## Application of cosolvent to reduce equilibration time of passive sampling for monitoring porewater concentrations of POPs in freshwater sediments

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The freely dissolved concentration of POPs in pore water ( $C_W$ ) has shown to be a better predictor of internal concentration in benthic organisms and sediment toxicity than total concentrations in sediment [1,2]. C<sub>w</sub> is directly proportional to chemical activity, i. e. the driving force of POPs accumulation in organisms and spontaneous diffusive transport between environmental compartments. Freely dissolved concentration in pore water can be determined by equilibration of a passive sampler, (e.g. an organic polymer) with sediment. Provided equilibrium was attained and the sediment was not significantly depleted, the C<sub>w</sub> can be estimated from the measured concentartion in the sampler and the passive sampler-water partition coefficient [3]. Attaining equilibrium for highly hydrophobic contaminants in a practical time span is a difficult task because the uptake rate by nonpolar passive sampler is limited by diffusive transport through water boundary layer at sampler surface and very low solubility of POPs in water. The uptake rate can partly be speed up by the intensive shaking of the sediment slurry. Application of thinner sampler films, e.g. micromiter thin, reduces the equilibrium time. Nevertherless, those actions only partly solve the problem. Secondly, solubility of hydrophobic contaminants in water can be increased by addition of modifiers, e.g. methanol, 2-hydroxypropyl-betacyclodextrin (HPCD) [4] that subsequently results in an increased transport through the water phase. In the present study we used silicone rubber as passive sampler known to have high permeability for hydrophobic contaminants. Solubility of POPs in water was increased by addition of methanol. The results show that addition of methanol up to 40% of water content in a freshwater sediment slurry from Morava river, Czech republic resulted indeed in faster equilibrium compared to water only for most of POPs (PAHs, PCBs, PBDEs). The addition of methanol did not affect the sediment/sampler distribution of the POPs. Therefore, derived porewater concentrations of POPs in a sediment with and without addition of methanol were not significantly different.

## **References:**

1. Burgess, R.M.; Berry, W.J.; Mount, D.R.; Di Toro, D.M. Mechanistic sediment quality guidelines based on contaminant bioavailability: Equilibrium partitioning sediment benchmarks. Environmental Toxicology and Chemistry 2013, 32 (1), 102-114; 10.1002/etc.2025.

2. Kraaij, R.; Mayer, P.; Busser, F.J.M.; Bolscher, M.V.; Seinen, W.; Tolls, J. Measured pore-water concentrations make equilibrium partitioning work - A data analysis. Environ. Sci. Technol. 2003, 37 (2), 268-274.

3. Smedes F., van Vliet L. A., and Booij K., 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., Jan. 2013, 47, 510–7.

4. Gouliarmou, V. and Mayer, P. Sorptive Bioaccessibility Extraction (SBE) of Soils: Combining a Mobilization Medium with an Absorption Sink. Environ. Sci. Technol. 2012, 46 (19), 10682-10689; 10.1021/es301515s.

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