2-Hydroxybenzothiazole**

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Sampling:

- Soils: four locations with suspected high and three with suspected low TW intake

  → Autobahn A4: exit 58b (acceleration lane)*: 3 samples with increasing distance of 0,05 m; 1,0 m; 2,0 m from the pavement + 1 from the adjacent trench

  →2 soils from small rivers‘ banks: Buttermilchwasser („BMW“) a. Löbauer Wasser („LW“), a. one from a remote field in Käbschütztal („HAU-2“)
- Snow: 3 with high expected TW concentrations from roadsides of S133 and (2) 1 with a low one (freshly fallen snow from a mountainous grove in the „Zittauer Gebirge“