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### Bioavailability of polycyclic aromatic hydrocarbons in sediments : experiments and modelling

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## **Chapter 7**

### **General discussion and conclusions**

## **Aim and research questions**

This thesis focuses on the environmental behaviour of polycyclic aromatic hydrocarbons (PAHs) in natural sediments. The following processes that determine the environmental fate of PAHs were therefore studied: vaporization, solubility, biodegradation, partitioning to dissolved organic matter (DOM) and adsorption to black carbon (BC). The chapters presented in this thesis originated from three main research questions:

1. What is the effect of DOM on the biodegradation of aqueous phase dissolved PAHs by bacteria? (Chapter 3)
2. Develop a method to measure DOM to water partition coefficients of PAHs in sedimentary pore water. (Chapters 3 and 4)
3. Develop a force field method to study interactions of PAHs with model structures for dissolved and particulate organic matter. (Chapters 5 and 6)

The last research question relied on accurate physicochemical data of the PAHs investigated. Supercooled liquid vapour pressures along with their temperature dependence were therefore determined in Chapter 2 of this thesis. The results obtained for the separate Chapters presented in this thesis are discussed below with regards to their environmental relevance. General conclusions are drawn on the effects of DOM on biodegradation and freely dissolved concentrations of PAHs and on the thermodynamic properties of PAHs relevant for this thesis. Finally, the consequences of the findings reported in this thesis for the risk assessment of contaminated sediments are discussed.

## **Physicochemical properties**

In Chapter 2, the determination of supercooled liquid vapour pressures of a wide range of compounds (unsubstituted, methylated and sulphur containing PAHs) by gas chromatography using Kováts retention indices has been described. The temperature dependent vapour pressures subsequently could be used to derive the enthalpy of vaporization and the heat capacity difference between the gas and liquid phase for these compounds. Differences in activity coefficients of test and reference compounds (*n*-alkanes) in the stationary phase were accounted for by including a correction factor that was dependent on both temperature and number of carbon atoms. The liquid vapour pressures of most compounds agreed well with literature values determined by gas chromatography within -0.15 to +0.15 log units.

The partitioning behaviour of PAHs between air and other compartments is largely determined by their liquid vapour pressures and several procedures have therefore been developed to estimate this parameter to predict the environmental distribution of PAHs. For

example, quantitative structure-property relationships (QSPR) with molecular polarizability as descriptor have been used by Staikova *et al.* [1] to predict liquid vapour pressures of unknown compounds. Furthermore, liquid vapour pressures have been used by Goss and Schwarzenbach [2] to predict and evaluate the partitioning behaviour of organic compounds between air and particulate (condensed) phases.

The calculation of liquid vapour pressures with gas chromatographic methods has been shown to be dependent on the similarity in physicochemical behaviour of test and reference compounds in the stationary phase. The liquid vapour pressures of unknown compounds belonging to structurally different organic compound groups can be determined by gas chromatography if the temperature dependence of the activity coefficients can be calculated directly from physicochemical or thermodynamic properties. The difference in activity coefficients can in theory be approximated to the difference in ideal gas solubility that is dependent on the entropy of vaporization and the boiling point temperature of the compound [3]. The activity coefficients in the stationary phase can in this way be estimated with structural descriptors such as the entropy of vaporization.

### **Biodegradation**

The effect of DOM on the absorption of PAHs by polydimethylsiloxane (PDMS) fibers and on the biodegradation of PAHs was studied in Chapter 3 of this thesis. In the presence of DOM, absorption and desorption rates of PAHs to and from PDMS fibers increased and the equilibrium between the fiber and the aqueous solution was reached more rapidly. This effect occurs when diffusion of PAHs through an unstirred boundary layer (UBL) surrounding the PDMS fibers forms the rate-limiting step in the absorption of PAHs and when desorption of PAHs from DOM is fast compared to the diffusion process. The presence of DOM also enhanced the mineralization of aqueous phase dissolved phenanthrene and pyrene by a PAH degrading bacterium. The presence of DOM induced significant differences in the initial rates of mineralization compared to the control. The mineralization of PAHs was shown to be independent of freely dissolved concentrations. Furthermore, residual PAH concentrations after biodegradation were similar for treatments containing DOM and control samples. This suggests that the biodegradation process was indiscriminate towards freely dissolved or DOM-bound PAHs. However, the results from biodegradation experiments cannot be directly compared to the PDMS fiber absorption experiments, because biodegradation is essentially a non-equilibrium process. The observed enhancement in PAH mineralization was explained by a combination of faster uptake kinetics in the UBL surrounding the microbial cells and direct microbial access to DOM-bound PAHs.

Biodegradation and absorption processes of PAHs rarely occur at equilibrium in the natural environment. The presence of DOM can therefore play an important role in enhancing biodegradation and absorption (or desorption) processes under non-equilibrium conditions as has been shown in Chapter 3 of this thesis. A small number of studies have already addressed

the phenomenon of DOM facilitated uptake of PAHs over the UBL in passive samplers [4, 5]. Facilitated transport of DOM-associated PAHs occurs when the rate-limiting step is diffusion through the UBL, when DOM-PAH complexes are labile and when a substantial amount of PAHs is associated to DOM. The latter process underlines the importance of both DOM concentration and hydrophobicity of PAHs on the extent of facilitated transport [5]. Apart from more rapid uptake kinetics in the presence of DOM, enhanced partitioning of PAHs between two disks of PDMS (excluding the UBL) by direct contact has been studied by Mayer *et al.* [4]. This mechanism has been shown to be even more important than facilitated transport of PAHs by DOM. Furthermore, the presence of humic acids sorbed on clay surfaces has been shown to stronger enhance biodegradation of phenanthrene than humic acids alone [6] further confirming the mechanism of direct contact in biodegradation of PAHs.

Although the presence of DOM can enhance transport in the kinetic phase of PAH absorption in passive samplers, the equilibrium level is not affected. The way in which passive samplers are exposed under non-equilibrium conditions in the kinetic regime is therefore important to obtain a realistic assessment of the bioavailability of PAHs considering that the equilibrium time of passive samplers is much longer (in the order of days to weeks) than biological processes of uptake and biodegradation. Additionally, enhanced biodegradation by PAH-degrading bacteria through addition of natural DOM (as opposed to the use of surfactants) can prove to be useful in the bioremediation of contaminated soils and sediments. The bioaccessibility (time integrated bioavailability, see Introduction) of PAHs sorbed to diagenetically matured organic matter and BC in soils and sediments could be affected by DOM via this pathway. The slow and very slowly desorbing fractions of PAHs sorbed to these condensed domains in soils and sediments can be mobilised through the addition of DOM which enhances the desorption kinetics over the UBL surrounding soil and sediment particles.

### **Partitioning to dissolved organic matter**

Chapter 4 describes the measurement of freely dissolved PAH concentrations with PDMS fibers in the presence of DOM extracted from different sediments. The DOM solutions used in these experiments were prepared by shaking sediment and water and subsequently centrifuging the supernatant of the sediment suspension at high speed to obtain a DOM solution devoid of colloids. The macromolecular structure of sedimentary DOM appears to be less affected by high speed centrifugation compared to filtration and is therefore considered to give a more representative and realistic view of pore water. The resulting DOM to water partition coefficients showed a large variability for the PAHs studied but no explanation could be found for this variability in terms of DOM properties such as specific ultraviolet absorbance. From the variation of the partition coefficients with temperature, enthalpies of sorption could be derived that were nearly equal (but opposite in sign) to the excess enthalpies of dissolution for supercooled liquid PAHs suggesting that only non-specific interactions are involved in the partition process.

Passive samplers can also be applied in field measurements of freely dissolved concentrations of PAHs and other hydrophobic organic compounds. Recent experiments have shown that passive samplers composed of polyoxymethylene and PDMS can be deployed directly in sediments to assess the bioavailability of PAHs, polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in pore water. The introduction of sediment-water activity ratios can subsequently be used to derive diffusive fluxes between the environmental compartments of sediment and water [7, 8]. The concept of chemical activity has been used in these studies to quantify the potential of PAHs to undergo processes such as diffusion and partitioning [9]. This concept however still relies on actual freely dissolved concentrations in both sedimentary pore water and overlying water.

Future studies that elucidate the thermodynamic aspects of the interactions between (a)polar compounds other than PAHs and DOM with variable composition can further improve the understanding of bioavailability issues due to different sorption affinities of DOM. Furthermore, the relationships between freely dissolved concentrations, internal concentrations of organisms and associated toxicological effects can be studied in more detail with passive samplers to strengthen the link between bioavailability and species specific effects [10] assuming that uptake of freely dissolved PAHs only occurs via passive membrane diffusion. Ingestion of soil or sediment particles by earthworms can however also lead to direct uptake of very hydrophobic compounds ( $\log K_{ow} > 5$ ) [11].

### **Simulation of thermodynamic properties of aromatic hydrocarbons**

The energies of vaporization, hydration and solution of aromatic hydrocarbons were calculated in Chapter 5 with a force field method based on molecular mechanics. Atomic charge scaling factors derived from Monte Carlo simulations of gaseous and liquid phases of benzene and water resulted into energies of vaporization, hydration and solution for fluoranthene that were equal to experimental values available from literature. It was concluded that the scaling factors derived can be applied to simulate gaseous, hydrated and liquid phases of other aromatic hydrocarbons as well.

The prediction of partitioning properties via the calculation of energies of phase transfer with force field methods seems applicable to provide input parameters for the prediction of the environmental fate of newly produced chemicals. The application of computational tools, however, to calculate physicochemical properties from molecular structure in order to predict the environmental behaviour of new chemicals should directly follow from chemical intuition of relevant environmental processes. For example, the calculation of  $\log K_{ow}$  as a descriptor of bioaccumulation of perfluorinated surfactants with the model of COSMOtherm [12] is not considered theoretically correct because of the dual molecular partitioning behaviour of these surfactants.

Accurate prediction of environmental partitioning properties may require relatively more computation time compared to the time required to experimentally determine partitioning

properties assuming the experimental method does not involve long equilibration times in the laboratory. Although computer speed has increased over the last decade for the simulation of large molecular systems, computing capacity in simulations is currently still limited by the amount of evaluated non-bonded interactions that are dependent on the size of the system, *i.e.* the type of model structure and number of water molecules included, the cut-off value applied (to modulate non-bonded interactions to zero) and the length of the simulations.

### **Simulation of sorption to environmental sorbents**

The application of force field methods to molecular systems of PAHs and BC with a free energy procedure based on Monte Carlo simulated potential energies of transfer described in Chapter 6 resulted in BC sorption coefficients for PAHs that are in agreement with literature values. Simulated structural and energetic properties of hydrated phases of sorbate and/or sorbent were used to calculate these sorption coefficients without requiring experimental values of related compounds or phases. The calculation of free energy in PAH sorption to BC can be considered an improvement compared to earlier simulations performed by Kubicki [13] where calculated energy differences between free and BC-bound PAHs were only approximated to enthalpy differences.

The presence of BC in the environment plays an important role in the fate of PAHs: adsorption to BC results into a reduced bioavailability and bioaccessibility of PAHs for benthic and terrestrial organisms. This environmental role of BC can be employed for the purpose of PAH immobilisation in contaminated soils or sediments. For instance, the biota to sediment accumulation factor for a polychaete in a study by Cornelissen *et al.* [14] was significantly reduced by amendment of activated carbon to harbour sediments. The *in situ* amendment of BC to contaminated soils or sediments thwarts however the possibility to employ bioremediation or natural attenuation involving PAH degrading microorganisms.

The application of the model presented in Chapter 6 of this thesis to calculate partition coefficients of PAHs for macromolecular structures such as DOM seems tempting provided that the polar interactions involved are well simulated. The method presented has been applied by us before to estimate the partitioning of fluoranthene to a model structure of DOM (Suwannee fulvic acid) adapted from Shin and Moon [15]. The partition coefficient obtained for fluoranthene and DOM was much lower than the experimental values from the literature. This was probably due to an incorrect description of polar interactions of DOM with water molecules via H-bonding. The differences in composition of fulvic acids and humic acids inherent to nature and their interactions with (a)polar organic compounds would therefore require further study in order to better estimate partition coefficients for these types of macromolecular structures.

## General conclusions

### *Effect of DOM on biodegradation*

The effect of DOM on the biodegradation of aqueous phase dissolved PAHs can play an important role in the bioremediation of contaminated soils and sediments. Potential bioremediation is dependent on the amount of freely available and accessible PAHs in the aqueous and solid phase. The assessment of bioavailability and bioaccessibility of PAHs sorbed to soils and sediments is strongly dependent on the time scale considered. Furthermore, the environmental risk is determined by the exposure of PAHs to specific terrestrial or benthic organisms that are most sensitive at the site of interest. Non-linear sorption to carbonaceous geosorbents such as BC decreases the bioavailability and bioaccessibility of PAHs by (partial) immobilisation in the solid phase assuming that these sorbents themselves remain stable in the terrestrial and aquatic environment. In case of bioremediation however, the bioavailability must be increased to reach the final clean-up goal. The bioremediation potential of contaminated soils and sediments can be enhanced by addition of synthetic or natural DOM to the soil or sediment, which will facilitate desorption of PAHs from the solid phase and subsequently enhance the biodegradation of aqueous phase dissolved PAHs. The results of Chapter 3 of this thesis have demonstrated that this enhancing effect of DOM on the bioavailability of PAHs to bacteria does occur in the aqueous phase. The use of passive samplers has provided the possibility to measure freely dissolved PAH concentrations in the presence of DOM under non-equilibrium conditions. In conclusion, the effect of DOM on absorption and desorption processes as well as bacterial uptake over aqueous boundary layers is important in the non-equilibrium exposure of passive samplers or bacteria to aqueous phase dissolved PAHs.

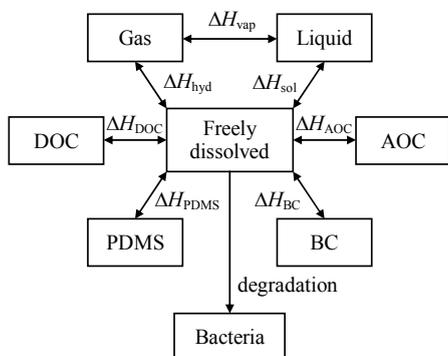
### *Effect of DOM on freely dissolved concentrations*

Freely dissolved PAH concentrations in pore water are affected by the composition of the solid and aqueous phases (soil or sediment type, organic matter content and presence of DOM) as well as by the physical conditions (*e.g.* temperature, water saturation, etc.) prevailing in the environment under study. In Chapter 4 of this thesis, passive samplers were applied in aqueous solutions containing DOM from different origins and the resulting DOM to water partition coefficients were highly diverging. The observed variability in partitioning of PAHs to DOM is not affected by normalization to organic carbon. Other factors related to the composition of DOM are obviously responsible for the variation in partitioning behaviour of PAHs. In order to standardise experiments that are performed to assess the effect of DOM on the bioavailability of PAHs, commercial humic acids have already been used to a large extent in environmental chemistry research. The composition and behaviour of these humic acids is however fundamentally different (due to weak polarity and high aromaticity) to that of natural DOM. The variability in composition and behaviour of natural DOM should therefore be explored further to be able to predict the freely dissolved PAH concentration in pore waters more accurately. The

freely dissolved concentration is also important in the thermodynamic description of the environmental fate and behaviour of PAHs, as will be discussed below.

### Thermodynamic properties

The research presented in this thesis is mainly focused on the freely dissolved concentration of PAHs. In Figure 1, a model with the freely dissolved concentration as central viewpoint is presented that summarizes the environmental processes of PAHs relevant for this thesis. The equilibrium processes that affect the freely dissolved concentration are hydration, solution, partitioning and sorption whereas a non-equilibrium process such as biodegradation depletes the freely dissolved concentration in pore water. Partitioning properties of PAHs such as Henry's Law constants, solubilities, DOM partition coefficients and AOC or BC sorption coefficients are related to the Gibbs free energies of phase transfer that can be dissected into enthalpies and entropies of phase transfer ( $\Delta G = \Delta H - T\Delta S$ ). The enthalpies of phase transfer directly follow from the measurement of the temperature dependence of any partitioning property or from the calculation of the difference in phase interactions in 3D force field models. These enthalpies of phase transfer have been measured and/ or calculated in this thesis (except for  $\Delta H_{\text{AOC}}$  and  $\Delta H_{\text{BC}}$ ).



**Figure 1.** Overview of environmental behaviour of PAHs relevant for this thesis.

The enthalpy of vaporization ( $\Delta H_{\text{vap}}$ ) has been determined experimentally from the temperature dependence of liquid vapour pressures in Chapter 2, and was also calculated from Monte Carlo simulations in Chapter 5 ( $\Delta H_{\text{vap}} = \Delta E_{\text{vap}} + RT$ ) along with the enthalpies of hydration ( $\Delta H_{\text{hyd}} = \Delta E_{\text{hyd}} - RT$ ) and solution ( $\Delta H_{\text{sol}} = \Delta E_{\text{sol}} = \Delta E_{\text{vap}} + \Delta E_{\text{hyd}}$ ). In Chapter 4, the sorption enthalpies ( $\Delta H_{\text{DOC}}$  and  $\Delta H_{\text{PDMS}}$ ) were determined experimentally from the temperature dependence of the partitioning behaviour of PAHs towards DOM and PDMS. In Chapter 6, the Helmholtz or Gibbs free energy of PAH sorption to BC (instead of  $\Delta H_{\text{BC}}$ ) was calculated directly from Monte Carlo simulations. The enthalpy and free energy differences of all processes depicted in Figure 1 and their associated partitioning properties can in principle be derived just from molecular

simulation using force field methods. Experimental data of partitioning properties will however still be required to obtain sensible and realistic results from theory.

### Implications for environmental risk assessment

Current risk assessment approaches performed in Europe and The Netherlands for the freshwater environment are (partly) based on the Water Framework Directive (WFD). The goal of the implementation of the WFD is to restore affected aquatic ecosystems to good ecological and chemical status by 2015. The ecological status refers to the quality of the structure and functioning of aquatic ecosystems. A good chemical status is reached when the water concentrations of priority substances are below the Environmental Quality Standards (EQS) laid down in Article 16 of the WFD (2000/60/EC). The EQS for freshwater have been established for 33 priority substances (including PAHs) and are expressed as total concentrations in the whole water sample to protect aquatic or pelagic organisms [16].

The long-term “annual average” EQS for organic contaminants in freshwater ecosystems (water and sediment) are preferably derived either from field studies or simulated ecosystems (mesocosms), or ecotoxicological data such as species sensitivity distributions (SSD) if data are available from at least eight taxonomic groups. In the SSD approach, hazardous concentrations at which 5% of the species are potentially affected ( $HC_5$ ), are calculated via statistical extrapolation and are subsequently converted to an Environmental Risk Limit (ERL) using an appropriate assessment factor [17]. The  $HC_5$  value for single compounds derived from laboratory experiments is however considered a rather conservative estimate for effects observed in field studies and mesocosms [18]. A more elaborate approach is the calculation of a potentially affected fraction of species in an ecosystem due to the presence of a mixture of compounds. This multisubstance potentially affected fraction (msPAF) expresses the total toxic pressure exerted by a compound mixture and is calculated by grouping compounds according to mode of action [19]. A field validation of the msPAF approach showed a correlation between an increase in toxic pressure and effects occurring on an ecosystem level [20]. In the derivation of ERLs for freshwater sediments in The Netherlands, a recently developed criterion is that dredged sediments cannot be disposed on land unless the msPAF for organic compounds is <20% (affected fraction of organisms) [21].

Apart from using statistical extrapolation, ERLs are also derived from acute and chronic effect data with assessment factors that are dependent on the type and amount of available ecotoxicological data. These assessment factors (already proposed by the OECD in 1992 [22]) are used to predict concentrations below which no unacceptable effects will likely occur. For example, No Observed Effect Concentrations (NOEC) for chronic effects determined for relevant taxonomic groups in freshwater (*Daphnia magna* or fish) are converted to a ERL using an assessment factor of 100. The lowest ERL (also based on ERLs derived from secondary poisoning of predators, human consumption of fishery products and drinking water abstraction) is subsequently selected as the EQS that represents an environmental concentration in freshwater

ecosystems that protects both humans and ecosystems from adverse effects [23]. Ecotoxicological data from acute effects are used to check the long-term EQS or to derive Maximum Acceptable Concentrations (MAC) to protect against effects from transient exposure peaks [17]. For sediments, the EQS are derived from ecotoxicological effects determined with benthic or sediment dwelling organisms. Because ecotoxicological data for benthic organisms are scarce, sediment EQS are often directly derived from water EQS by the equilibrium partitioning method [17]. To that end, generic  $K_{\text{TOC}}$  values are being used and the resulting EQS are expressed as total sediment concentrations. In these calculations, only absorption of organic compounds into amorphous organic carbon is taken into account while elevated distribution coefficients due to strong adsorption of organic compounds to BC have been observed in sediments [24].

Total PAH concentrations in sediments are generally not considered representative for the *in situ* exposure of pelagic and benthic organisms, because only freely dissolved PAH concentrations are bioavailable in aquatic systems (excluding direct uptake by ingestion of food) [10, 24]. For the characterization of risks due to PAH-contaminated sediments, total PAH concentrations cannot be used. Hence, existing EQS for sediments should be reconsidered, and freely dissolved PAH concentrations should be compared directly to EQS for water [24]. These freely dissolved concentrations can be easily determined in a site-specific risk assessment by using solid phase extractions of the aqueous phase with polymer coatings such as polydimethylsiloxane as demonstrated in Chapters 3 and 4 (see also [7]), polyoxomethylene [7] or polyethylene [25]. Passive samplers based on PDMS have already been proposed as a promising method in an international standard (ISO 17402:2008) to predict the bioavailable fraction of organic contaminants in soils and sediments [26]. On an European level, the use of passive samplers has been recently proposed in a technical guidance document [27] as a (possible) complimentary method for the monitoring of surface water to improve the quality of the risk assessment under the WFD. The application of passive samplers such as Semi-Permeable Membrane Devices (SPMD) and Polar Organic Chemical Integrative Samplers (POCIS) have been mentioned in this report for the measurement of a time integrated exposure (days to weeks) of (a)polar organic contaminants in the aquatic environment [27]. Finally, several methods to measure bioavailable or bioaccessible concentrations of organic contaminants have been suggested in The Netherlands to improve the risk assessment of contaminated soils and sediments within the Dutch regulatory framework. The methods selected involve the application of passive samplers (SPME, polyoxomethylene and silicone rubber) to measure actual or bioavailable concentrations and solid phase extractions (Tenax and cyclodextrin) to measure potential or bioaccessible concentrations of organic contaminants. No clear preference was made for any of the methods evaluated, because the most appropriate method has to be selected on a site-specific basis [28].

Following from the research presented in this thesis, a suggested refinement in the current risk assessment approach could be to express the water EQS as a freely dissolved concentration, because this is considered more environmentally relevant in terms of exposure of organic

contaminants to pelagic and benthic organisms. The water EQS values of the priority substances anthracene, fluoranthene and benzo[*a*]pyrene for freshwater [29-31] have all been derived from NOEC values determined for *Daphnia* species using an assessment factor of 10. This assessment factor is applied when ecotoxicological data are available for a base set of three trophic levels comprised of primary producers (algae), primary consumers (*Daphnia* species) and secondary consumers (fish) [32]. The water EQS for anthracene, fluoranthene and benzo[*a*]pyrene have been set at 0.11, 0.12, and 0.05  $\mu\text{g/L}$ , respectively [29-31]. The EQS have been recalculated here in the presence of suspended particulate matter (15 mg/L SPM,  $f_{\text{OC}} = 0.10$  [33]) as well as DOM (5 mg C/L, average value for river and lakes from [34]) with a mass balance approach (analogous to Eq. 1 in Chapter 4) assuming equilibrium partitioning between SPM, DOM and water. The log  $K_{\text{TOC}}$  values for SPM were taken from the Substance Data Sheets [29-31] and the log  $K_{\text{DOC}}$  values were taken from Chapter 4 for DOM extracted from Mekrijärvi sediment. The log  $K_{\text{DOC}}$  value of benzo[*a*]pyrene is assumed to be comparable to the log  $K_{\text{DOC}}$  value determined for benzo[*e*]pyrene due to the close similarity in molecular size and physicochemical properties (see Figure 2 and Table 1 in the Introduction). The freely dissolved concentrations of anthracene, fluoranthene and benzo[*a*]pyrene decreased in the presence of only SPM to concentrations of 0.10, 0.08, and 0.003  $\mu\text{g/L}$ , respectively, and decreased further to 0.05, 0.03, and 0.001  $\mu\text{g/L}$ , respectively, when both DOM and SPM are taken into account. These recalculated EQS show a small influence of DOM on the freely dissolved concentration (1.1 to 2.0 times lower) compared to partitioning to SPM due to the presence of a relatively low but environmentally relevant DOM concentration. An increase in DOM concentration to 50 mg C/L would have a larger influence of DOM with freely dissolved concentrations decreasing by a much higher factor (2.1 to 11.0 times lower) compared to the decrease in freely dissolved concentrations by SPM. In addition, the origin of DOM as well as temperature will further influence these calculations of freely dissolved PAH concentrations in pore water (as was demonstrated in Chapter 4).

The comparison of freely dissolved PAH concentrations (measured with passive samplers) with EQS expressed as bioavailable concentrations occurring in sedimentary pore water would result into protection levels (protecting 50% or 95% of the species present) that are less overprotective compared to the currently used sediment EQS based on total concentrations. An expert group from The Netherlands [28] recommended recently to keep the first tier of risk assessment essentially unchanged, *i.e.* by comparing measured total solid phase concentrations of organic contaminants with sediment EQS based on total concentrations. It was further proposed to only implement bioavailability measurements in a second tier of risk assessment in which a combination of methods can be applied to measure actual and potential concentrations of organic contaminants (*e.g.* with SPME and Tenax). The bioavailable or bioaccessible concentrations can subsequently be converted to total solid phase concentrations with the equilibrium partitioning method. These total concentrations can be compared with sediment EQS that are derived from water toxicity data obtained with the same approach maintaining the current protection levels for ecosystems [28]. In this way, the current risk assessment of

contaminated sediments would be improved by taking both bioavailability and bioaccessibility into account, although sediment EQS based on bioavailable concentrations should be derived directly from ecotoxicological data determined with benthic organisms.

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