

Sediment-water partitioning of PCBs, PAHs, PCDDs and PCDFs.

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Abstract

The equilibrium partitioning of polychlorinated biphenyls (PCBs), hexachlorobenzene (HCBz), polycyclic aromatic hydrocarbons (PAHs), polychlorinated-*p*-dioxins (PCDDs) and -dibenzofurans (PCDFs) between field contaminated estuarine sediments and water was determined using the co-solvent method. With thermostated batch stir experiments apparent K'_{oc} - and compound specific K_{oc} -values were measured. Apparent K'_{oc} -values were influenced by the amount and characteristics of the sediment and porewater organic carbon and the separation technique. The compound specific K_{oc} -values were found to be independent of the separation technique used and hardly influenced by the amount and origin of the sediment. These K_{oc} -values closely reflected the hydrophobic characteristics of the compounds. An approximately linear inverse relationship between the $\log K_{oc}$ values and the fraction cosolvent was observed. The results of these determinations are discussed and compared to literature values obtained with other experimental methods and with several types of structure-activity relationships.

1. Introduction

Sorption of nonionic organic chemicals to natural sediments, soils and dissolved organic matter strongly controls their environmental transport, fate and uptake by organisms. The influence of sorption can be quantified by the equilibrium partitioning of these chemicals between solid and aqueous phases as well as by the kinetics of the ad- and desorption processes. A growing number of regulatory agencies utilize the equilibrium partitioning concept for the derivation of sediment quality criteria for these chemicals from water quality criteria^{1,2}). Additionally, most water quality and transport models are based on equilibrium partitioning of the chemicals concerned.

Field observations showed that PCBs and other hydrophobic compounds sorb much lesser to suspended sediments than would be predicted on the basis of either the solubility or the octanol-water partition coefficient ($K_{d, oct}$)³). This "reduced apparent" sorption coefficient K'_p has been explained in terms of numerous potential factors including enhanced solubility due to the presence of dissolved organic matter in the aqueous phase and inappropriate separation techniques⁴). Various methods have been developed for the determination of equilibrium partitioning coefficients (K_{oc}) for extremely hydrophobic compounds. Methods that use mechanical separation techniques, such as filtration³) and centrifugation⁵), suffer from incomplete phase separation and usually underestimate the K_{oc} . It was shown that centrifugation up to 2000 g could not distinguish dissolved PCDDs/PCDFs from bound phases⁶).

Gas-purging dissolved contaminants from the water phase cannot be applied for low volatile compounds such as most PAHs and PCDDs/PCDFs and might erroneously include sorbed contaminants in the dissolved phase, through particle-mediated transport across the water/air interface⁷.

Other techniques, however, that rely on chromatographic principles⁸ (solid-liquid partitioning on chromatographic columns), membrane diffusion⁹ (dialysis membranes) or solubility enhancement^{10,11} (cosolvents) may be suitable for the determination of K_{oc} 's related to either dissolved organic phases or solids. However, it was found that the determination of K_{oc} -values of PCDDs and PCDFs with the reversed phase technique was influenced by the amount of particles present (the so-called *particle concentration effect*)⁶.

Cosolvent solutions have been suggested as experimental tools for estimating hardly measurable sediment- or soil-water partition coefficients of highly hydrophobic compounds^{10,12}. In this research, we report on the applicability of the solvophobic model to explain experimental data of K_{oc} determinations for sorption of PCBs, PAHs, PCDDs and PCDFs by "field contaminated" sediments from binary mixed solvents. Using methanol as cosolvent, K_p values for 14 PCBs, 13 PAHs, 12 PCDDs/PCDFs and HCBz were measured at our laboratory. The results of these determinations are discussed and compared to literature values obtained by other methods.

2. Materials and methods

A detailed description of the experimental procedures can be found in the papers of Smedes *et al.*¹³ (1994) and Loonen *et al.*¹⁴ (1994).

Materials. All individual PCBs and PAHs were obtained from Promochem (Wesel, FRG). The organic solvents were from Mallinckrodt (St. Louis, USA) except MeOH that was from Labscan (Dublin, Ireland). ¹³C-labelled PCDDs and PCDFs were from Cambridge Isotope Laboratories Inc. (USA).

Batch stir testing and analytical protocols

The batch stir experiments for the determination of the K_p 's were performed in 18 L stainless steel pressure containers at a constant temperature. Sediments from the estuary of the rivers Rhine and Meuse were stirred for at least 72 hours with water-methanol mixtures in order to reach equilibrium between bound and dissolved contaminants. After stirring the mixtures were left for 48 hours to let the sediment settle. For mass-balance control both the concentration of the contaminants in the waterphase (C_w) and sediment (C_s) were determined. Analytical procedures for both waterphase and sediment consisted of extraction of organic contaminants, concentration, clean-up and analytical separation and determination as described elsewhere^{13,14}. PCBs were detected by use of dual capillary column HRGC, PAHs by fluorescence RP-HPLC and PCDDs/PCDFs by HRGC-HRMS.

Cosolvent theory

Based on the log-linear relationship between the solubility of organic compounds in water and the volume fraction cosolvent¹⁵, the decrease of the K_p with increasing volume fraction cosolvent can be described with the solvophobic model¹⁶:

$$\log K_{p,m} = \log K_{p,w} - \alpha \sigma_c f_c \quad (1)$$

where the subscripts m and w refer to mixed and aqueous solvents, respectively. The parameter α whose value may vary among chemical families¹⁰, is related to solute-sediment and solvent-sediment interactions. The parameter σ_c varies with the cosolvent

and the solute under consideration, and is known as the solubilizing power of the cosolvent¹⁵. σ_c is theoretically predicted and experimentally verified to be proportional to the $\log K_{d,oct}$ of the solute¹⁰. Thus, the more hydrophobic compounds exhibit a larger enhancement of solubility relative to less hydrophobic compounds. Methanol was chosen as cosolvent because in several studies it was found that the reduction in sorption due to methanol addition was induced solely by the increase in sorbate solution-phase activity coefficient and not by swelling of the organic matter matrix when compared to acetone and DMSO as cosolvents¹⁷.

3. Results

Sorption coefficients in pure water were obtained by linear extrapolation of $\log K_{p,m}$ to 0% methanol as shown in figure 1. The molar based K_p^* -values decrease log-linear with increasing methanol concentration of the PCBs. Similar relationships were found for PCDDs/PCDFs and PAHs. The two- and three-ringed PAH-compounds exhibited fast aqueous biodegradation resulting in an upward deviation (low aqueous concentration) from linearity at 0% methanol. The more hydrophobic compounds ($\log K_{d,oct} > 5.5$) apparently interact with dissolved or particulate organic matter remaining in the water phase after separation as shown in figure 1 at low methanol concentrations. Compared to the truly dissolved fraction, aqueous concentrations are overestimated at 0% methanol - and hence the K_p underestimated.

No particle concentration effect could be observed for sediment concentrations ranging from 3 to 10 g/L. The K_p -values agreed well with reported values for compounds having a $\log K_{d,oct} < 5$. Above this value our measurements always exceed reported K_p -values except for some values determined from desorption experiments²⁰.

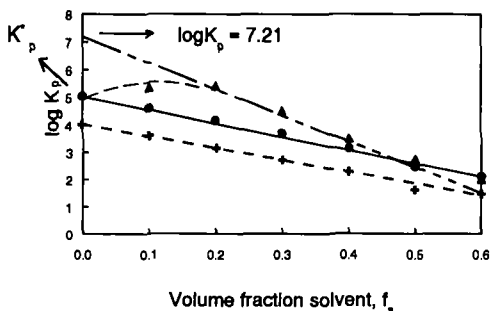


Figure 1. Log-linear plot of sorption partition coefficients K_p^* versus f_c determined for sorption of PCBs and HxCBz by sediments from water/methanol mixtures. + = 2,4,4'-tricB; Δ = 2,2',3,3',4,4',5-heptaCB; \bullet = HxCBz.

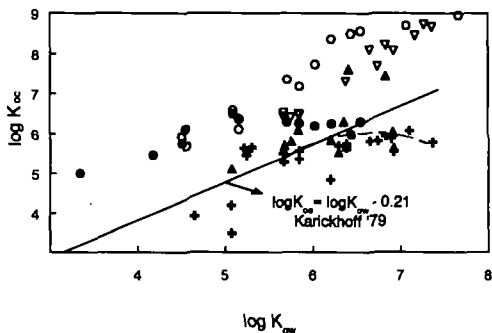


Figure 2. Plot of $\log K_{d,oct}$ versus $\log K_{oc}$ for PCBs and PAHs. K_{oc} -data: \bullet = PAHs^{18,19}; Δ , + = PCBs^{3,20-23}; \circ = PAHs (this work); ∇ = PCBs (this work). The plotted K_{oc} vs $K_{d,oct}$ relationship is from Karickhoff²⁴.

Reported values seem to level off at $\log K_{d,oct} = \pm 6$, which is in strong contrast with the hydrophobic nature of these compounds. We suggest that this is caused by extremely difficult to avoid experimental artifacts - basically due to various sorption phenomena and inexact phase separation - and not by physico-chemical interactions such as particle-particle interactions^{26j}.

4. Conclusions

Using the cosolvent technique reproducible $\log K_{oc}$ -values could be determined for PCBs, PAHs, HxCBz and PCDDs/PCDFs. The measured K_{oc} -values were higher than reported values depending on the hydrophobic nature of the compounds studied and correlated well with octanol-water partition coefficients. Over a range of 3-10 g/L sediment no indication of the "particle concentration effect" was found as the measurements gave comparable results.

5. References

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