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Distribution of Hydrophobic Contaminants between Sediment, Water, and Colloids in Batch Incubations

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The sediment-water partition coefficient of hydrophobic contaminants is an important parameter for modelling the transport of these compounds in the aquatic environment. Therefore, the methodology of determining sediment-water partition coefficients has received a great deal of attention. The most widely used procedure for determining partition coefficients is the batch method, which involves shaking of sediment, water, and an amount of contaminant in a flask for several days. After equilibrium is attained, the phases are separated by either filtration or centrifugation. The partition coefficient (K_d) is calculated from the concentrations in the water phase (C^w) and the sediment phase (C^s) :

$$K_d = \frac{C^s}{C^w} \qquad (1)$$

A complete phase separation between solids and water is necessary to obtain a valid K_d value. Generally, this cannot be achieved due to the fact that the very fine particles pass through the filter, or do not settle during centrifugation. As a result the concentration of contaminants in the water phase is overestimated, and the sediment-water partition coefficient is underestimated. This phenomenon has been identified by Voice and Weber (1985), Gschwend and Wu (1985), Brownawell and Farrington (1986), among others. The particles that remain in the water phase after phase separation are commonly referred to as colloids.

A separation between the dissolved and the bound fraction can be achieved by liquid-solid chromatography. It has been shown that the presence of colloids prevents the retention of cholesterol and atrazine in gel permeation chromatography (Hassett and Anderson 1979; Wijayaratne and Means 1984). Landrum et al. (1984) and

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Backhus and Gschwend (1990) have separated dissolved and bound aromatic compounds using solid phase extraction with Sep-Pack C18 cartridges. In the present study solid phase extraction with PFA teflon beads was used for the determination of sediment-water partition coefficients.

MATERIALS AND METHODS

PFA teflon beads (median diameter 300 μm) were supplied by Fluorplast, Raamsdonkveer, The Netherlands.

Spike solutions in hexane contained α- and γ- hexachlorocyclohexane, penta- and hexachlorobenzene (1 μg/ml each), and the technical PCB mixtures Clophen A30 (8 μg/ml) and Clophen A60 (7 μg/ml).

Clean-up of the extracts was done according to Duinker and Hillebrand (1983). Samples were analyzed with a Carlo Erba MEGA 5300 gas chromatograph equipped with an electron capture detector and a 50 m CP-Sil 8 capillary column (id 0.25 mm, film thickness 0.12 μm).

PFA columns (6 mm id) were conditioned by rinsing with 2 ml hexane, 3 ml acetone and 3 ml bidistilled water. Columns were not allowed to run dry. Dissolved contaminants were extracted by passing the water phase over the PFA column. The amount of PFA needed to quantitatively extract the contaminants was determined by eluting a 100 ml spike solution in bidistilled water over columns filled with 0, 1, 2, 4 g PFA and analyzing the eluate. Adsorbed contaminants were extracted from the columns by eluting with 2x1 ml bidistilled water, 3x1 ml acetone and 2x1 ml hexane, soaking for 20 min and flushing with 5 ml hexane. The residence time of the water in the PFA columns was 20 s.

Eluates from the PFA columns, which contained the colloidally bound fraction, were extracted with 20 ml dichloromethane under reflux and stirring overnight. Sediments were extracted overnight with acetone and acetone-hexane (30/70) according to Jensen et al. (1977).

Sediment-water partition coefficients were determined by plating 0.4 or 1 ml spike solution on the wall of a 100 ml glass jar, adding 1 to 4 g of sediment from the Southern North Sea and 70 ml sea water (salinity ≈ 30). The jars were shaken for 10 days at 9 °C, and centrifuged for 20 min at 3000 RPM. The water phase was siphoned off to 5 mm above the solid surface.

Octanol-water partition coefficients (K_{ow}) were obtained from Shiu and Mackay (1986) for PCBs, from de Bruijn

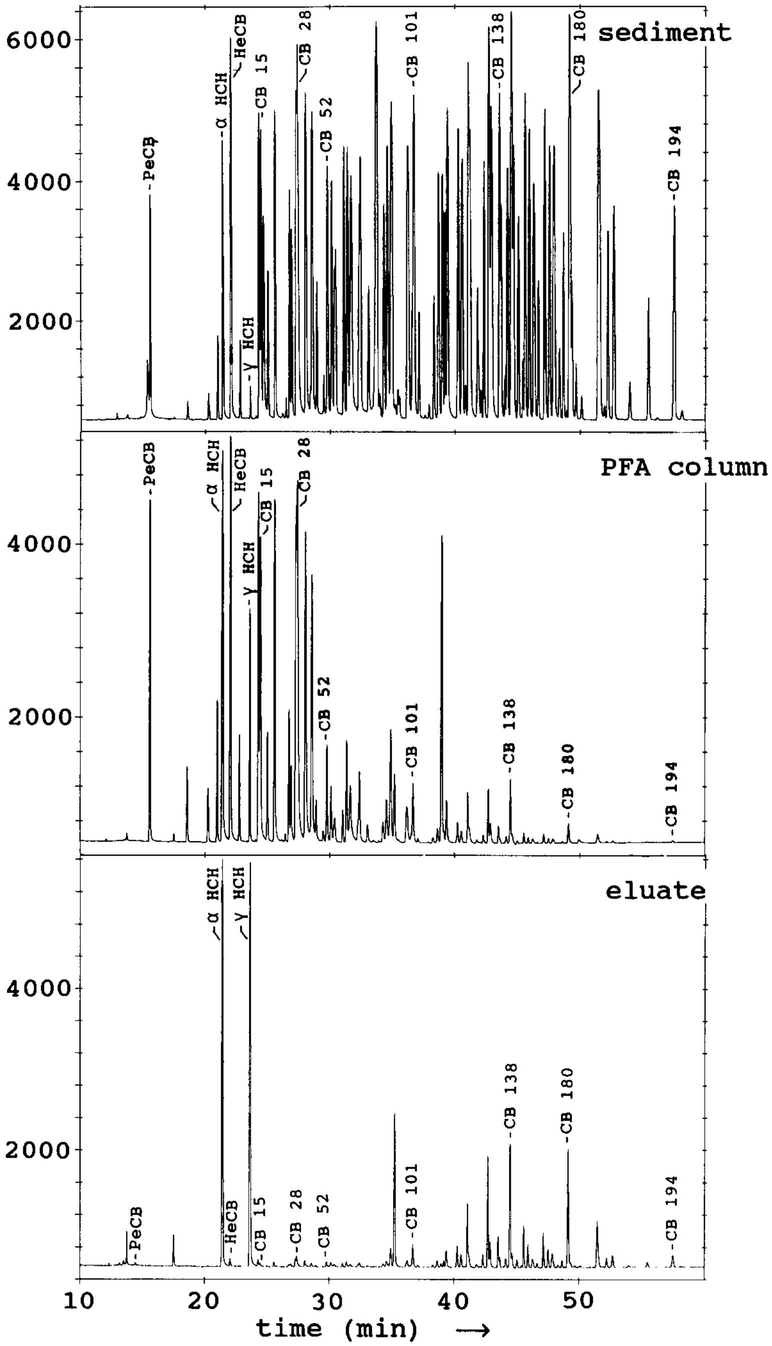

Figure 1. Chromatograms of extracts of sediment, PFA column (dissolved fraction) and PFA eluate (bound fraction). PeCB=pentachlorobenzene, HeCB=hexachlorobenzene, HCH=hexachlorocyclohexane, PCBs are indicated by their IUPAC numbers.

and Hermens (1990) for chlorinated benzenes and from Suntio et al. (1988) for HCHs.

RESULTS AND DISCUSSION

Columns containing 1 and 2 g PFA retained 94% and 99% of the chlorobenzenes and PCBs and 44% and 49% of the HCHs. Therefore, the 2 g loading was used in the later experiments, bearing in mind that the HCHs are not sufficiently retained.

Figure 1 shows typical chromatograms of sediment extracts, PFA extracts (dissolved fraction) and dichloromethane extracts of the PFA eluate (colloidally bound fraction). The eluate is relatively enriched in compounds with a large octanol-water partition coefficient (K_{ow}). In pilot experiments it was observed that contaminants in the eluate of the PFA column (the bound fraction) could not quantitatively be extracted by triple extraction in a separatory funnel with dichloromethane. A 16 hour extraction with 20 ml dichloromethane under vigorous stirring and reflux proved to be sufficient. This result indicates that the bound fraction is relatively resistant to liquid-liquid extraction.

If the contaminants associated with the colloids are not separated from the dissolved contaminants (which is the case when the water phase is extracted by liquid-liquid extraction directly after phase separation) the apparent partition coefficient is

$$K_{d,app} = \frac{C^{s}}{C^{w} + [COLL]\ C^{coll}} \qquad (2)$$

where [COLL] is the concentration of colloids in the water phase, and C^{coll} is the concentration of contaminants in the colloid phase (i.e. the amount of contaminant per unit mass of colloid). Dividing the right hand side of equation 2 by the concentration in the water phase gives the relation between the true and the apparent K_d:

$$K_{d,app} = \frac{K_{d}}{1 + [COLL]\ K_{d,coll}} \qquad (3)$$

where $K_{d,coll}$ is the partition coefficient between colloids and water. It follows from equation 3 that the errors resulting from incomplete phase separation are large when the colloid concentration is large, and when the contaminant shows a high affinity for the colloids (high $K_{d,coll}$).

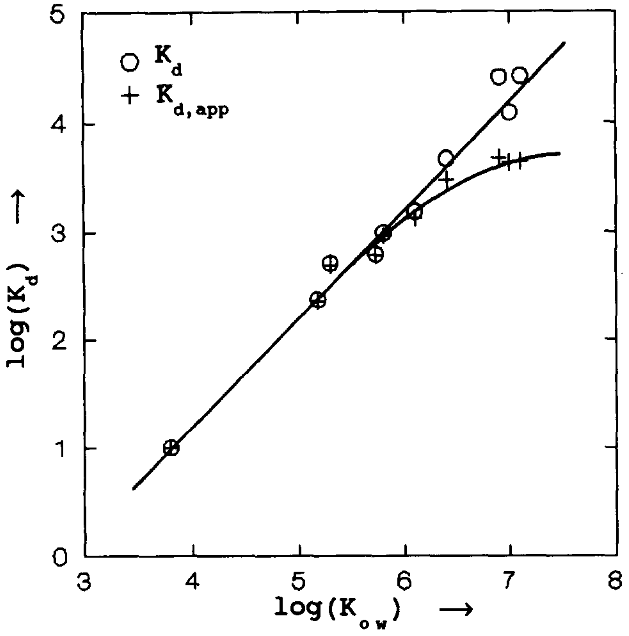

Figure 2. Apparent and true partition coefficients calculated from equations 1 and 2 as a function of the octanol-water partition coefficient.

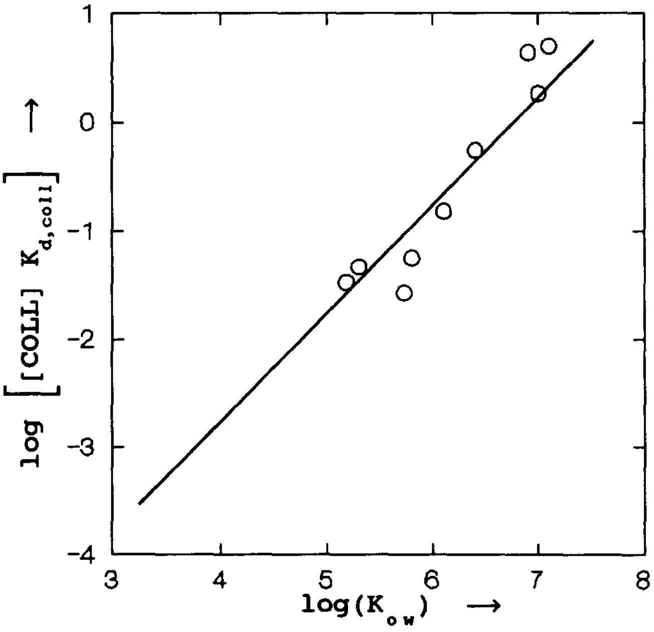

Figure 3. Partition coefficients between colloids and water calculated from equation 4 as a function of the octanol-water partition coefficient.

Figure 2 shows apparent and true partition coefficients (calculated from equations 1 and 2) as a function of the octanol water partition coefficient. Since HCHs are not quantitatively retained by the PFA columns, the amounts adsorbed by the PFA and the amounts in the eluate were added to obtain the dissolved fraction for these compounds. The apparent partition coefficient levels off at $\log(K_{d,app}) = 3.7$. The difference between apparent and real K_d increases when K_{ow} increases, to a maximum of 0.7 log units at $\log(K_{ow}) = 7$. The slope of the $\log(K_d)$ vs $\log(K_{ow})$ plot did not differ significantly from 1 (95% confidence range 0.91-1.14).

The contaminant distribution between colloids and water was calculated from the true and the apparent partition coefficients by substitution in equation 3:

$$[COLL]\ K_{d,coll} = \frac{K_d}{K_{d,app}} - 1 \qquad (4)$$

Figure 4 shows $[COLL]\ K_{d,coll}$ as a function of K_{ow}. The slope in this figure does not differ significantly from 1 (95% confidence range 0.86-1.55), which indicates that organic matter dominates the sorption of these compounds to colloids (Karickhoff 1984).

The results of the experiment reported in this paper have been confirmed in other adsorption experiments with marine sediments (organic carbon content 0.1 to 0.5%). Differences between true and apparent K_d values were negligible for compounds with $\log(K_{ow})<6$, and were up to 1 log unit for more hydrophobic compounds. Fresh water sediments probably will yield different results due to their higher organic carbon contents and higher amounts of colloidal material.

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