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Sediment cores and bottom water samples from across the Baltic Sea region were analyzed for freely dissolved concentrations (C\text{free}), total sediment concentrations (C\text{T}), and the dissolved aqueous fraction in water of seven indicator PCBs. Ex-situ equilibrium sampling of sediment samples was conducted with polydimethylsiloxane (PDMS) coated glass fibers that were analyzed by automated thermal desorption GC-MS, which yielded PCB concentrations in the fiber coating (C\text{PDMS}). Measurements of C\text{PDMS} and C\text{T} were then applied to determine (i) spatially resolved freely dissolved PCB concentrations; (ii) baseline toxicity potential based on chemical activities (a); (iii) site specific mixture compositions; (iv) diffusion gradients at the sediment water interface and within the sediment cores; and (vi) site specific distribution ratios (K\text{D}). The contamination levels were low in the Gulf of Finland and moderate to elevated in the Baltic Proper, with the highest levels observed in the western Baltic Sea. The SPME method has been demonstrated to be an appropriate and sensitive tool for area surveys presenting new opportunities to study the in-situ distribution and thermodynamics of hydrophobic organic chemicals at trace levels in marine environments.

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