

Application of equilibrium passive sampling to profile pore water and accessible concentrations of hydrophobic organic contaminants in Danube sediments<sup>1</sup>

<sup>1</sup>Submitted to Environmental Pollution

Introduction

Freely dissolved concentrations in pore water ( $C_w$ ) as well as the accessible/releasable ( $C_{AS}$ ) concentrations in the sediment can be determined by equilibration of a partitioning passive sampler (silicone rubber polymer with a high sorption capacity for non-polar compounds) with sediment using various sampler-sediment ratios. This method allows construct a sorption isotherm yielding the concentration in the pore water at low sampler/sediment ratio (minor depletion of the sediment phase) or at high sampler/sediment ratio (maximum depletion of the sediment phase) - the accessible concentration in the sediment.

We demonstrated the application of the multi-ratio equilibrium passive sampling method<sup>2</sup> (five different sampler-sediment phase ratios ranging from 0.0005 to 0.2) to measure freely dissolved concentrations and accessible concentrations of polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) in sediments that were collected at 9 locations of the Danube River.

Exposed silicone rubbers were Soxhlet extracted for 8 h in 100 mL of methanol. Subsequently, the extracts were quantitatively split in two portions for further analysis. 20% extract aliquots for analysis of PAHs were further cleaned-up on a silica gel column using diethylether/acetone elution. The 80% extract aliquots for analysis PCBs, OCPs and PBDEs were purified by a cleanup using activated silica gel modified with sulfuric acid. Target compounds were instrumentally analysed using GC-MS/MS method.

<sup>2</sup>Smedes, F., Van Vliet, L.A., Booi, K., 2013. Multi-ratio equilibrium passive sampling method to estimate accessible and pore water concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in sediment. Environ. Sci. Technol. 47, 510–517. <https://doi.org/10.1021/es3040945>

Results

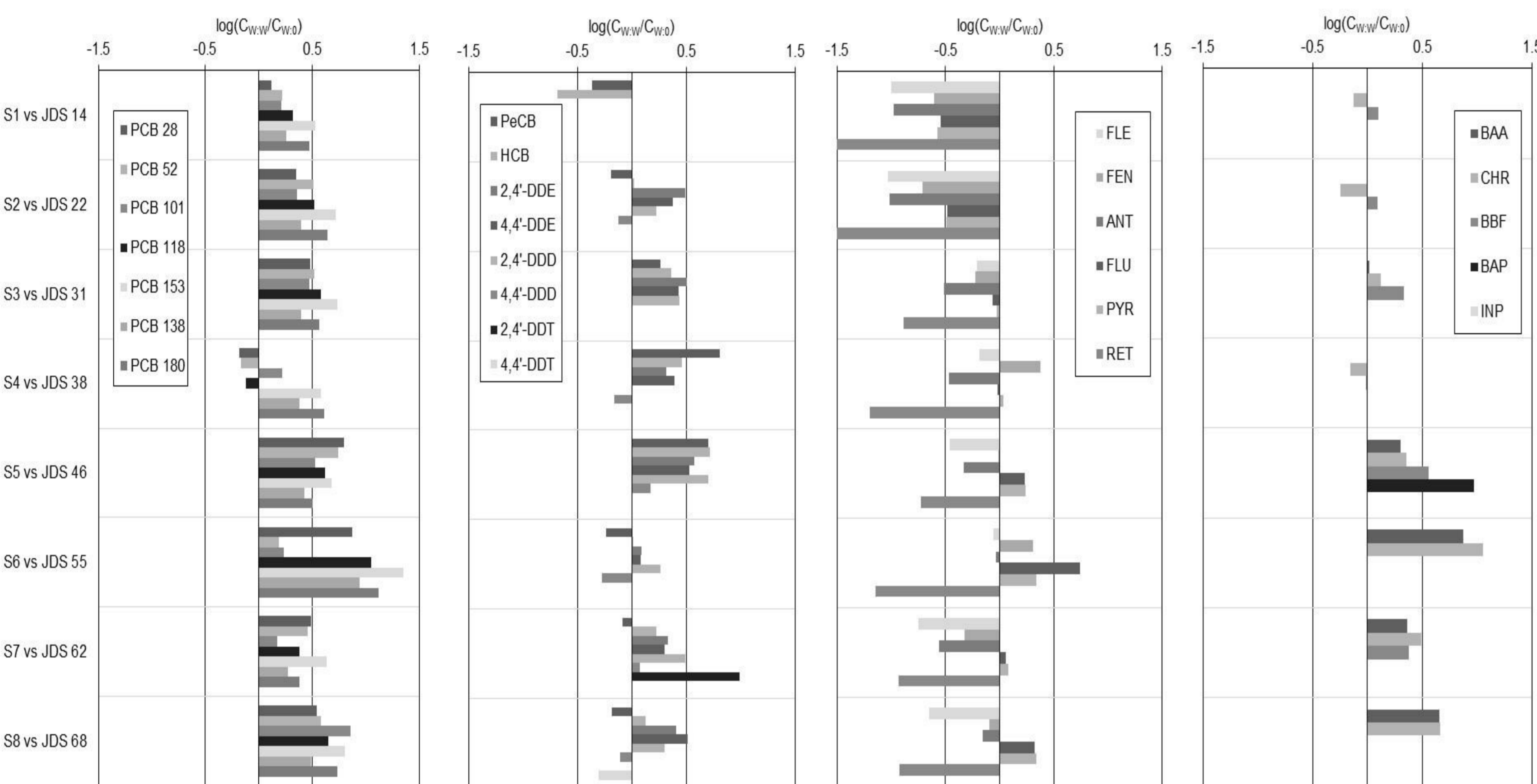


Fig. 1. Comparison of the ratio (log units) of the freely dissolved concentration in surface water ( $C_{w,w}$ ) measured by mobile passive sampling<sup>3</sup> during JDS 3 versus freely dissolved concentration in pore water ( $C_{w,o}$ ).

<sup>3</sup>Vrana, B., Smedes, F., Allan, I., Rusina, T., Okonski, K., Hilscherová, K., Novák, J., Tarábek, P., Slobodník, J., 2018. Mobile dynamic passive sampling of trace organic compounds: Evaluation of sampler performance in the Danube River. Sci. Total Environ. 636, 1597–1607. <https://doi.org/10.1016/j.scitotenv.2018.03.242>

Conclusions & Highlights

- Equilibrium passive sampling characterized sorption of organic contaminants to river sediments
- Sediment pore water concentrations were in the same range as those in the water column
- $K_{OC}$  for the accessible contaminant fraction correlated well with  $K_{OW}$
- Lower accessibility in sediment was observed for compounds with planar molecular geometry

Investigation of cosolvent application to enhance POPs' mass transfer in partitioning passive sampling in sediment<sup>4</sup>

<sup>4</sup>Belháčová-Minaříková, M., Rusina, T., Smedes, F., Vrana, B., 2017. Investigation of cosolvent application to enhance POPs' mass transfer in partitioning passive sampling in sediment. Environ. Sci. Pollut. Res. 24, 27334–27344. <https://doi.org/10.1007/s11356-017-0223-8>

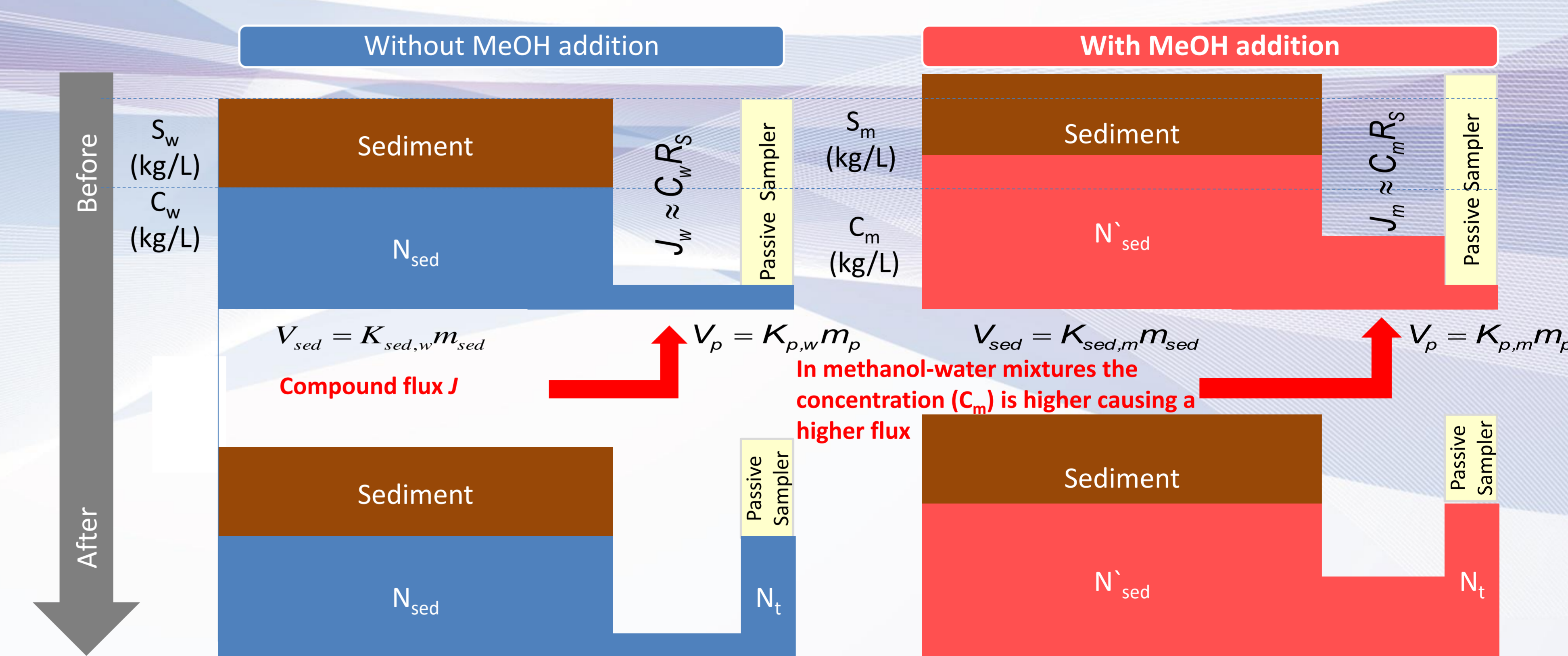
Introduction

Equilibration of POPs in the sediment - passive sampler system is slow, since concentrations of most POPs in the water phase, which is the main route for mass transfer, are very low. Uptake rates of most POPs are influenced by diffusive mass transfer through the water boundary layer (WBL) located at the external surface of the sampler.

There are several options how to accelerate attainment of sampler-water/sediment partition equilibrium. First, equilibrium is attained faster with increasing the surface area - volume ratio (application of thin samplers); the selection of passive sampler material - polymer with low sampler/water partition coefficients; exposing samplers in turbulent water or by intensive turbulent shaking of sediment in dense suspension to disrupt the WBL and decrease diffusion distance. Secondly, equilibration time can be shortened by addition of modifiers - humic acids, surfactants, cyclodextrins or alcohols to maximize mass transfer coefficients.

In water - methanol mixture sediment suspension increases the POPs' solubility and, consequently, the permeability in the water phase, resulting in higher aqueous concentrations enhance POPs mass transfer. Thus, with cosolvent addition, faster equilibration of the sampler with sediment suspension is expected.

Uptake of compounds from sediment to passive sampler in negligible depletion



Results

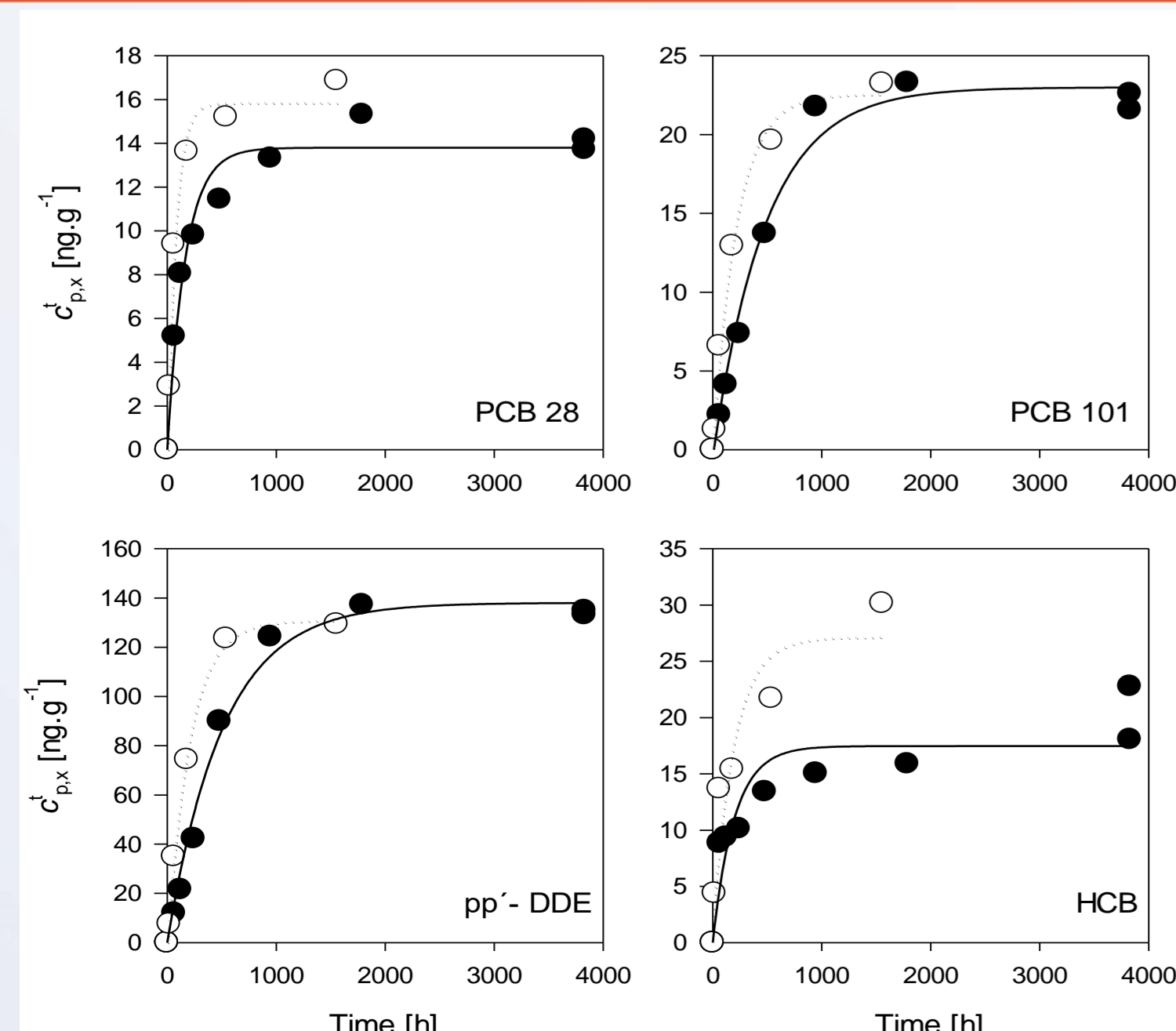


Fig. 2. Comparison of uptake curves for POPs partitioned from sediment to passive sampler without (black dots) and with (white dots) addition of methanol having molar fraction of  $x=0.1$ .

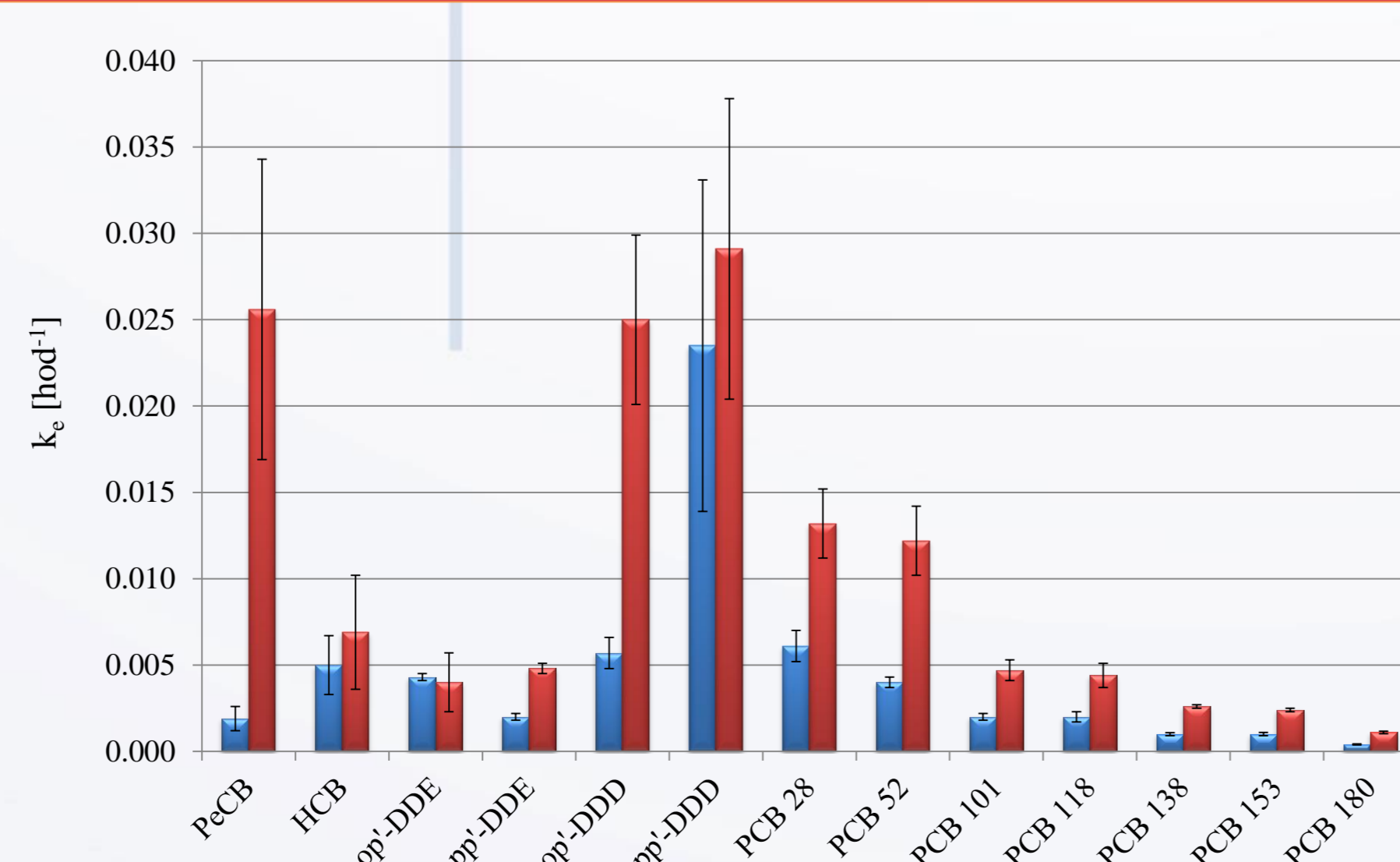
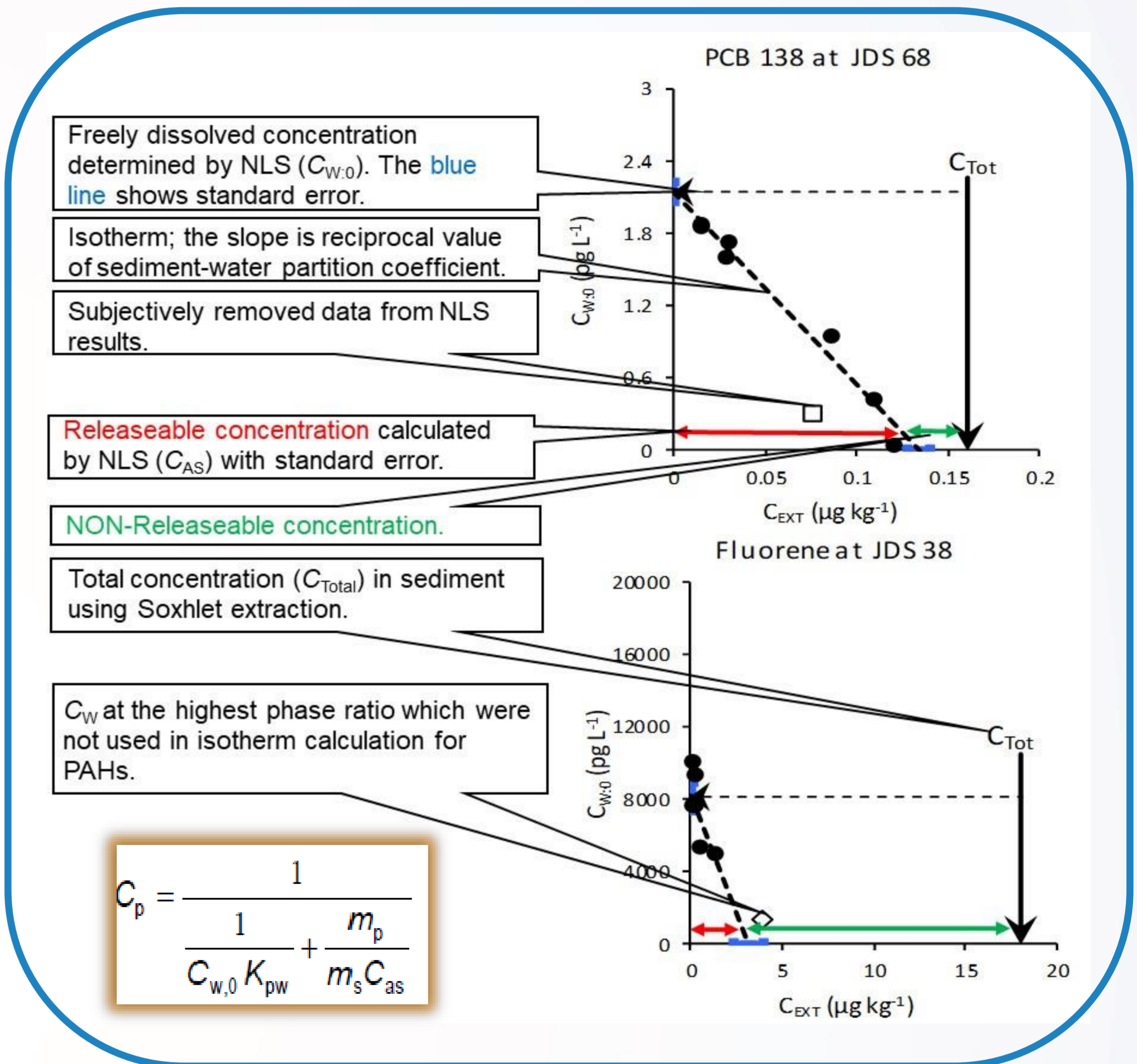
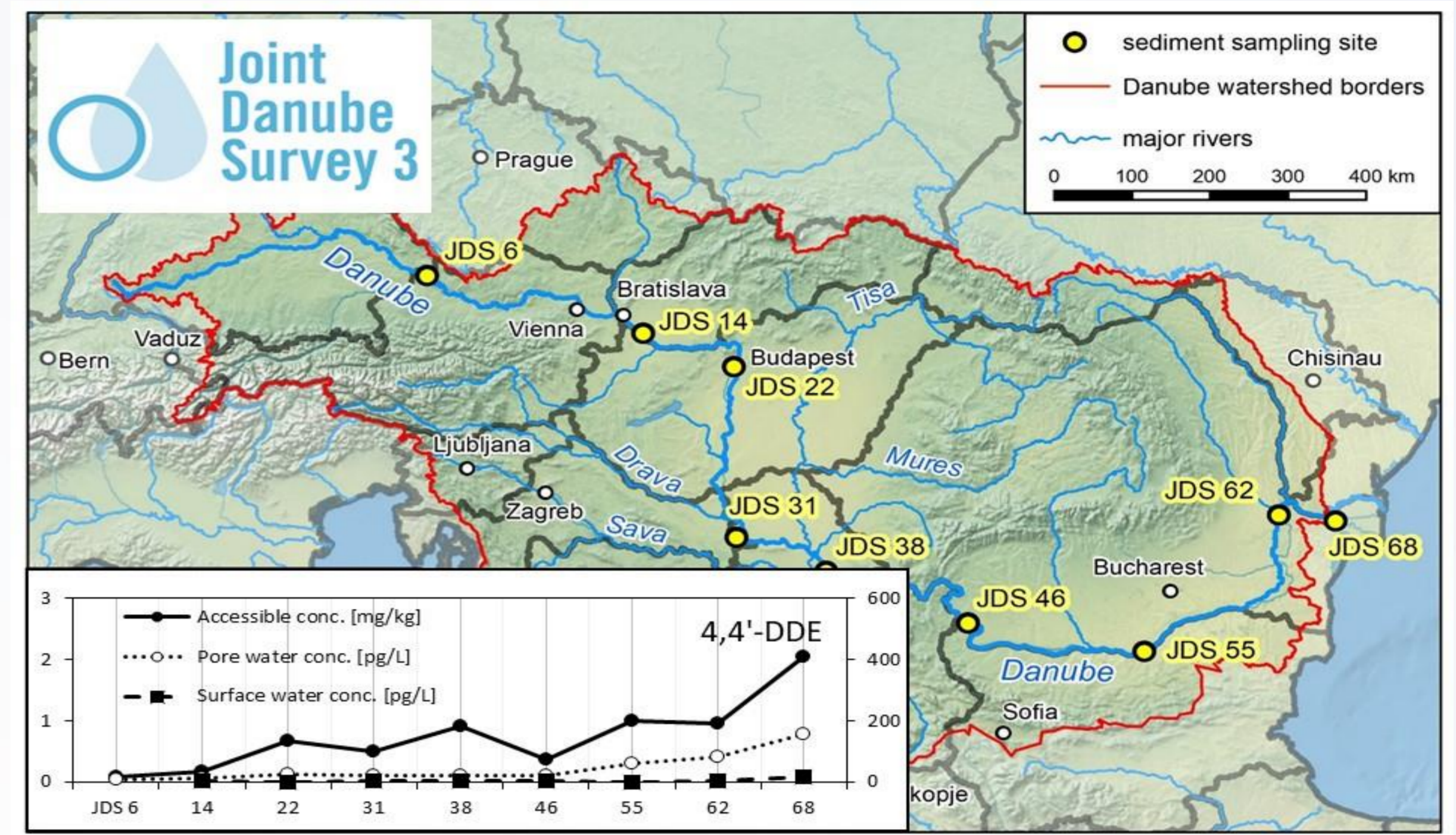


Fig. 3. Comparison of the first order rate constants ( $k_1$ ) of sorption kinetics of POPs without (blue column) and with (red column) addition of methanol.

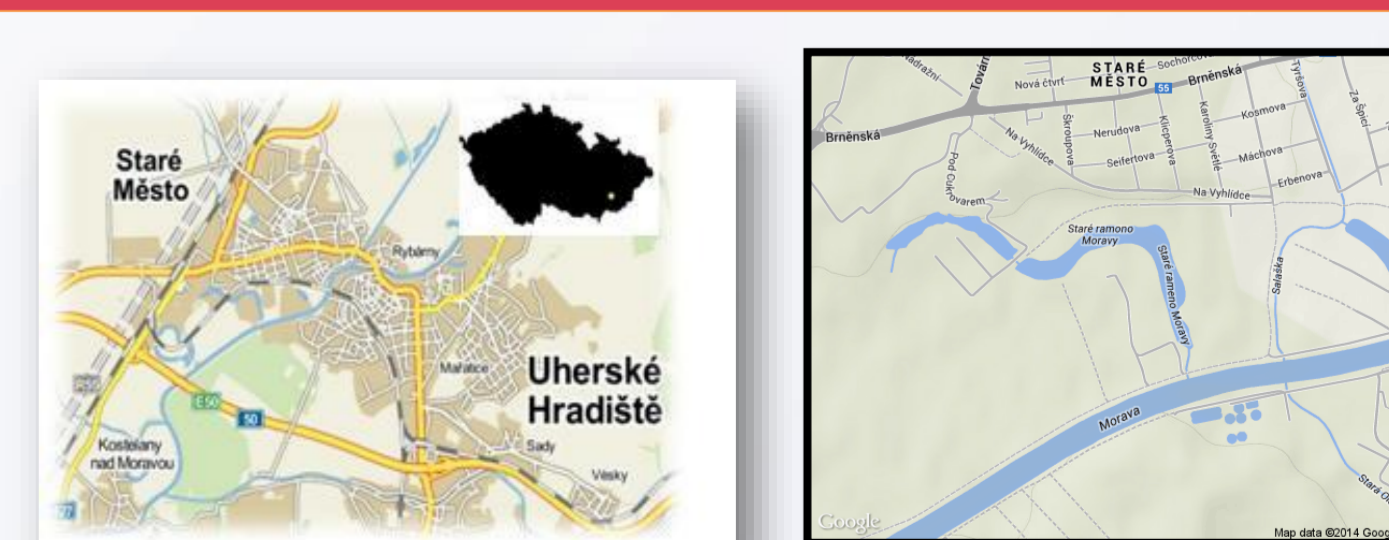
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Multi-ratio equilibrium passive sampling



Experiment design

Exposed silicone rubbers were cold extracted for 3x8 h in 3x20 mL of methanol. Subsequently, the extracts were quantitatively split in two portions for further analysis and processed as mentioned above. Sediment was collected in oxbow lake of Morava river - „Čerták“



Conclusions & Highlights

- Equilibrium can be achieved for a POPs with a broader hydrophobicity range
- Addition of methanol up to a molar fraction of 0.1 did not dramatically affected equilibrium partitioning of POPs between sediment and passive samplers while it significantly accelerated mass transfer and reduced the required equilibration time
- This approach, in agreement with the precautionary principle, will unlikely fail identifying sites at potential contamination risk. Therefore, we recommend the procedure for a fast screening of contaminated sediment sites in a tiered approach