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Influence of sampling strategies on the assessment of concentrations and loads of trace contaminants in surface waters

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Research questions

Do 12 grab samples in a year lead to a significant deviation in the estimation of mean & maximum concentrations and annual riverine loads for different groups of trace contaminants?

If yes, how large is the deviation?

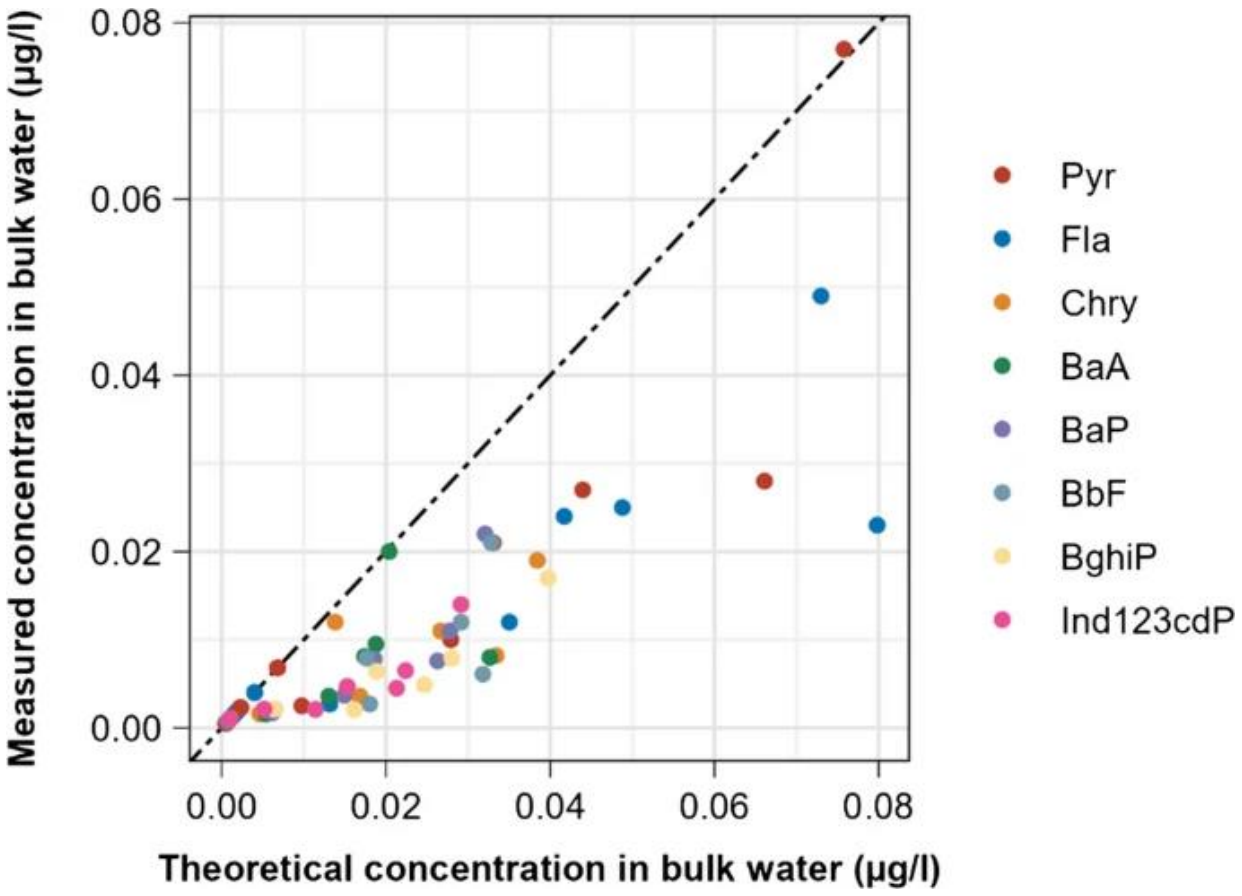
Do surveys based on bulk water samples lead to a significant deviation in the estimation of concentrations and loads for polycyclic aromatic hydrocarbons (PAHs)?

PAHs - Methods

- 6 high-turbidity events
- 3 rivers (MQ 0.1-7 m^3/s)
- Online sensors
- Simultaneous samples of:
  - River water via autosampler (total + filtered)
  - SPM via Phillips samplers or large volume sampler
  - Supernatant
- Analysis of 8 PAHs (4-6 rings)
- Comparison of measured vs. calculated conc.

Zoboli et al. (2024) doi: 10.1007/s11356-024-33787-9

PAHs - Results



- Average underestimation of 60%
  - confirmed when quantitatively including analytical uncertainty
- Tendency for increase in underestimation with increase in molecular weight and logK_{ow}
- Higher recovery rate in SPM than in water samples
- Probable incomplete extraction

Compliance with EQS: biota as alternative

River load calculation, understanding of fate and dynamics, validation of models: **SPM (+ turbidity measument) essential**

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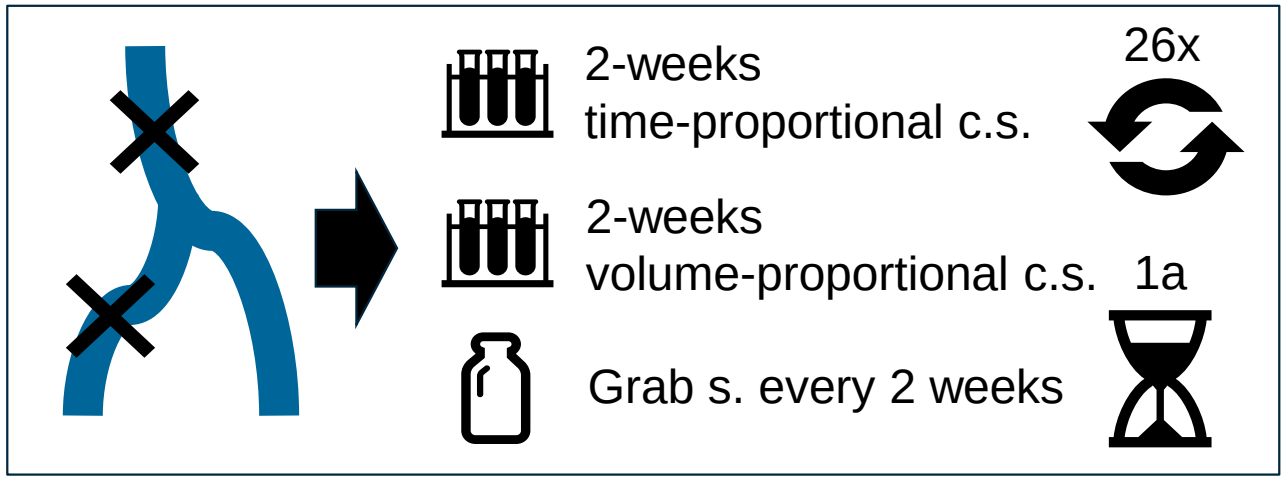
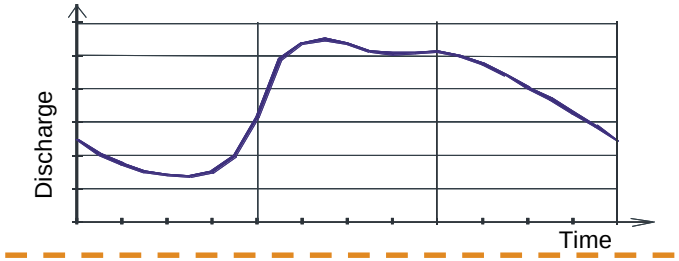
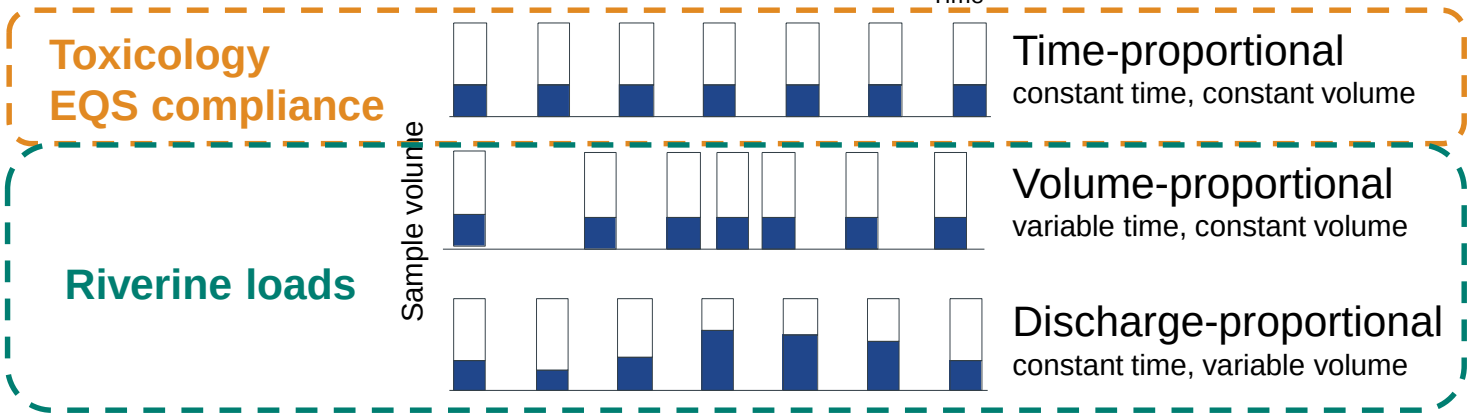
Sampling strategies - concept



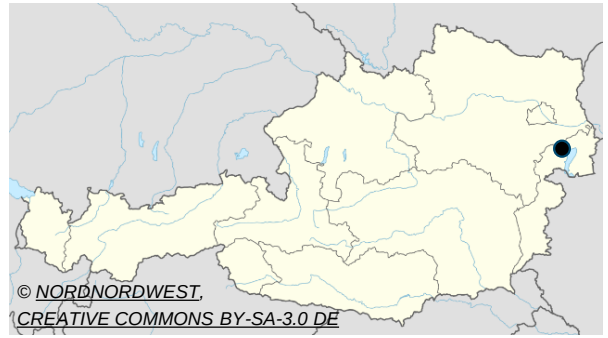


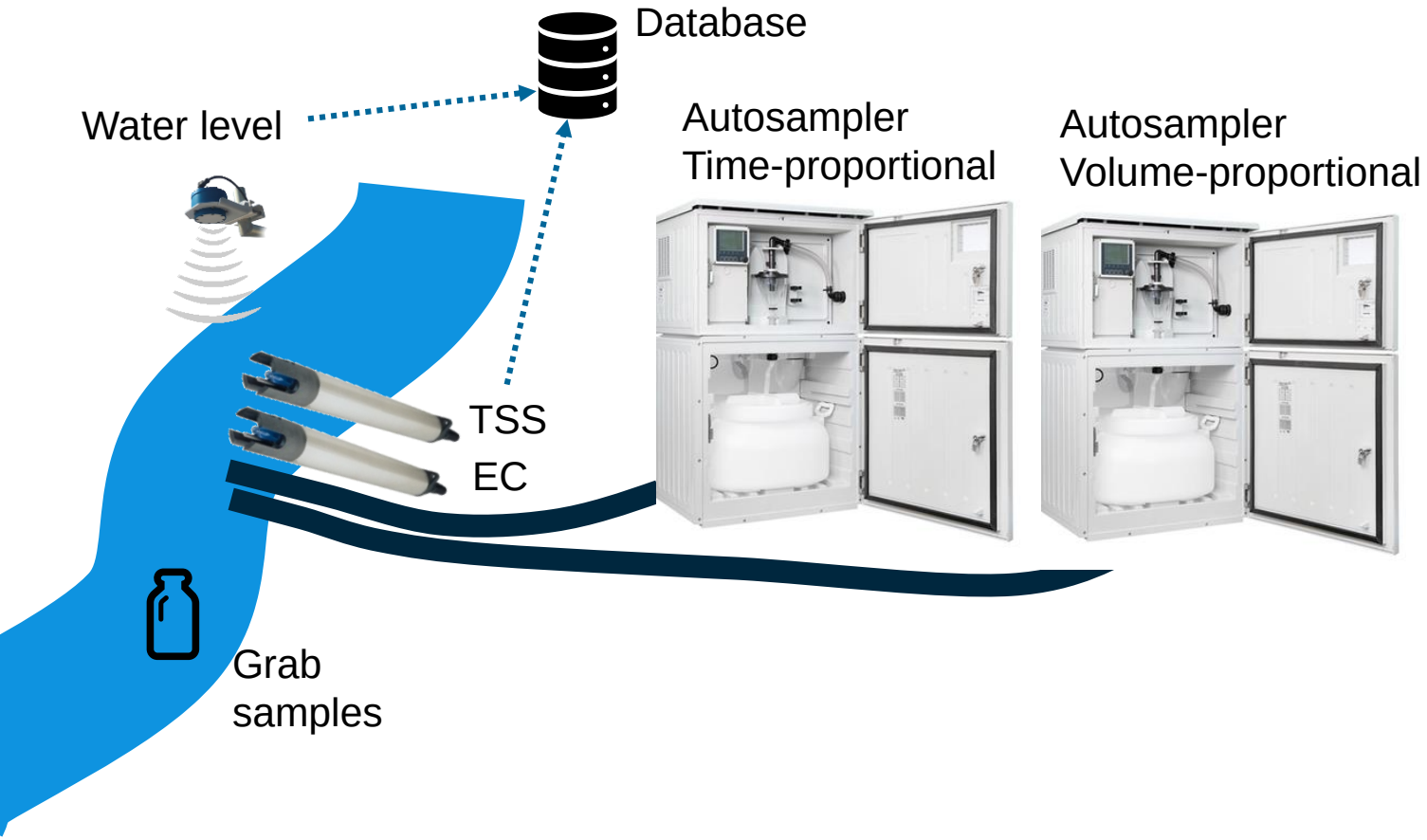
Scope of contaminants:

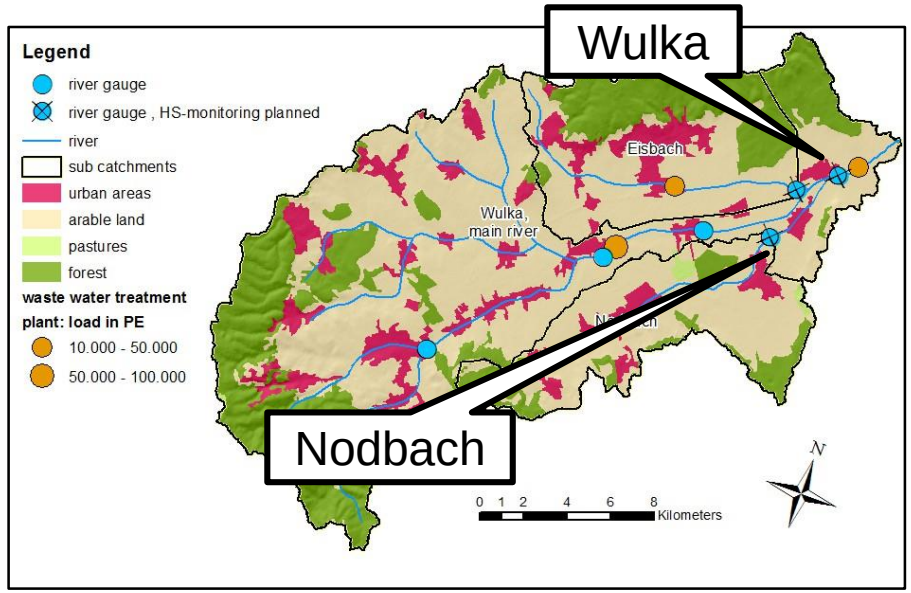
- 4 pharmaceuticals
- 8 metals
- 34 PFAS
- 404 pesticides (screening)



Sampling strategies - setup

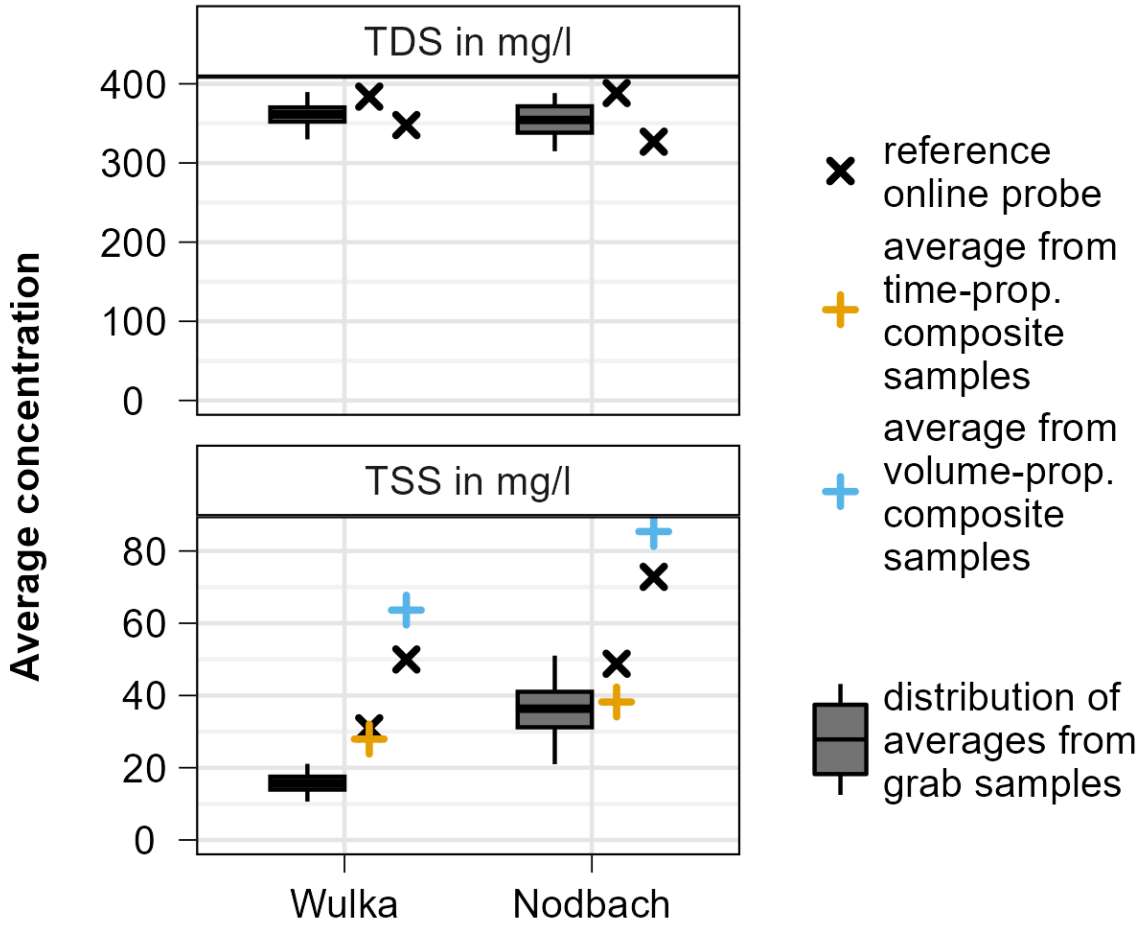






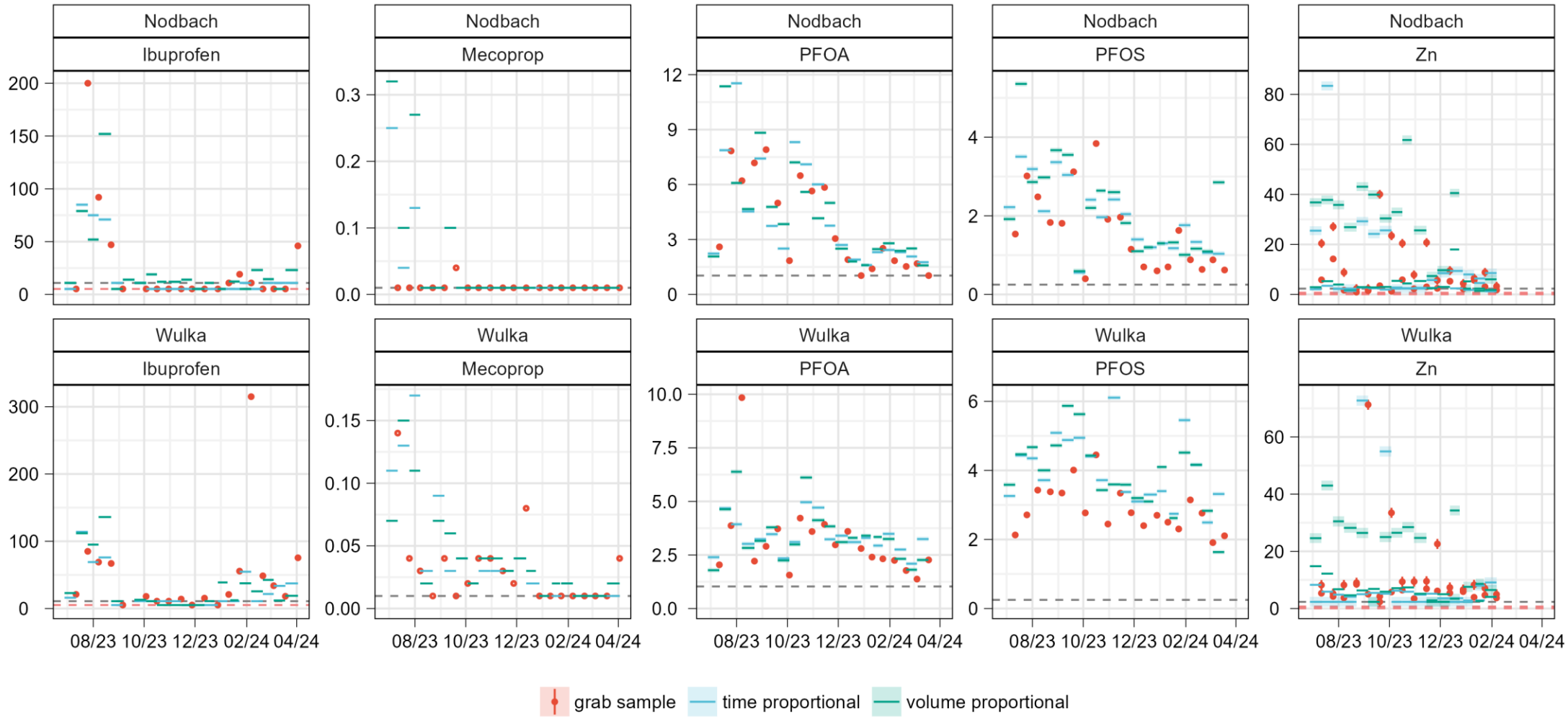
Sampling plausibility and efficiency

- Samples vs. sensors
- Total Dissolved Solids (Electrical Conductivity)
- Total Suspended Solids (Turbidity)

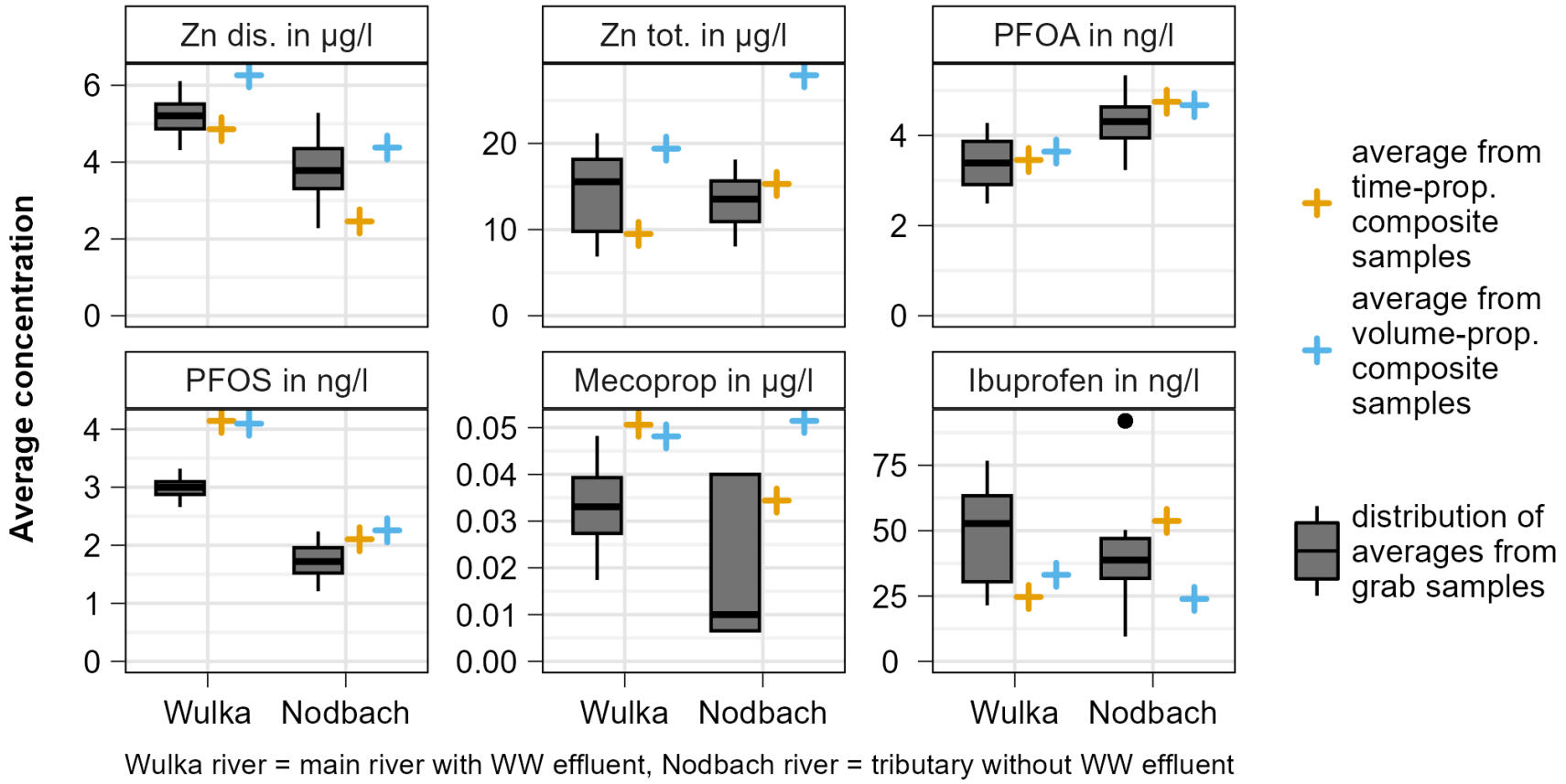


WEBER ET AL. (2024) EGU 2024, VIENNA, AUSTRIA, HTTPS://DOI.ORG/10.5194/EGUSPHERE-EGU24-6153, 2024.

Temporal variability



Average concentration by sampling method



Wulka river = main river with WW effluent, Nodbach river = tributary without WW effluent

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Wrap-up and outlook

Main (preliminary) outcomes

- Grab samples present problems to determine average concentrations of:
  - dissolved trace contaminants when highly variable inputs with short peak concentrations dominate
  - particle-bound trace contaminants
- Only volume-proportional samples reliable for flow-weighted mean concentrations to a high extent
- Even with volume-proportional samples, PAHs concentrations can be considerably underestimated
- Separate collection and analysis of SPM, combined with turbidity measurements, is essential for high-molecular PAHs

Main lessons learned in the field

- High difference between base and high flow make volume-prop. sampling very challenging in small streams
- Events above HQ1 are difficult to sample due to extreme high sampling rates (practicability of vessels and travels!)

Outlook

- Statistical significance of deviations for all contaminants for mean, max and loads
- Quantitative inclusion of analytical uncertainty (3 replicates for subset of samples)
- Repeated sampling during music festival
- … **final report by end of summer 2024**!

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