Passive sampling for the assessment of contaminant bioavailability in sediment management

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Contaminant bioavailability

- In sediment management risk assessment is usually based on total concentrations of contaminants determined by conventional solvent extraction of sediments
- Only a fraction of the contaminants that are bound to sediment particles is bioavailable
- Contaminant bioavailability can indirectly be assessed by monitoring chemicals in biota (biomonitoring)
- Accumulation of chemicals in biota (bioaccumulation) depends on many abiotic and biotic factors that have to be considered (e.g. species, age, sex)
- Biomonitoring may be hampered by availability of monitoring species due to their natural occurence

Species used for monitoring bioaccumulation in sediment management (from left to right: white furrow shell (*Abra alba*), common whelk (*Buccinum undatum*), common dab (*Limanda limanda*), blue mussels (*Mytilus edulis*)

Passive samplers

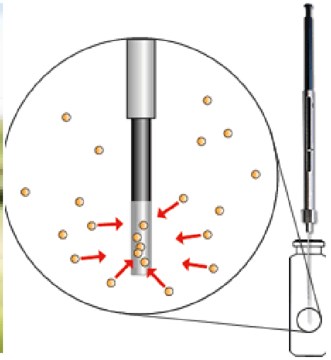
„techniques that quantify bioavailability based on the diffusion and subsequent partitioning of contaminants from sediments to a reference sampling phase“
Parkerton et al. 2013 Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments. Summary of a SETAC Technical Workshop

- Directly measure freely dissolved contaminant concentrations
- Reference phase (i.e. polymer) accumulates (target)analytes when it gets in contact with the sample or exposed in environment
- Various sampler types for different contaminant classes and matrices (e.g. water, sediment)

SPMD on holder (www.est-lab.com)

DGT (www.mn.uio.no)

POCIS (www.im-weiss.de)



SPME (www.labhut.com)

Silicone-based passive samplers

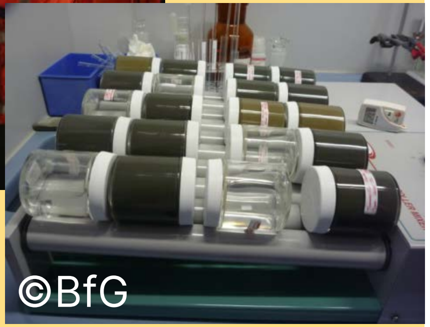
- Particularly suited to study hydrophobic organic chemicals

Water

- Silicone rubber sheets
- Exposure: several weeks (e.g. 4 weeks), *in situ*
- Kinetic samplers
- Time-weighted averaged concentrations (C_{twa}) in water phase

Sediment

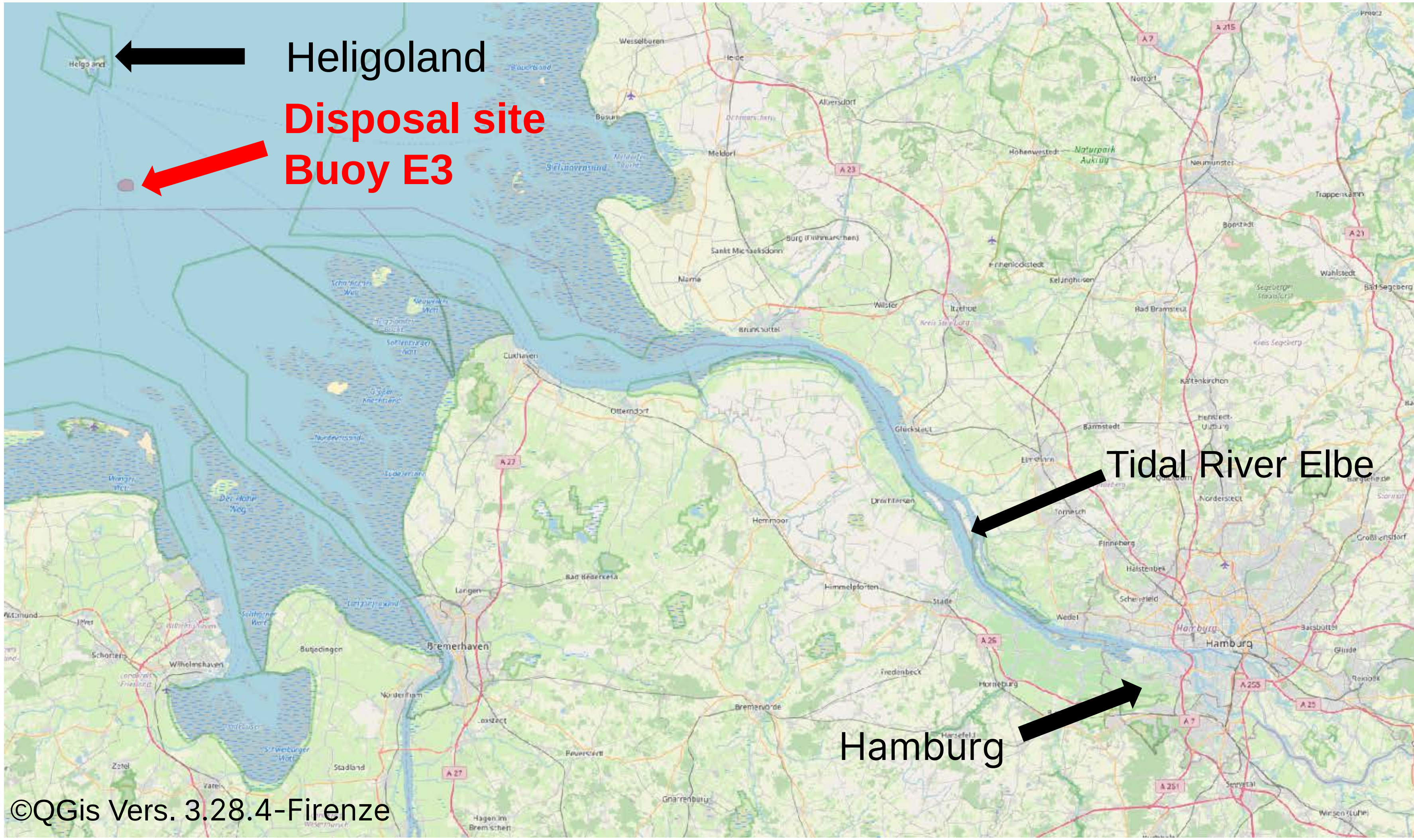
- Silicone coated glass jars
- Incubation: 4 weeks, *ex situ*
- Equilibrium samplers
- Freely dissolved concentrations in sediment porewater (C_{free})



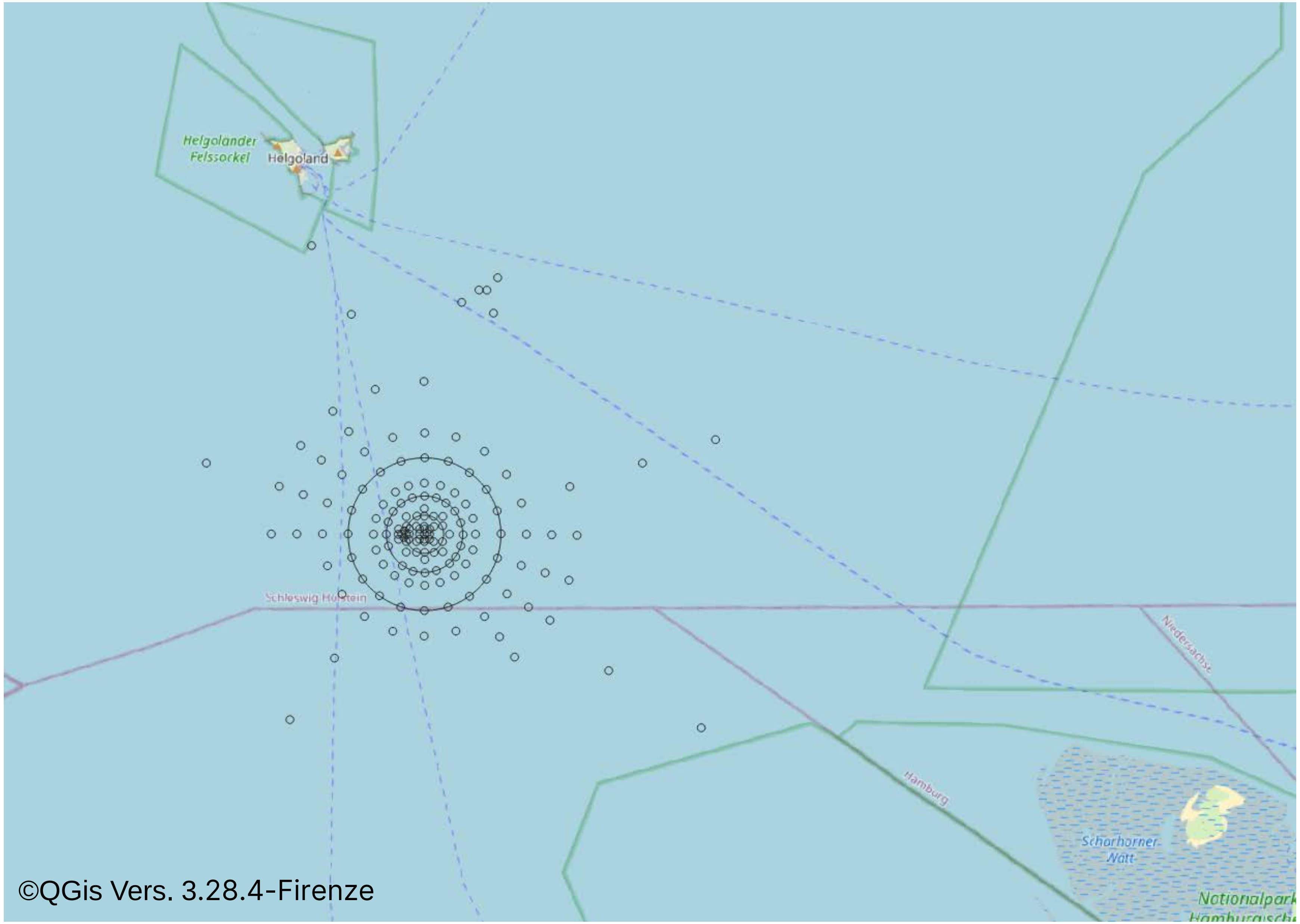
Contaminant biovailability at a disposal site

BfG

- Disposal site for dredged sediment in the German North Sea (near the Island of Heligoland)
- Since 2005 disposal of fresh sediments with low contamination
- 0,5 – 1,5 Mio. t dw dredged material / year (exception: 2011 – 2013)
- Site with low currents and sediments that naturally originate from the river Elbe → minor ecological impact



- Regular extensive monitoring campaigns
- conducted by the Hamburg Port Authority and scientifically accompanied by the BfG
- Monitoring: hydrology, morphology, contaminants in sediment and biota, ecotoxicology, ecology



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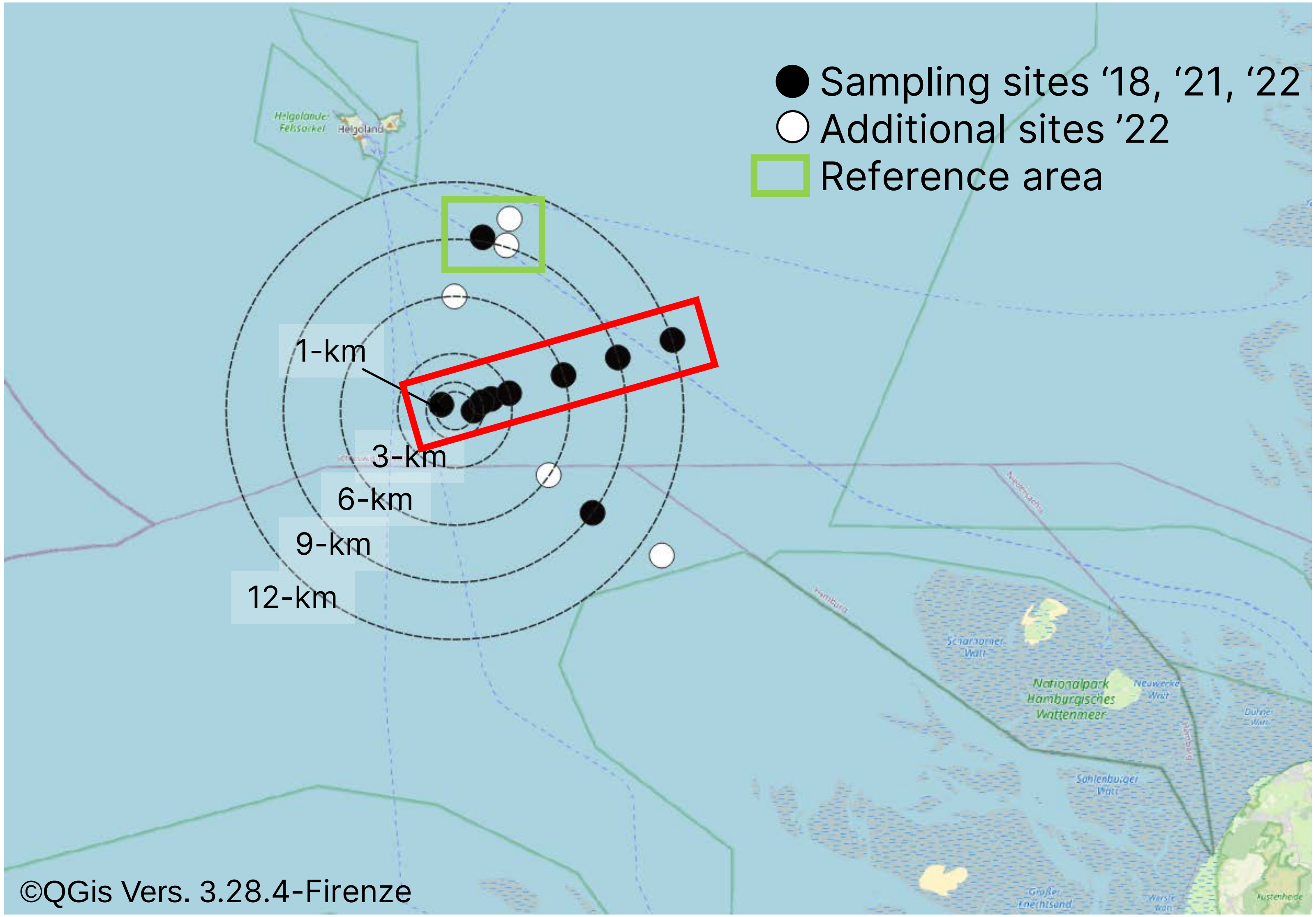
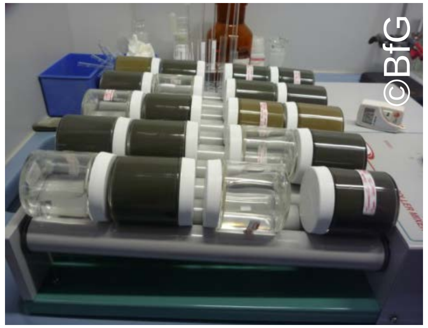
- For passive sampling sediments were sampled at the disposal site and reference site
- 2018, 2021, 2022
- In the laboratory: measuring freely dissolved concentration of HOCs in sediment pore water
- Target analytes: PCBs, PAHs, DDT and metabolites



Methodology

Sampling sediments
& transport to lab

Preparing samplers



Incubate sediments
in samplers
(4wks, in the dark)

Remove sediments

Extract silicone

Clean-up

GC-MS/MS

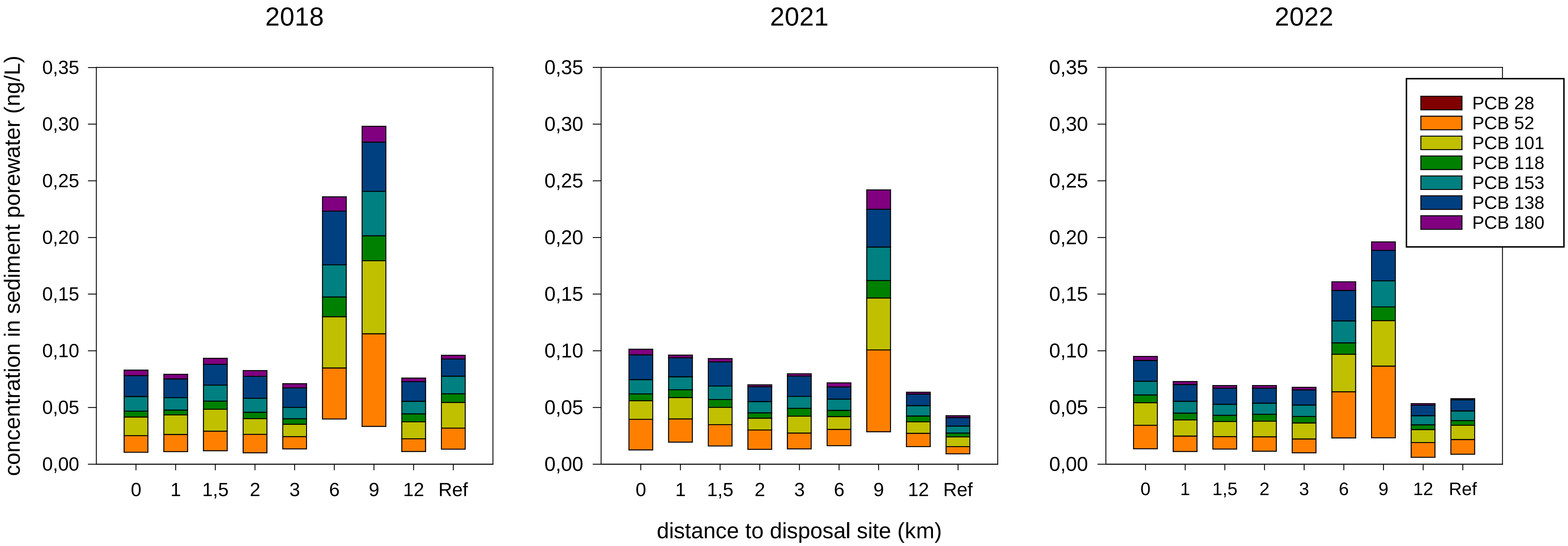
$$C_{free} = C_{silicone} / K_{silicone,aq}$$

analyte-specific silicone to water partitioning coefficients

Witt G. et al.. (2020) In: Seiler TB , Brinkmann M (Editors), Toolbox for assessment of in situ bioavailability and toxicity of organic chemicals in aquatic systems. Springer Protocols

Freely dissolved PCB concentrations

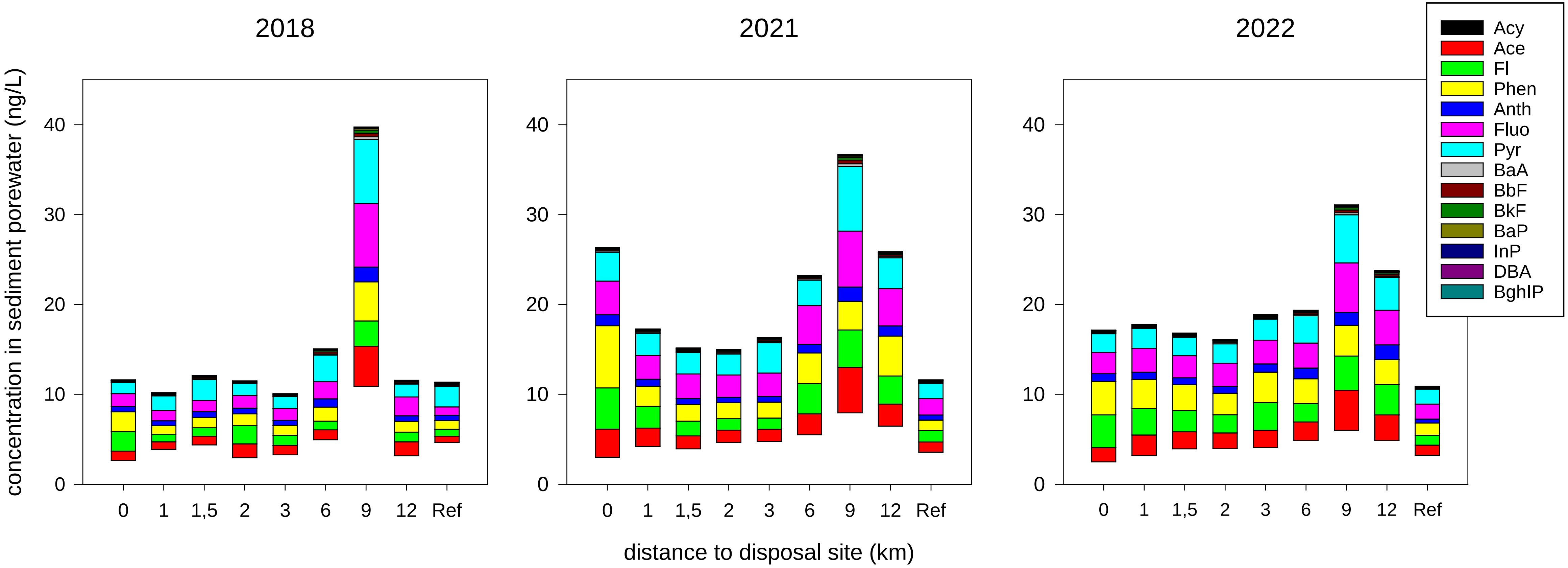
Northeastern part of disposal site



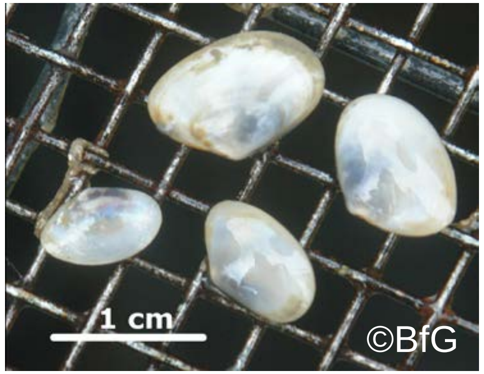
River Elbe sediments: 0.02 – 0.3 pg/L sum 7 Indic. PCB (Schäfer et al. (2015) Chemosphere 138)

Freely dissolved PAH concentrations

Northeastern part of disposal site

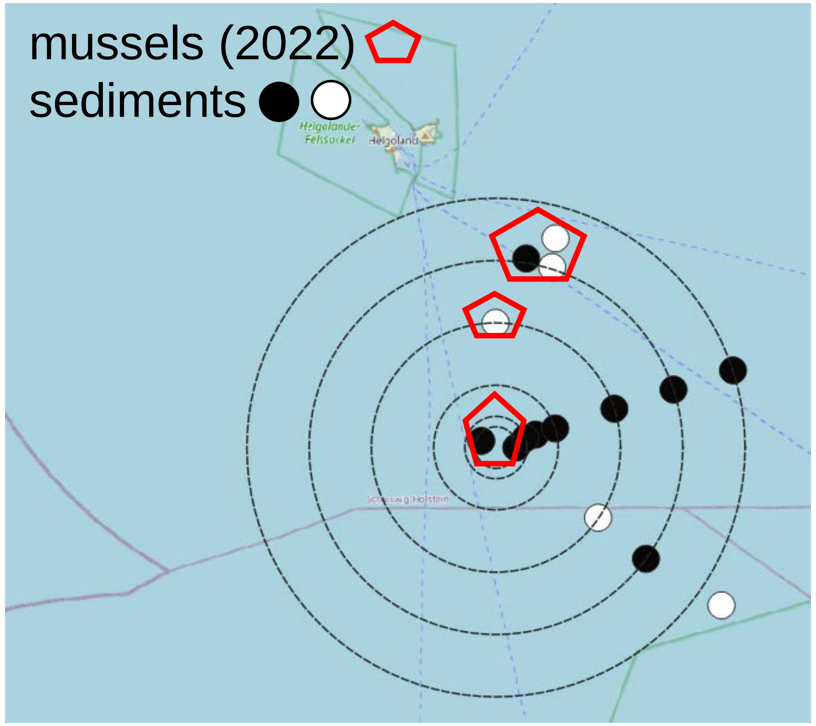


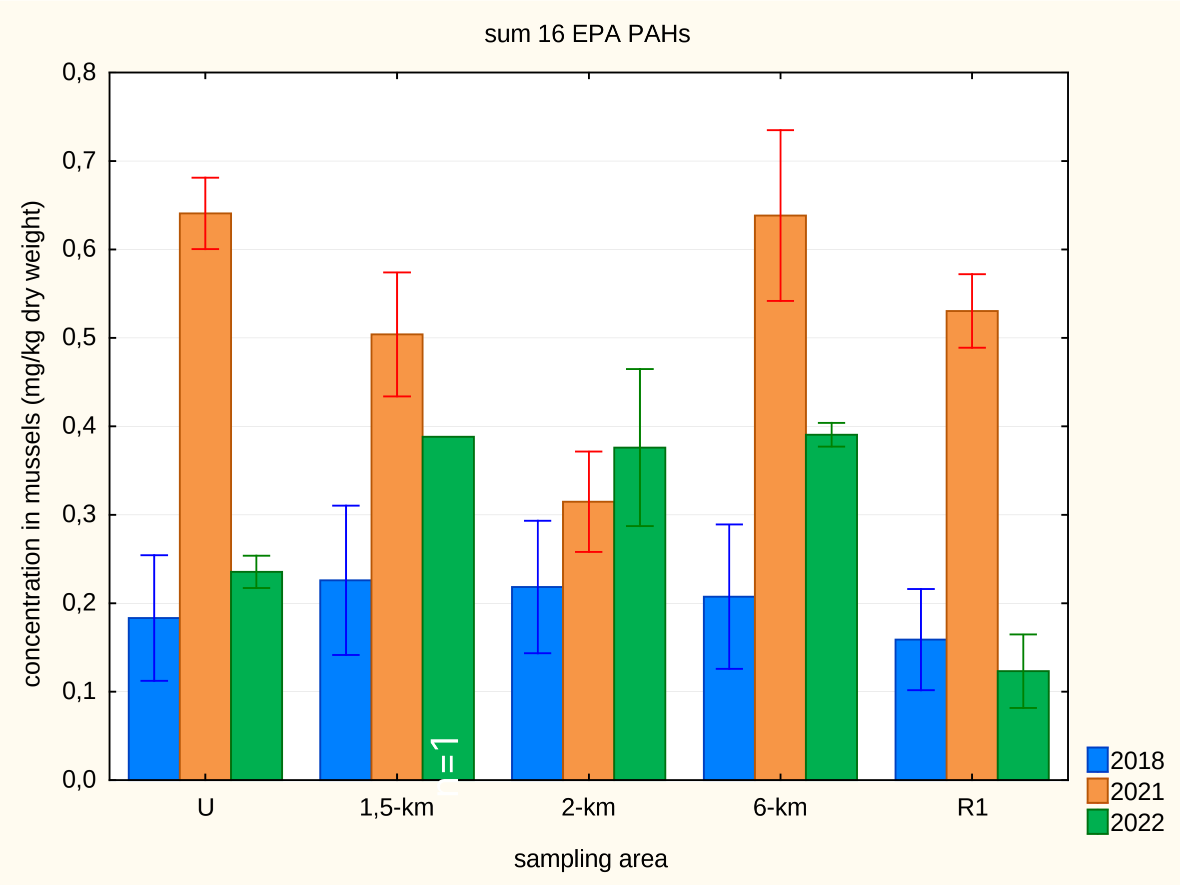
Concentrations in deposit feeding mussels



White furrow shell (*Abra alba*)

Sampling sites



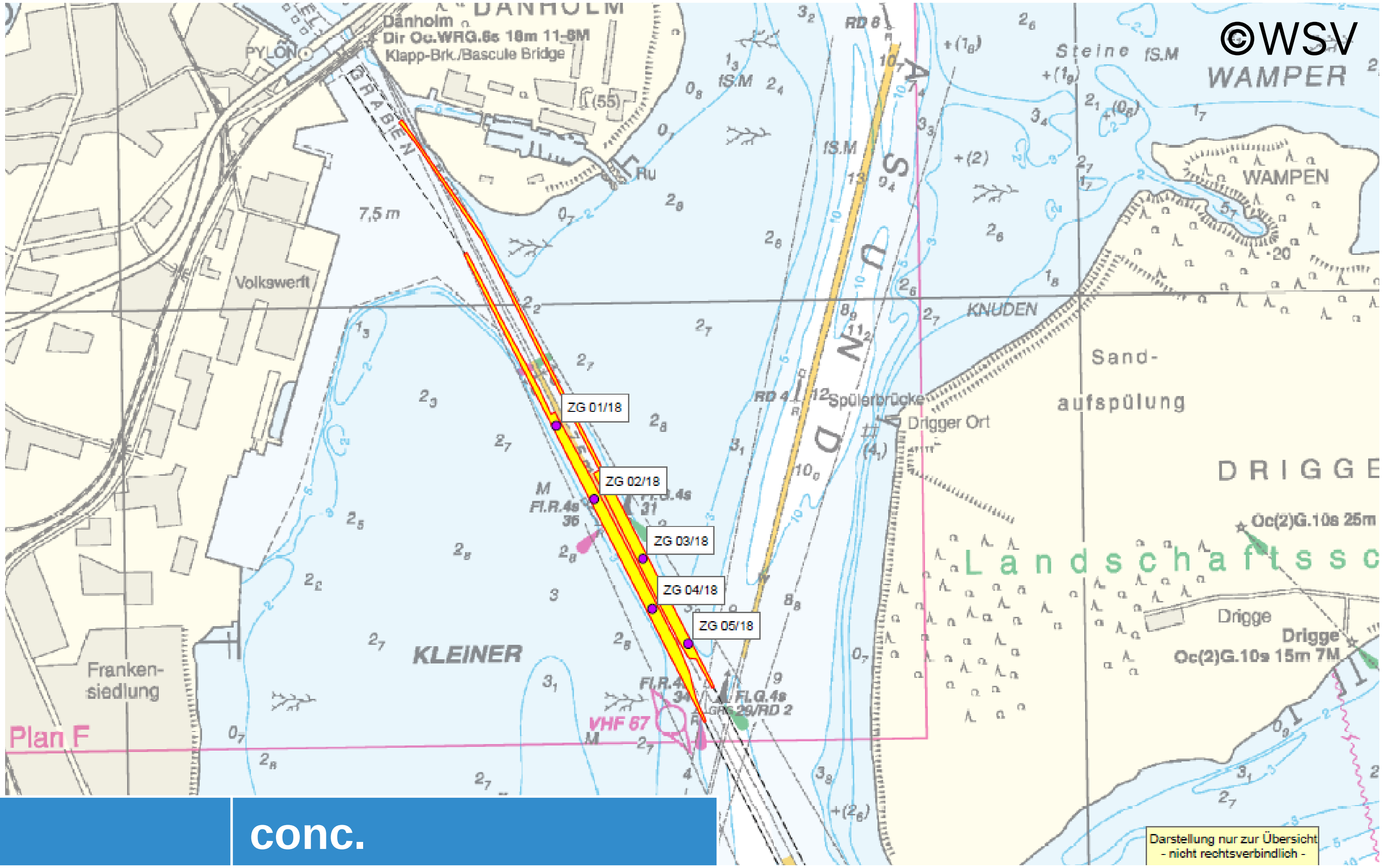


- Mussels also show increased PAH levels in 2021
- Disposal of dredged sediments does not result in increased bioavailability of PAHs at the disposal site

Contaminant bioavailability during sediment dredging activity

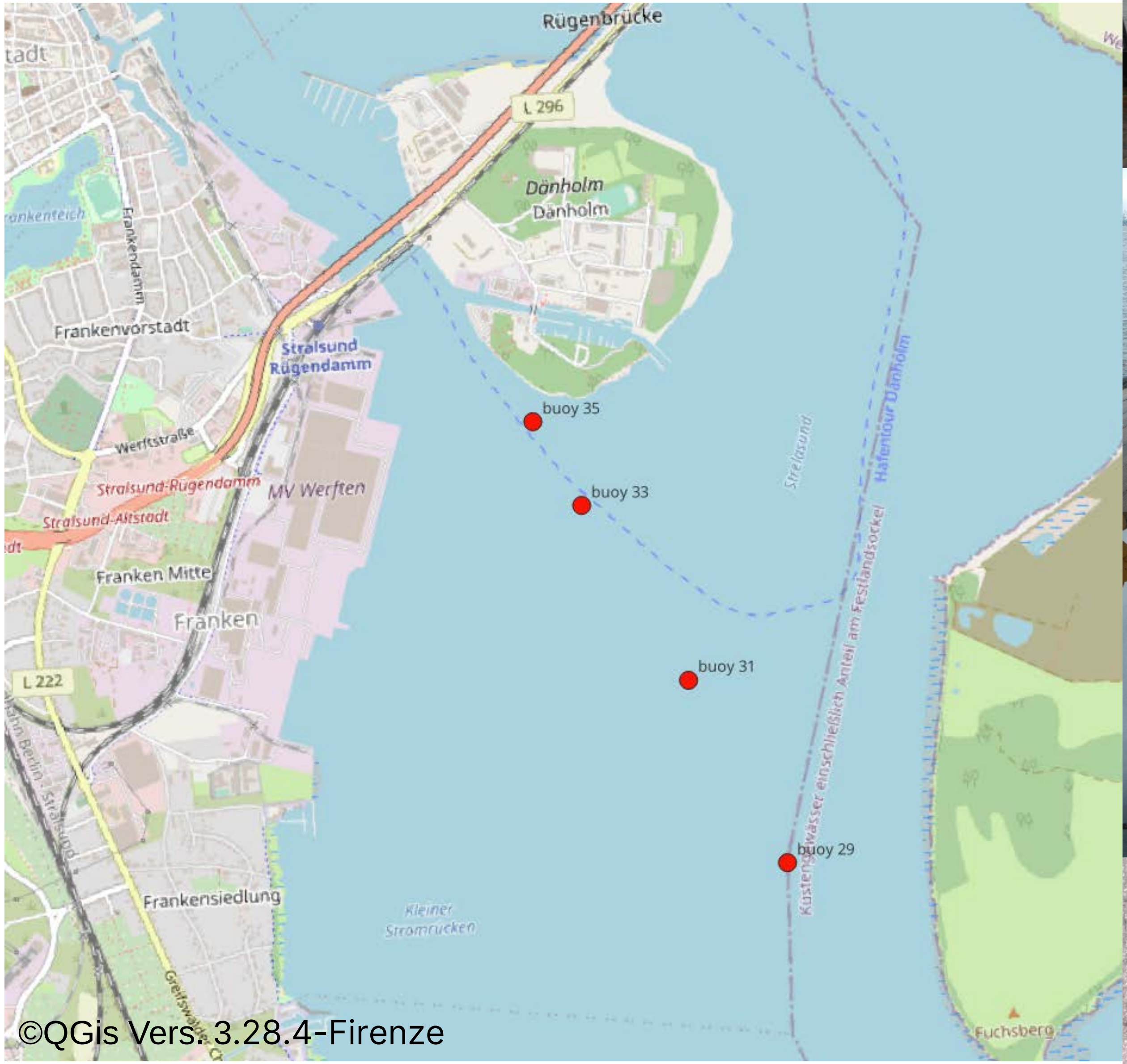
BfG

- Dredging activity in a waterway in a coastal strait in the German Baltic Sea
- Strela Sound – between the Island of Rügen and the hanseatic city Stralsund
- Overall contaminant concentrations in sediments are low
- Concentrations of As in sediment eluate are considered critical
- August 2019: appr. 200.000 m³ sediment were dredged



analytes	conc.
Sum 6 Indicator PCB	< 8 µg/kg dw
Sum 16 U.S. EPA PAH	< 1 mg/kg dw
As	≤ 80 µg/L

- Exposure of passive samplers
  - before (Dec/Jan 18/19)
  - during (July 2019)
  - after (Aug 2019) the dredging operation
- Passive samplers: silicone rubber sheets
- Exposure: for four weeks *in situ*, at buoys
- During and after the dredging operation: parallel exposure of blue mussels (*Mytilus edulis*)



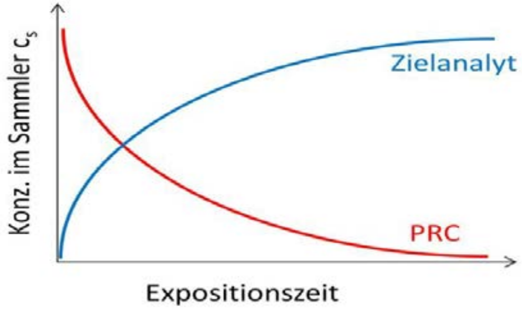
Methodology

Cleaning silicone & spiking with reference compounds → Field exposure (4 wks)

→ Recovery of samplers & transport

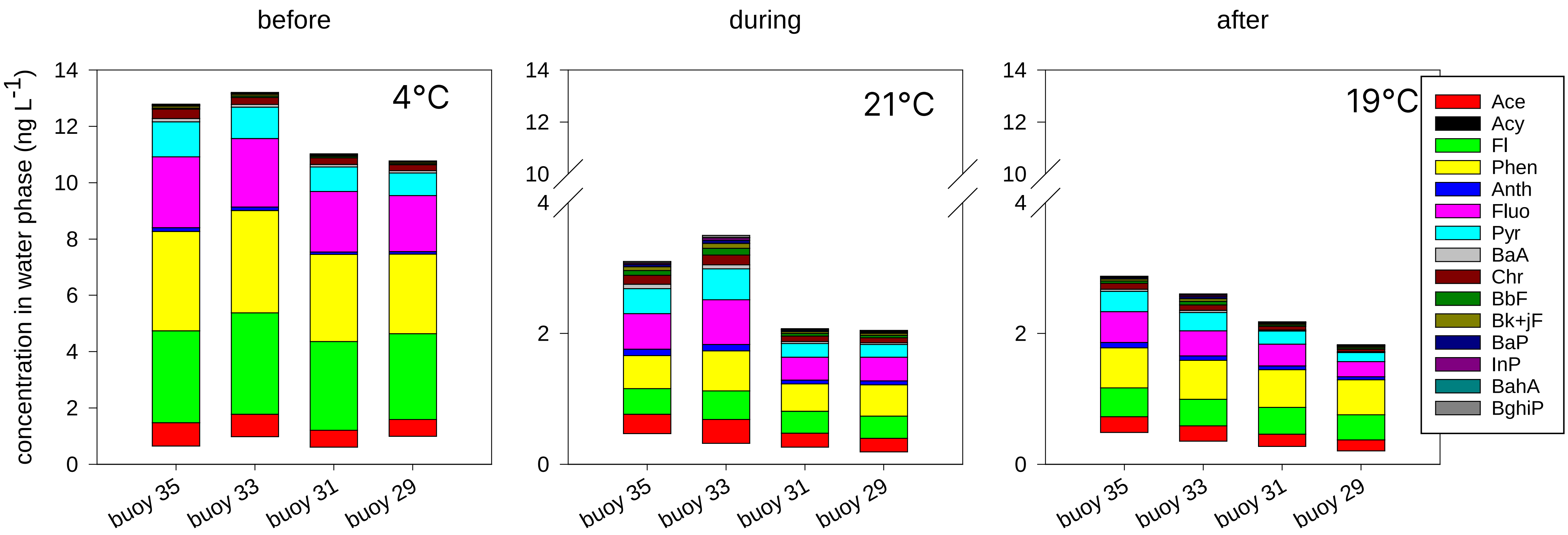
→ Extraction

→ Clean-up of extracts → GC-MS/MS → $C_{Silikon}$ → Determine sampling rates → C_{TWA}



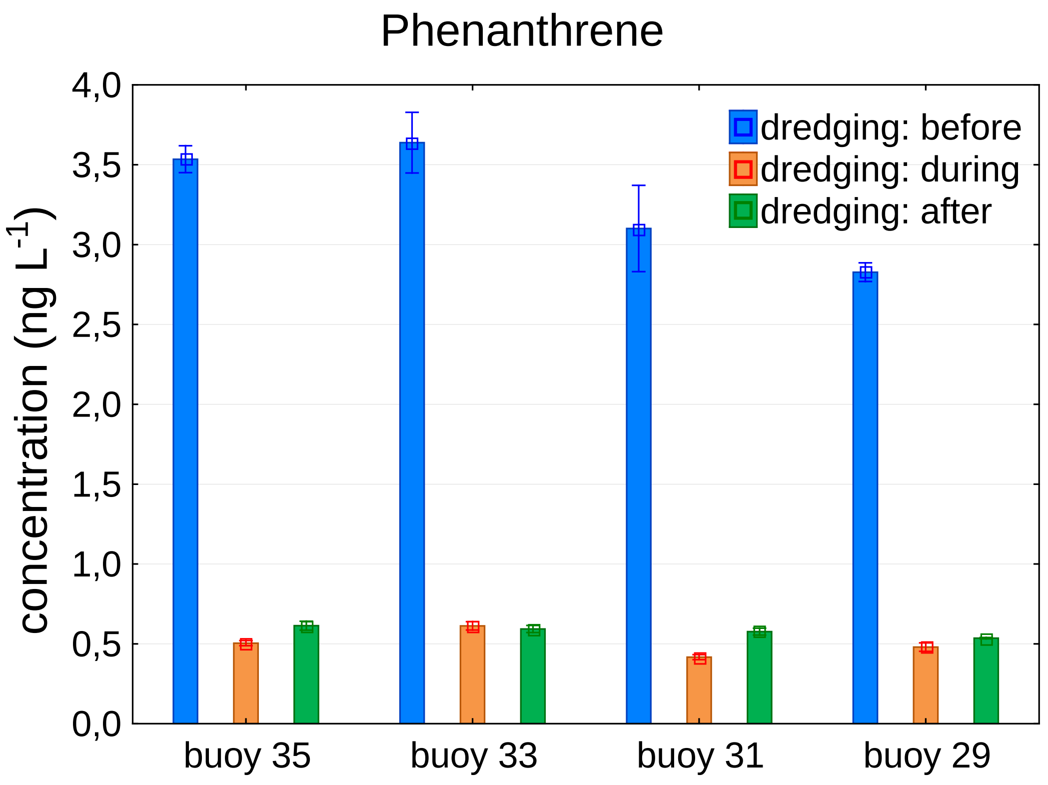
Becker et al. (2020) UBA Texte 110

PAHs in water phase



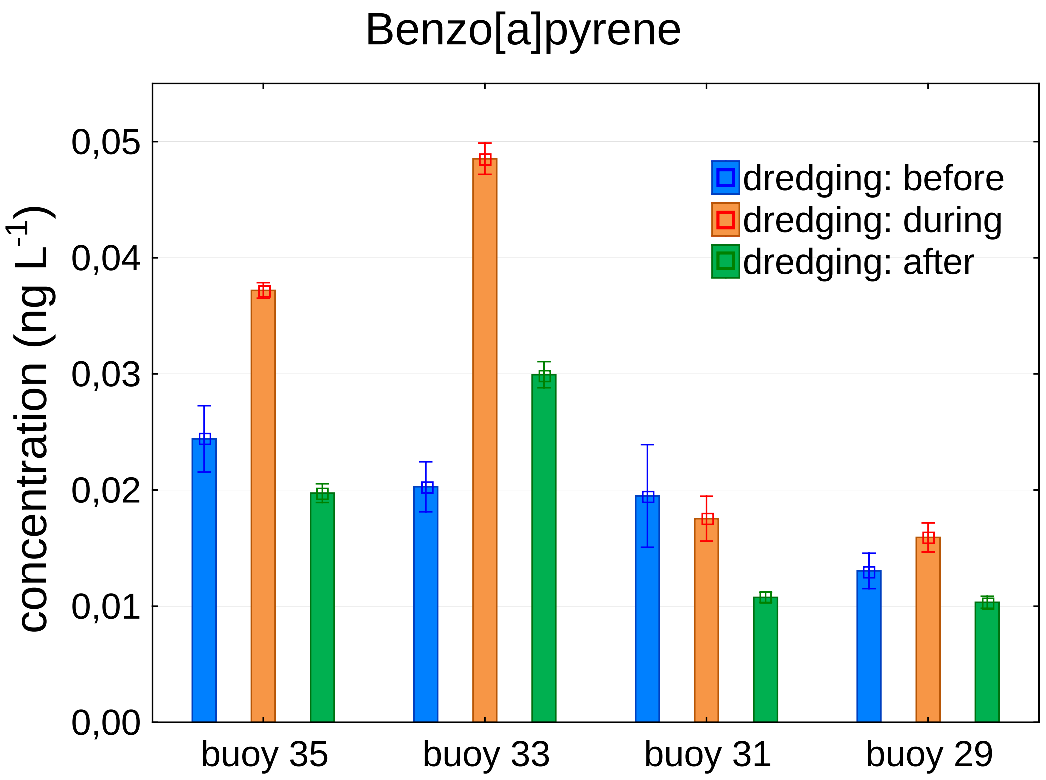
PAHs in water phase

Log Kow < 5.7



- Markedly increased levels in winter months
- No effect of dredging activity

Log Kow > 5.7



- Slightly increased levels at two buoys that are close to peninsula with its marina during dredging activity
- Levels decrease again after dreging activity

Summary

Disposal site North Sea

- Levels of PAHs and PCBs were not increased at the disposal site but at a site influenced by tidal current influenced from the river Elbe
- 2021: Increased levels of PAHs were also found in mussels in the monitoring area (unkwown source)

Dredging activity waterway

- Concentrations of HOCs were low in dredged material
- Dredging activity did not result in increased freely dissolved concentrations of sum PAHs
- Levels of PAHs with log Kow < 5.7 were highest in winter months despite temperature correction of data (unkown source)
- Levels of more hydrophobic PAHs were slightly increased during dredging activity, levels decreased again after dredging activity
- Levels of PCBs and DDT metabolites were partly < LOQ (0.4 to 30 pg/L)

Conclusions

- In both studies passive samplers enabled quantification of freely dissolved contaminant concentrations (sediment porewater or water)
- Silicone coated glass jars are advantageous in routine monitoring campagins since sediments can be exposed *ex situ* in samplers
- Silicone rubber sheets can be exposed in the field in parallel to dredging activities and time averaged concentrations are obtained
- Passive sampling can be combined with biotamonitoring (active or passive)
- Biotamonitoring and passive sampling can complement each other
- Expert knowledge for proper application of passive samplers and evaluation of passive sampling data are necessary (e.g. temperature correction)
- Passive samplers specific for certain group of contaminants → may be used as complementary tool only when studying dredged material contaminated with diverse range of chemicals

Thank you for your attention!

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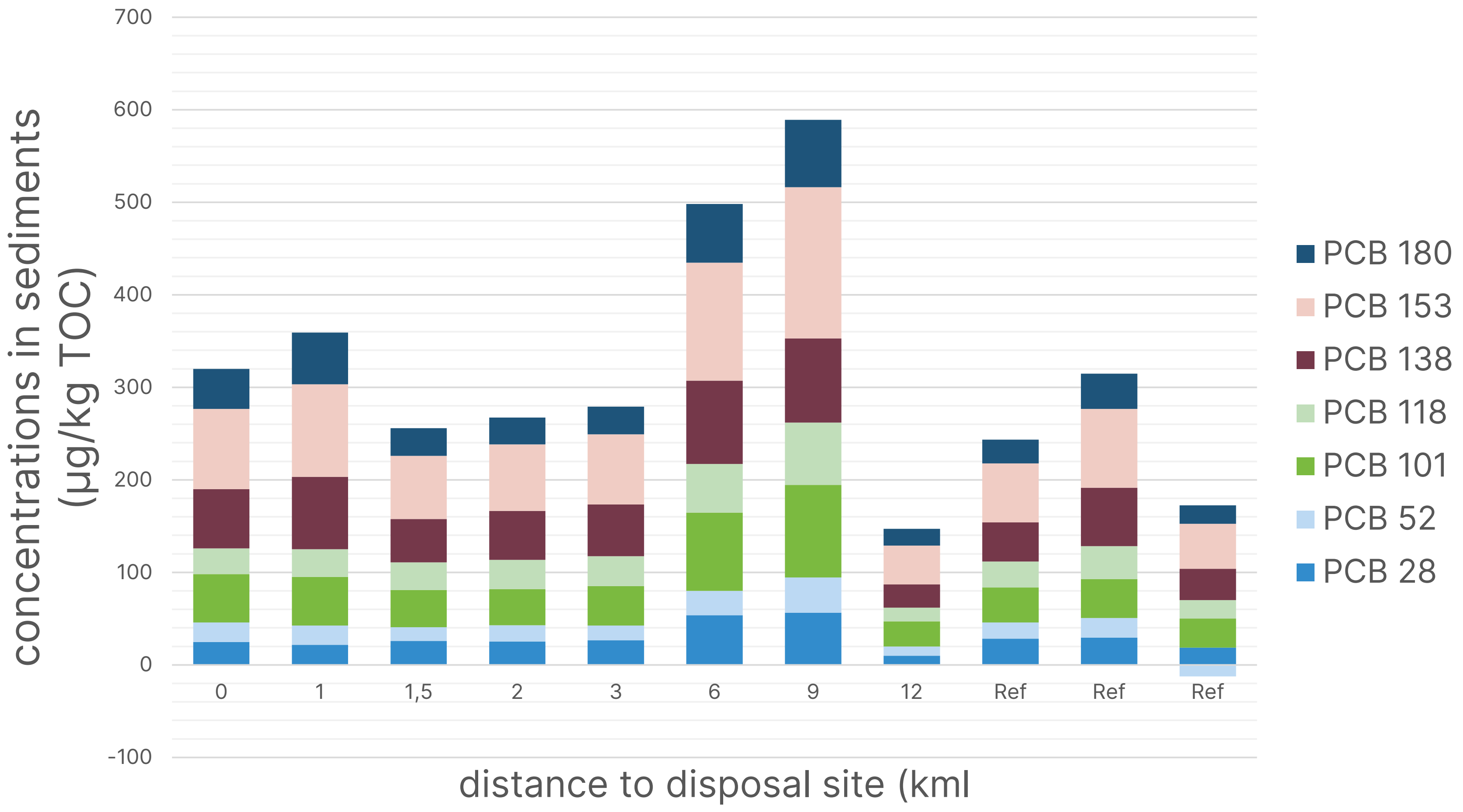
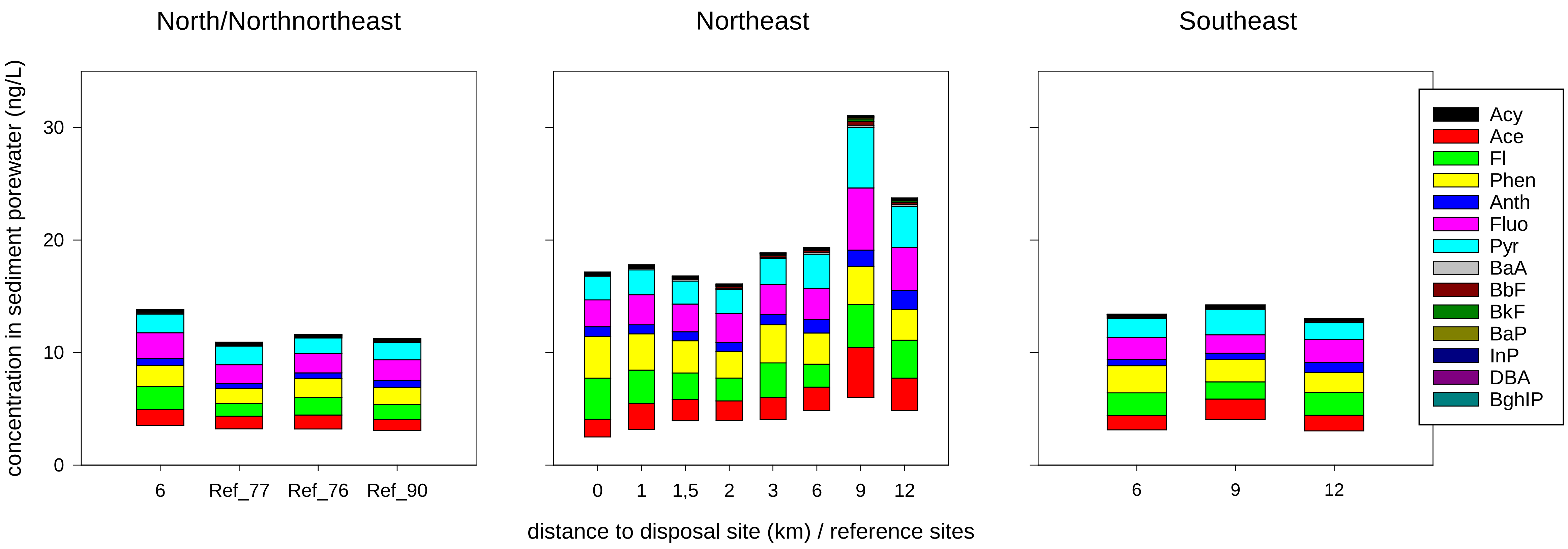
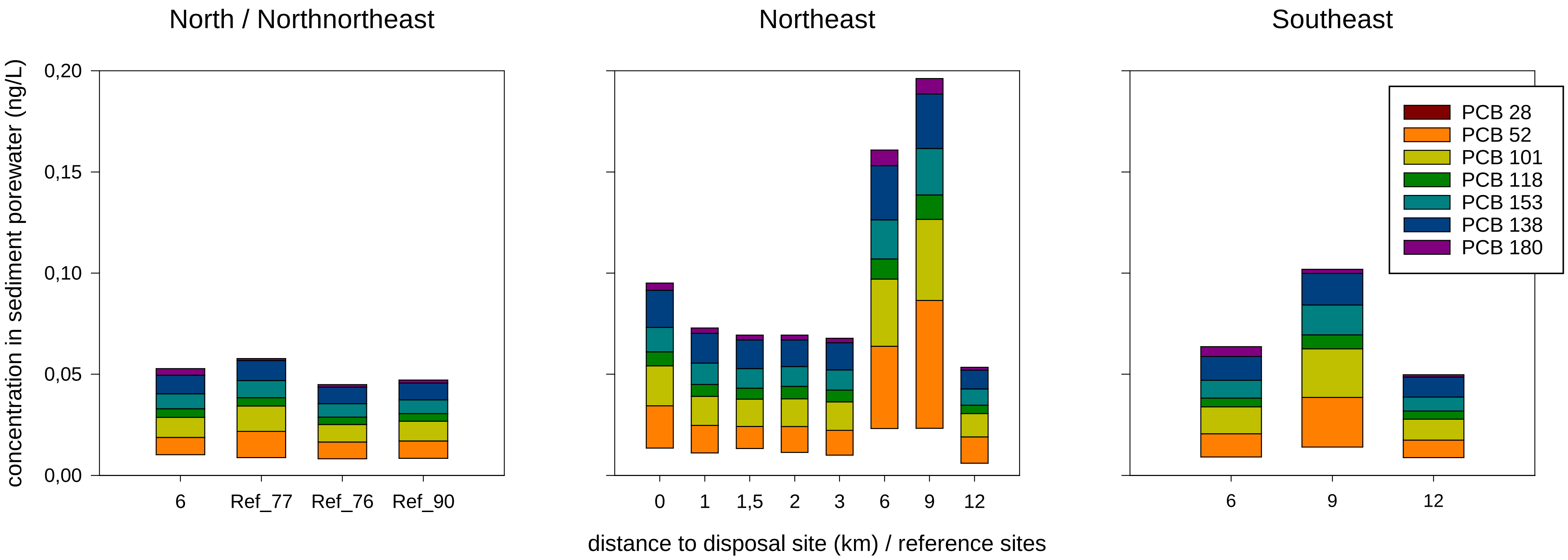
Total PCB concentrations in sediments

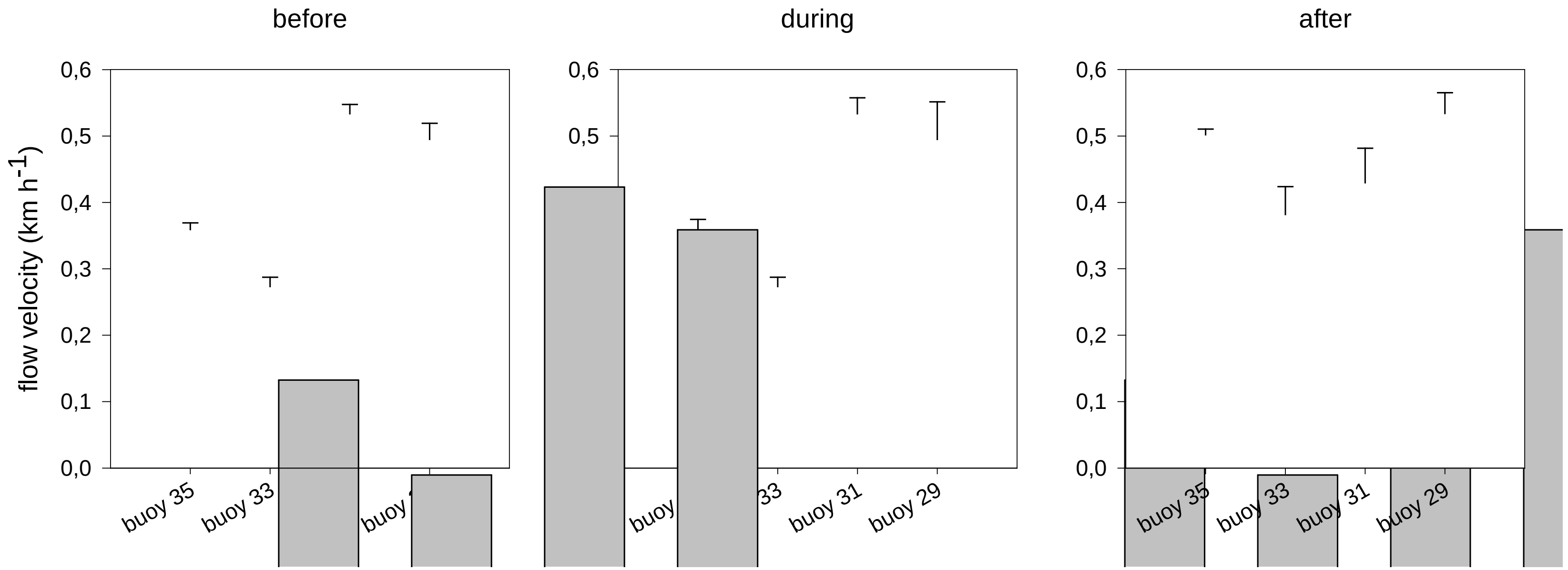


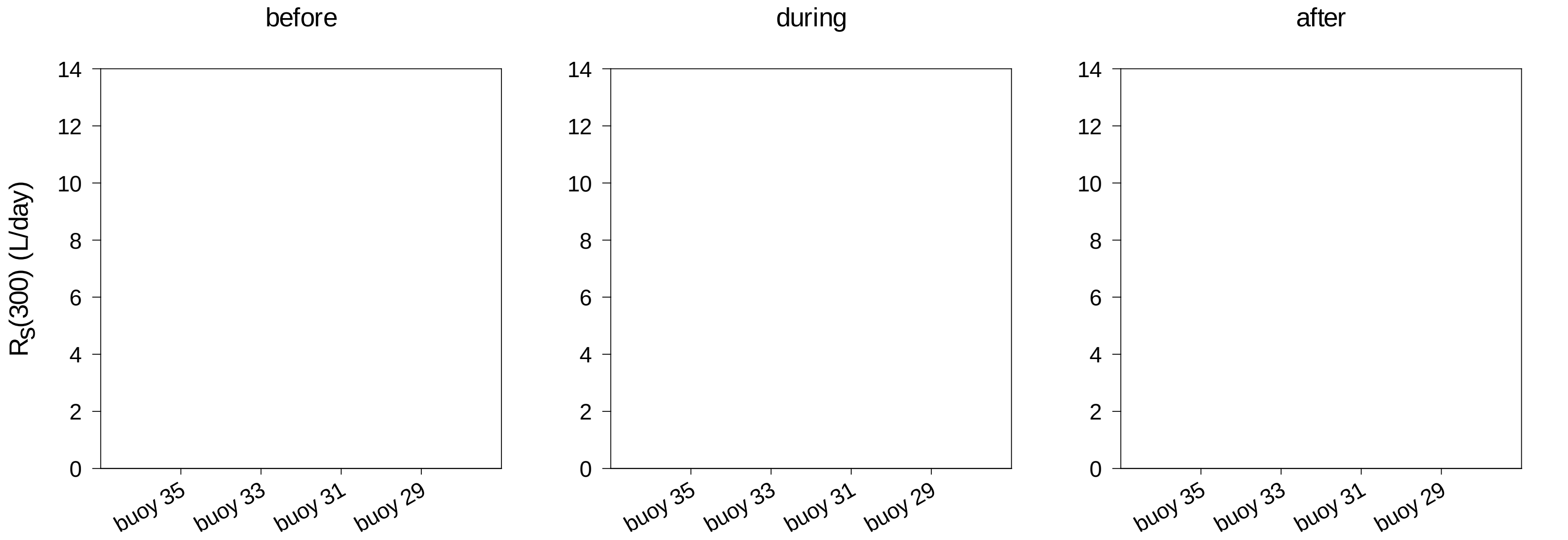
2022: Sediment porewater concentration of PAHs



2022: PCB sediment porewater concentrations




before
during
after
flow velocity (km h-1)
0,0
0,1
0,2
0,3
0,4
0,5
0,6
buoy 35
buoy 33
buoy 31
buoy 29


before
during
after
RS(300) (L/day)
0
2
4
6
8
10
12
14
buoy 35
buoy 33
buoy 31
buoy 29

Metals in mussels