

Determination of DOC-water partition coefficients using disposable SPME fibres

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Introduction

Dissolved organic carbon (DOC) present in sediment pore waters plays an important role in the bioavailability issues by affecting mobility and freely dissolved concentrations of hydrophobic organic compounds. Interactions between DOC and PAHs have been studied before in various ways by measuring freely dissolved PAH concentrations with SPME glass fibres in the presence of DOC originating from different sources^{1,2,3}. In this study, an equilibrium method using disposable SPME fibres has been applied. In this method, the distribution of PAHs between water, fibre and DOC requires knowledge of the fibre to water partition coefficients (K_{fibre}) in order to be able to calculate the DOC to water partition coefficient (K_{doc}). Values of K_{doc} for a selection of PAHs were determined in the presence of increasing concentrations of DOC extracted from freshwater sediments. These sediments show a range of varying properties (0.12 - 21.03 % TOC) and originate from the Netherlands, Finland and Sweden. The effect of three different temperatures has also been studied to gain information on the strength of the interactions involved.

Materials and methods

DOC was extracted from sediment-water suspensions by shaking sediment and artificial freshwater with a ratio of 4:1 (w/w) for 1 hour. Separation of water and sediment was achieved by centrifuging for 1 hour at 7,400 g and the supernatant was subsequently centrifuged for 3 hours at 31,000 g to remove all colloidal matter. A glass fibre with a core diameter of 110 μm and a 28.5 mm PDMS coating (12.4 ml/m) was cut into pieces of 2 cm and thermally cleaned under a He flow for 2 hours at 250 °C. Freely dissolved PAH concentrations were determined by exposing the fibres to diluted DOC solutions (total volume: 50 ml) spiked with a PAH mixture in thermostatted environments (4, 20 and 36 °C) under continuous shaking. After equilibrium between water, fibre and DOC had been reached (after 10 days at 20°C and 36°C and 21 days at 4°C), the fibres were desorbed in 150 ml of acetonitrile and analysed with isocratic liquid chromatography and fluorescence detection. As a significant amount of the PAHs was extracted from solution (3-31% of total dissolved PAHs are sorbed to the fibre at 0 mg/l TOC), the fibre to water partition coefficient (K_{fibre}) was determined in a kinetic way by equilibration in time (for 330 to 380 hours).

Results

Values for K_{fiber} of 6 PAHs have been determined by assuming a one-compartment model with first order kinetics (see equation 1), where $c_{\text{spme},t}$ is the fibre concentration at $t=t$, $c_{\text{total},0}$ is the initial aqueous concentration at $t=0$, V_{fibre} and V_{water} are the fibre and water volume and k_1 and k_2 are the uptake and elimination rate constants, respectively.

$$c_{\text{spme},t} = \frac{k_1}{k_1 \frac{V_{\text{fibre}}}{V_{\text{water}}} + k_2} c_{\text{total},0} (1 - e^{-k_1 (\frac{V_{\text{fibre}}}{V_{\text{water}}} + k_2) t}) \quad (1)$$

Fibre concentrations for pyrene at three different temperatures in time are shown in Fig. 1. With a temperature increase from 4 to 36 °C, the equilibrium between water and fibre is achieved faster, but fibre concentrations are lower.

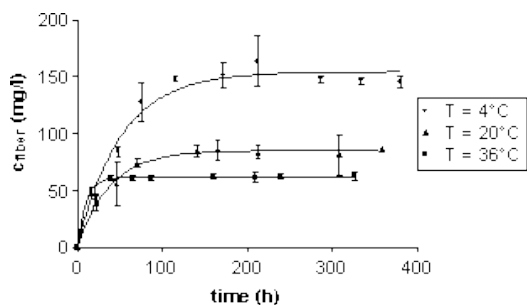


Figure 1: Equilibrium profile of pyrene sorption to fibres at three different temperatures in time (measured in triplicate, SE shown)

The values of K_{fibre} obtained with the equilibration method have been used to determine K_{doc} of the selected PAHs. The value of K_{doc} is determined indirectly by measuring the amount sorbed to the fibre with increasing concentrations of DOC. As this sorbed amount is directly proportional to the freely aqueous concentration (by calculation with K_{fibre}), the remainder is assumed to be sorbed to DOC. K_{doc} values are calculated by fitting the freely dissolved fraction ($c_{\text{free}}/c_{\text{total}}$) to the rearranged mass balance equation 2 given below, where c_{free} and c_{total} is the free and total concentration, respectively and $\{\text{doc}\}$ is the measured DOC concentration.

$$\frac{c_{\text{free}}}{c_{\text{total}}} = \frac{1}{1 + \frac{V_{\text{fibre}}}{V_{\text{water}}} K_{\text{fibre}} + \{\text{doc}\} K_{\text{doc}}} \quad (2)$$

As shown in figure 2, ratios of free over total concentrations of pyrene sorbed to DOC from different sediments decrease with increasing DOC concentrations due to partitioning. The resulting K_{doc} values show variable sorption, indicating that the DOC extracted from the different sediments exhibits different properties as sorbents.

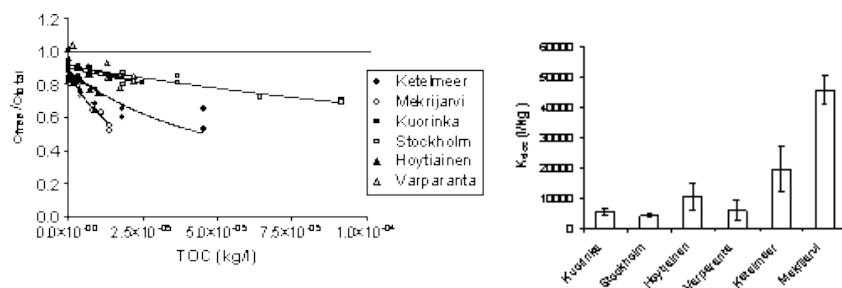


Fig. 2: Fraction freely dissolved pyrene with DOC from different sediments and the resulting K_{doc} values ($n=8-12$; SE shown).

The effect of three different temperatures (4 - 36 °C) is shown in fig. 3 for K_{doc} values of pyrene sorption to DOC extracted from Mekrijärvi sediment (FI). With the obtained values, van 't Hoff plots were constructed to calculate sorption enthalpies from the slopes by linear regression (see fig. 3). Enthalpy values of K_{doc} show increasing negative (exothermic) values with increasing hydrophobicity of the compounds. Sorption enthalpies for pyrene and benzo(e)pyrene amount to -32.57 ± 1.74 and -39.19 ± 4.82 kJ/mol, respectively, indicating an increase of the sorption strength.

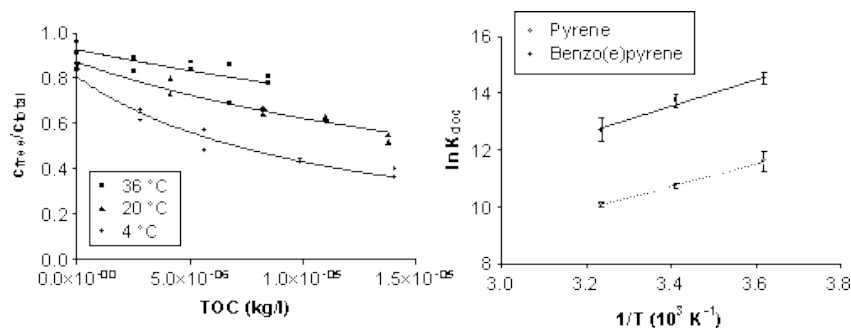


Fig. 3: Determination of K_{doc} values (Mekrijärvi sediment) for pyrene at different temperatures and their temperature dependence ($\ln K_{doc} \pm SE$; $DH = -R \cdot \text{slope}$).

Conclusions

Among the studied sediments, a range in $\log K_{doc}$ values was found because of different sorbing potentials of the DOC extracted. The $\log K_{doc}$ values of the sandy sediments of Varparanta and Kuorinka showed the weakest sorption in comparison with the more organic-rich Mekrijärvi sediment. Stronger sorption to fibre and DOC was observed at lower temperatures: an increase of 10 degrees Kelvin corresponded to a decrease of $\log K_{fibre}$ and $\log K_{doc}$ with 0.16-0.18 and 0.20-0.24, respectively. The sorption enthalpies resulting from this study are lower than values previously reported for the temperature dependence of sorption of PAHs with similar hydrophobicity to DOC from Lake Ketelmeer, the Netherlands (-18.28 and -31.28 kJ/mol for fluoranthene and benzo(a)pyrene, respectively⁴). This is in agreement with the lower sorption potential for Lake Ketelmeer as shown in this study compared to Mekrijärvi sediment.

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