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TU123 Equilibrium sampling of hydrophobic organic chemicals in sediments: challenges and new approaches

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The exposure risk of contaminated sediments is traditionally assessed by exhaustive extraction methods that measure total concentrations (c_{total}) including bound and freely dissolved contaminants. However, freely dissolved concentrations (c_{free}) of hydrophobic organic chemicals (HOCs) are considered to be the effective concentrations for diffusive uptake and partitioning, and they can be measured by equilibrium sampling. We have thus applied glass jars with multiple coating thicknesses for equilibrium sampling of HOCs in sediment samples from various sites in different German rivers. The coated glass jars were very convenient for routine monitoring campaigns since (1) equilibration times are minimized by the very thin coatings, (2) the equilibration is done in the laboratory and (3) equilibrium sampling is confirmed by equal analyte concentrations in various silicone coating thicknesses without tedious time-serious measurements. However, for some sediment samples analyte concentrations decreased towards thicker silicone coating possibly caused by depletion of the sediment or equilibrium partitioning not being attained. In this study, we investigated the application of sediment depletion and kinetic uptake models. Sediment depletion was tested by the model for multi ratio equilibrium sampling (Smedes et al. ES&T 2013). If non-depletion was assumed by a sufficient capacity ratio between sampler and sediment (< 0.05) and by low hydrophobic PCBs attaining equilibrium, the lower analyte concentrations in thicker silicone coating for more hydrophobic PCBs can be explained by non-equilibrium. Equilibrium concentrations in silicone were then determined by non-linear least square regression of analyte concentrations in polymer as a function of silicone mass using a first order kinetic model. Finally, the model was used to determine c_{free} of PCBs at different sites. Next to non-equilibrium partitioning for some compounds, we had difficulties in detecting target analytes such as p,p'-DDT in coated glass extracts despite high c_{total} in the respective sediment samples. We will demonstrate that microbial degradation can play a significant role during equilibrium sampling of biodegradable compounds even during short incubation times and despite confirmation of equilibrium partitioning.