ROLE OF DESORPTION AND BLACK CARBON IN BIOAVAILABILITY OF SEDIMENT-ASSOCIATED POLYCHLORINATED BIPHENYLS

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ABSTRACT
Kinetically limited desorption and superadsorbent black carbon (BC) have probably a significant influence on the fate of hydrophobic organic contaminants in soils and sediments. This study evaluated their role in explaining often observed variations in biota sediment accumulation factors (BSAFs). Desorption of PCBs was studied with a single 24 h Tenax extraction and freely dissolved porewater concentration was determined using polyoxymethylene solid phase extraction. Oligochaetes (Lumbricus variegatus) were exposed in sediments from three PCB field-contaminated sites in a two-week kinetic bioaccumulation laboratory study. So called rapidly desorbing fraction decreased with the PCB hydrophobicity and the solids - water partitioning coefficients (KOC, KPC) followed the respective KOC values but were larger. Most of the analysed 29 congeners reached steady state in worm tissue in two weeks. Three Biota Sediment Accumulation Factor (BSAF) models were applied: 1) Animal lipid - sediment OC based basic BSAFs, 2) BC and sediment ingestion included BSAF model and 3) a model based on freely dissolved pore water concentration and bioconcentration factor. The basic BSAFs (means range 1.3-2.1) were generally larger than the BSAFs from the other models. BC and sediment ingestion term inclusive model provided closer BSAF estimates than porewater concentration based model when compared to basic BSAFs. The results confirm the role of desorption in bioavailability of sediment-associated PCBs and suggest the influence of BC. Bioaccumulation of PCBs in sediment foraging animals is not only dependent on freely dissolved, active chemical concentration in porewater but also dependent on processes derived from ingestion and assimilation of contaminated sediment particles. The model by Moermont et al. (2005) provides an interesting framework to study the effect of sediment ingestion and black carbon sorption on bioavailability.

INTRODUCTION AND AIMS
• Sediments efficiently sorb hydrophobic organic contaminants in aquatic environment
• These contaminants are persistent in anoxic and UV-light poor sediments and may accumulate to biota and food webs
• Fate assessment of these contaminants requires knowledge on factors affecting bioavailability
• Traditionally, only the total organic carbon content in sediment has assumed to be sufficient when determining bioavailable fraction
• Recent investigations suggest that kinetically limited desorption and strong sorption by pyrogenic "black" carbon influence bioavailability as well
• Freely dissolved concentration in pore water should reflect rapidly desorbing chemical and, thus, could be used to detect bioavailable pool (Kraaij et al., 2003)
• Inclusion of black carbon and sediment ingestion in bioavailability model should improve bioavailability estimates even further (Moermont et al., 2005)
• Our aims were to test different models to estimate bioavailability (biota sediment accumulation factors; BSAFs) of sediment sorbed polychlorinated (PCBs) congeners:
  1) Basic BSAF model (observed values)
  2) Black carbon (BC) and sediment ingestion included bioavailability model
  3) Freely dissolved chemical concentration in pore water and bioconcentration factor – model

MATERIALS AND METHODS
• Oligochaete worms (Lumbricus variegatus) were exposed to three PCB contaminated field sediments in a two week exposure and BSAFs (PCB conc. in worm lipid/PCB conc. in sediment OC) were determined at the end (apparent steady state) for 29 congeners using GC-MS detection
• Rapidly desorbing PCB fractions in sediments were determined using 24 hour Tenax extraction
• Freely dissolved PCB pore water concentrations (expressed as KOC) were determined using polyoxymethylene (POM) solid phase extraction (Jonker & Koelmans, 2001)
• Steady state partitioning models, BSAFs (BSAFwater): BSAFwater = (C1 fC1 fOC)/(COC)
  • Observed partitioning:
  • BC and sediment ingestion included partitioning (Moermont et al., 2005):
  BSAFwater = (C1 fC1 fOC)/(COC)
  • The BSAFwater model was applied using KOC = KPC assumption, q = a food chain multiplier including e.g. chemical assimilation efficiency, OC consumption rate, growth rate and respiration rate

RESULTS
• Estimates for the rapidly desorbing fractions were clearly dependent on PCB hydrophobicity (KOC(Figure 1))
• Polyoxymethylene extraction provided OC – water partitioning coefficients were larger than KOC for each PCB congener in all three sediment but had the same slope (Figure 2) than the 1:1 line
• Model based black carbon – water partitioning coefficients were generally larger than KOC
• BSAFs calculated from the measured porewater dissolved concentrations and BCF were, on average, 5 to 6 times smaller than the observed BSAFs in all three sediments (Figure 3).
• BC and worm sediment ingestion included model (BSAFwater) estimated partitioning much better, observed values were only two times larger in all three sediments (Figure 3).

CONCLUSIONS
• Kinetically limited desorption has a major role in bioavailability of PCBs
• Bioaccumulation of PCBs in sediment foraging animals is not only dependent on freely dissolved, active chemical concentration in porewater (desorption governed) but also dependent on processes derived from ingestion and assimilation of contaminated sediment particles.
• The model by Moermont et al. (2005) provides an interesting framework to study the effect of sediment ingestion and black carbon sorption on bioavailability.

REFERENCES