Bioavailability of polycyclic aromatic hydrocarbons in sediments : experiments and modelling

Haftka, J.J.H.

Link to publication

Summary

Environmental contamination with polycyclic aromatic hydrocarbons (PAHs) during most of the twentieth century has been mainly caused by incomplete combustion of organic matter as well as by other industrial processes such as coal gasification. Contaminated soils and sediments have therefore received increasing attention in the past decades for the possibility of site remediation. The presence of PAHs in soils and sediments can pose a serious environmental risk for terrestrial and aquatic organisms depending on the bioavailable rather than the total concentration of PAHs. The bioavailable concentration of PAHs refers here to the freely dissolved amount that can be taken up by organisms or that can be biodegraded by bacteria. The bioavailability of PAHs in the aqueous phase is dependent on the amount of PAHs sorbed to different organic carbon fractions in soils and sediments. Rapid and slow desorption of PAHs from amorphous organic carbon and black carbon (BC), respectively, results in either partitioning to dissolved organic matter (DOM), biodegradation by bacteria or uptake by organisms. The freely dissolved concentration of PAHs in the pore water of soils and sediments therefore directly determines the risk of contaminated environments. In this thesis, the environmental behaviour of PAHs in processes such as vaporization, solubility, biodegradation, partitioning to DOM and adsorption to BC has been studied. The research described in this thesis is focused on: the effect of DOM on the biodegradation of PAHs in the aqueous phase (Research question 1), the measurement of freely dissolved PAH concentrations in the presence of DOM using passive samplers (Research question 2) and the development of a method based on computer simulations to study interactions of PAHs with model structures of BC (Research question 3).

The last research question relies on accurate vapour pressure data of the PAHs investigated. Supercooled liquid vapour pressures along with their temperature dependence are therefore determined in Chapter 2 of this thesis with a gas chromatographic method. Differences in vapour pressure (amounting to a factor of 10) have been observed between experimental values and literature values due to differences in chromatographic behaviour of reference compounds and PAHs in the stationary phase of the gas chromatograph. A compound and temperature dependent correction has therefore been applied to the experimental values which results in vapour pressures that are consistent with literature values determined by gas chromatography (within -0.15 and +0.15 log units).

The effect of DOM on the biodegradation of PAHs by bacteria has been studied in Chapter 3 where biodegradation kinetics of bacteria are compared to absorption kinetics of polydimethylsiloxane (PDMS) fibers. In the presence of DOM, the absorption and desorption rates to and from PDMS fibers are increased and the equilibrium between fiber and water is more rapidly established. The presence of DOM has also increased the mineralization rates of PAHs by bacteria. The enhanced effect of DOM on biodegradation of PAHs is proposed to be

caused by faster uptake kinetics (analogous to the PDMS fiber experiment) combined with the possibility of direct access of bacteria to DOM-sorbed PAHs.

Partitioning of PAHs to DOM of different origin has been studied in Chapter 4 by using PDMS fibers. The DOM partition coefficients determined in these experiments show a large variability depending on the origin of extracted DOM. The effect of temperature on the partitioning behaviour of PAHs towards DOM or PDMS fibers has also been studied. These results show a relatively weak influence of temperature on the (non-specific) partitioning behaviour and interactions between PAHs and PDMS fibers or DOM are similar to interactions between PAHs in their pure liquid.

Computer simulations have been applied in Chapter 5 to calculate thermodynamic properties of gaseous, hydrated and liquid phases of aromatic hydrocarbons. The difference in energy between gaseous and liquid phases of benzene and water results in energies of vaporization that have been used to fit the electrostatic interactions to literature values. The energies required to vaporize a gas phase molecule from its pure liquid as well as to dissolve a gas phase molecule into water are subsequently calculated for fluoranthene. The resulting energies of vaporization, hydration and solution for fluoranthene are consistent with literature values.

The simulation method employed in Chapter 5 has been extended in Chapter 6 to simulate the sorption behaviour of PAHs to BC. The model structure used for BC is a truncated aromatic sheet of carbon that mimics the structure of BC. The sorption of PAHs to BC mainly involves van der Waals interactions and the calculated sorption coefficients for phenanthrene, fluoranthene and benzo[*a*]pyrene are in close agreement with literature values. In addition, geometrical distances between PAHs and BC during the simulations agree well with an experimental value from literature.

From the main research questions, a number of conclusions can be drawn. Bioremediation of contaminated soils and sediments can be limited by the amount of freely available PAHs in the aqueous and solid phase. Non-linear sorption to carbonaceous geosorbents such as BC decreases the bioavailability of PAHs by (partial) immobilisation in the solid phase. The bioavailability has to be increased, however, to reach the final clean-up goal in case of bioremediation. The bioremediation potential of contaminated soils and sediments could be enhanced by addition of synthetic or natural DOM to facilitate desorption of PAHs from the solid phase and to subsequently enhance the biodegradation of aqueous phase dissolved PAHs (Research question 1).

Freely dissolved PAH concentrations are more relevant in the risk assessment of contaminated soils and sediments than total PAH contents. Soil and sediment quality criteria should therefore be reconsidered in environmental risk assessment by comparing freely dissolved concentrations directly to aqueous quality criteria, because total concentrations are not useful to characterize the risk of contaminated sites. Passive samplers form a suitable tool in environmental risk assessment to accurately analyse freely dissolved concentrations of PAHs. The application in this thesis of passive samplers to aqueous solutions containing DOM of different origin has resulted in variable partition coefficients and the bioavailability of PAHs is therefore strongly dependent on the type and amount of DOM (Research question 2).

The central viewpoint in this thesis is the freely dissolved concentration that determines the risk and exposure of PAHs to benthic and terrestrial organisms in soils and sediments. The freely dissolved PAH concentration is affected by environmental processes such as partitioning to DOM and adsorption to BC that decrease the bioavailability of PAHs. These equilibrium processes can in principle be calculated from molecular simulation only (Research question 3), because the thermodynamic quantities (free energies) are directly connected to the partitioning properties (BC sorption coefficients). Experimental data of partitioning properties will however still be required to obtain sensible and realistic results from theory.