Bioaccumulation of persistent organic pollutants from floodplain lake sediments: linking models to measurements

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Abstract

The main research questions of this research were (1) what is the extent and nature of bioavailability of sediment-bound polychlorobiphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) and (2) what are the effects of lake ecosystem structure on fate and bioaccumulation of PCBs and PAHs. Fast-desorbing fractions in the sediment of floodplain lakes were estimated by the 6-h Tenax-extractable fractions with a correction factor. These fractions varied between 1 and 40% and did not show a clear trend with log K_{OW}. This means that contaminants in these sediments were available, but to a smaller extent than total concentrations would suggest. The 6-h Tenax extractable concentration often correlated better with bioaccumulation than the total extractable concentration in sediment. Despite the reduced availability, benthivorous fish and invertebrates in floodplain lakes still rapidly accumulated substantial amounts of PCBs. PAHs were accumulated relatively less because PAHs were relatively less available than PCBs due to their stronger sorption to carbonaceous materials, also referred to as soot or black carbon. For fish, metabolic transformation caused even lower PAH concentrations. Contaminants that have been present in the sediment for longer periods of time (years to decades), were less available for Tenax extractions as well as for uptake by biota in different parts of the food web than contaminants that were recently added. Thus, aging may translate directly into reduced uptake at higher trophic levels. Nutrient additions in enclosures with benthivorous fish had a positive effect on PCB accumulation by these fish. Measured bioaccumulated concentrations of PCBs and PAHs in invertebrates in flood plain lakes were not influenced greatly by seasonal effects or ecological structure. Although effects were statistically significant, their magnitude in terms of accumulation factors was small, which may have been caused by the similar sediment composition and bioavailability of contaminants in our systems. Differences between compounds were much larger than differences due to ecosystem structure, seasons, or species composition. As for total masses of PCBs and PAHs in certain compartments however, lake ecosystem structure appeared to have a large influence on the biomass of biota and therefore also on the mass distribution of PCBs and PAHs in biotic compartments. Thus, changes in ecosystem structure strongly influenced PCB and PAH dynamics, although concentrations within the biotic compartments were not significantly influenced by biotic biomass. As for bioaccumulation modelling, when aquatic exposure concentrations were quantified accounting for sorption to carbonaceous materials, model results improved substantially. Including metabolic transformation and sediment uptake in the model accounted for a further improvement of the model fit. Implications are discussed for food chain bioaccumulation modeling, bioavailability assessment, sediment policy making and floodplain lake management.

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Chapter 1

General introduction

General Introduction

Background, research questions and thesis outline

Contaminated sediments are a major problem in many countries, and may limit development of ecosystem health [*1*]. At present, to determine if sediment meets quality criteria, total concentrations of sediment-bound contaminants are analyzed. However, particular fractions of sediment-bound toxicants seem to be unavailable to organisms, irrespective of the uptake route [*2-5*]. Consequently, bioavailable concentrations in sediment may be much lower in the field than what is estimated using total sediment concentrations and laboratory-derived partitioning coefficients [*2-5*]. To decide if sediment needs to be remediated, actual risks of these sediments need to be determined. To assess this risk, it could therefore be better to use bioavailable rather than total concentrations of contaminants. How to measure or predict bioavailability of organic compounds and to assess which factors influence bioavailability, has been the focus of research projects world wide (e.g., [*2,4-12*]).

It is not only necessary to develop practical concepts to accurately determine bioavailability. There is also a great need for knowledge on the effects of food web structure on bioavailability and bioaccumulation, and models that can describe these processes. Food web structure partly depends on the amount of nutrients present in the system (trophic state). Interactions between trophic state or food web structure and contaminant fate and effects (Figure 1.1) have recently been the focus of several research projects in the USA [*13,14*], Canada [*15,16*], Sweden [*17*], and the Netherlands [*18-21*]. The Dutch NWO-sponsored Stimulation Programme for System-oriented Ecotoxicological Research, which includes the research described in this thesis, also addressed these issues.

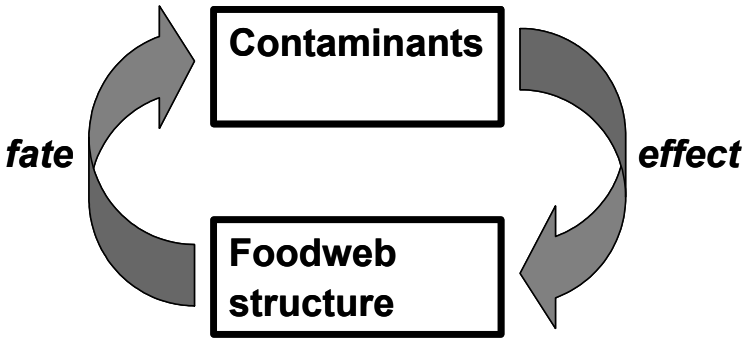

Figure 1.1. *Interactions between nutrients and contaminants. After Koelmans et al., 1999* [*19*].

These interactions may play a large role in floodplain lakes in the Rhine catchment area in the Netherlands, which are historically polluted with trace metals and organic chemicals such as PAHs, PCBs, and mineral oil [*22*], together with nutrients. Many of these pollutants cannot be degraded by microorganisms and thus are very persistent in the environment. Although river water quality has improved the last decades [*23*], floodplain lake sediment remains polluted with these persistent contaminants, and may have changed from sink to source. The extent and nature of bioavailability of sediment-bound persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs) in floodplain lakes still needs to be identified.

Sediments in floodplain lakes do not only contain contaminants, but are also rich in nutrients [*23-26*]. Many floodplain lakes can be categorized as mesotrophic or eutrophic, and are dominated by algal blooms, although shifts to a clear, macrophyte-dominated structure may occur [*27,28*]. Of course, when compared with other lakes, dynamics in floodplain lakes are influenced very much by inundations, which can occur several times a year, usually in winter and spring. Insight in the way food web structure affects fate and bioaccumulation of PCBs and PAHs in these shallow floodplain lakes is lacking.

Because of their unique combination of varying ecological conditions and pollution characteristics, floodplain lakes are a suitable area to study the interactions between contaminants and nutrient cycles on the ecosystem level, to assess the effect of these interactions on bioavailability of sediment-bound contaminants and to apply existing models to analyze these interactions.

The **objectives** of this research were to assess the interactions between nutrients or ecological structure and contaminant cycles and effects in floodplain lakes, and to model contaminant flows in these systems. The main **research questions** were:

- What is the extent and nature of bioavailability of sediment-bound PCBs and PAHs?
- What are the effects of lake ecosystem structure on fate and bioaccumulation of PCBs and PAHs?

Sub goals described in this thesis are:
- To measure and model uptake of PCBs and PAHs by benthivorous fish in field enclosures treated with different nutrient regimes.
- To determine bioavailable fractions of PCBs and PAHs in sediment and evaluate the 6h Tenax-extraction method.
- To estimate fate and availability of PCBs and PAHs in flood plain lakes with different ecological structures in different seasons and in model ecosystems with different ecological structures.
- To determine the effect of aging on uptake of PCBs and PAHs by biota.
- To develop and improve models that describe bioaccumulation of organic contaminants.

In Chapter 2, an experiment is described in which the effect of nutrient additions on bioaccumulation of PCBs by benthivorous carp (*Cyprinus carpio*) in enclosures in a floodplain lake is assessed. In this chapter, also the 6h Tenax-extraction method is evaluated. Accumulated amounts of PCBs were compared to these 6h Tenax-extractable amounts, which were used as a measure for bioavailability. The effect of nutrient additions on bioaccumulation was also assessed. Finally, an uptake model was applied, including uptake of PCBs through sediment ingestion.

Chapter 3 describes bioavailability and bioaccumulation of PCBs and PAHs by benthic invertebrates in three ecologically different floodplain lakes. A monitoring study that lasted from September 2000 until March 2002 was described. A model was developed to describe BSAFs for invertebrates, including a term to account for a lesser bioavailability due to very strong sorption to carboneceous materials such as black carbon, coal and kerogens, and a term to account for uptake of the bioavailable fraction of the contaminants through ingested sediment.

In Chapter 4, the effect of aging (and the subsequent reduction of bioavailability) and ecosystem structure on bioaccumulation in biota are described. To assess the effect of ecosystem structure on fate and bioaccumulation of PCBs and PAHs, polluted floodplain lake sediment was brought into indoor model ecosystems, in which four different ecological structures were created. To determine the effect of aging on bioavailability and bioaccumulation in these systems, the sediment was spiked with two PCBs and a deuterated PAH, which subsequently could be compared with their 'native' counterparts. The 6h Tenax-extraction method was evaluated with respect to its capability to capture PCB and PAH fractions that are available to various biotic compartments.

In Chapter 5, fate of all analyzed PCBs and PAHs in these model ecosystems is described. An extensive statistical analysis was performed on lipid-normalized concentrations and total mass distribution of the contaminants in biota, suspended solids and sediments. Also, the effect of ecosystem structure on species composition and the amount of PCBs and PAHs in the biological compartments was analyzed thoroughly.

In Chapter 6, model results from earlier chapters are combined with existing models to obtain a bioaccumulation model for PAHs and PCBs in all biological compartments of the model ecosystems described in chapters 4 and 5. This new model included a term for strong sorption to hard carbonaceous materials and was optimized for metabolic transformation rates for PAHs. Finally, a sensitivity analysis was performed to assess model sensitivity of the newly introduced parameters compared to the most sensitive parameters in the original model.

Finally, in Chapter 7 this thesis ends with some concluding remarks and the main implications of the results.

Sorption and bioavailability of HOCs to field sediments

Figure 1.2 shows a schematic overview of the partitioning of a hydrophobic organic compound between sediment and water, and water and biota.

Sorption of HOCs (hydrophobic organic compounds) to sediments has been described by several authors (e.g., [*3,9,11,29-31*], starting with Karickhoff et al. [*32*].

Karickhoff, 1979 [*33*] described the partitioning of a compound between sediment and water using a partitioning coefficient K_P:

$$K_P = \frac{C_{sed}}{C_w} \quad (1)$$

with C_{sed} the concentration in sediment and C_w the freely dissolved concentration in the water phase. When it is taken into account that organic contaminants are mainly present in the organic matter fraction of sediment (f_{om}, or if given on an organic carbon basis: f_{OC}) and concentrations in the mineral fraction (f_{min}) can be neglected, concentrations are usually given on an organic carbon-basis (C_{oc}). Partitioning of the compound between water and sediment is then described using an organic-carbon-to-water partitioning coefficient K_{OC} [*34*]:

$$K_{OC} = \frac{C_{sed}/f_{OC}}{C_w} = \frac{C_{OC}}{C_w} \quad (2)$$

In general, K_{OC} correlates with the octanol-water partitioning coefficient (K_{OW}) of a compound (an overview of different correlations is given in Ten Hulscher, 2005 [*10*].

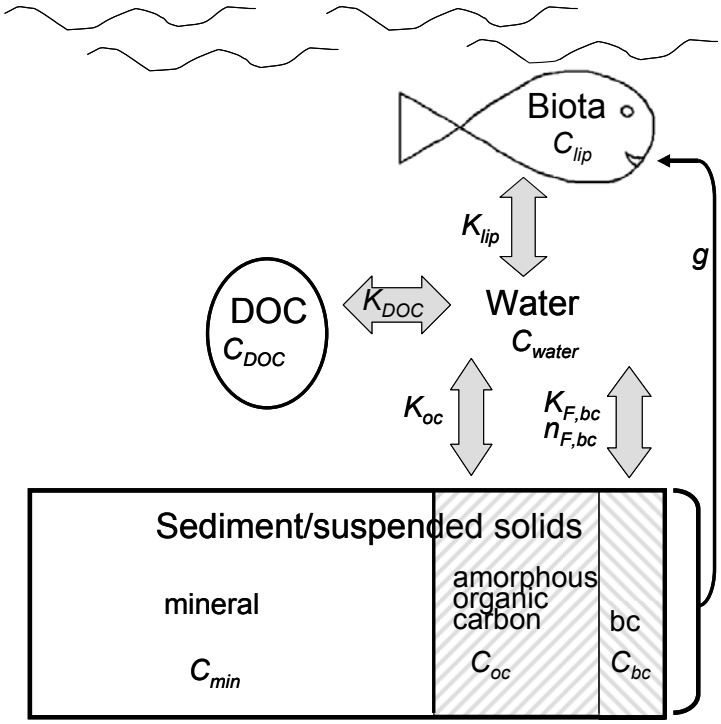

Figure 1.2. *Equilibrium partitioning of an organic compound between sediment and/or suspended solids, water, and biota. C_{sed} = concentration in sediment/suspended solids; C_{min} = concentration in mineral fraction; C_{OC} = concentration in organic carbon fraction; C_{bc} = concentration in black carbon fraction; C_{lip} = concentration in lipid fraction of biota; C_{water} = freely dissolved concentration in water; C_{DOC} = concentration in dissolved organic carbon (DOC); K_{lip} = lipid/water partitioning coefficient; K_{OC} = organic carbon/water partitioning coefficient; $K_{F,bc}$ and $n_{F,bc}$= Freundlich coefficient and exponent for sorption to the black carbon fraction; K_{DOC} = DOC/water partitioning coefficient; g = food chain magnifier for digestive uptake of sediment.*

It has been recognized that various different types of organic carbon exist, each with its own partitioning coefficient [*33*]:

$$K_{OC} = \sum f_{OC,i} K_{OC,i} \quad (3)$$

With $f_{OC,i}$ the fraction of a specific type of organic carbon, and $K_{OC,i}$ the partitioning coefficient of that organic carbon. More recently, it has been observed that one of these OC phases can be characterized as BC, and sorption to organic carbon can be split into a term for linear sorption to amorphous OC and a term for strong non-linear sorption to BC [*35*].

When a generic, often laboratory derived, value for K_{OC} is used however, water concentrations in the field can be overestimated up to a factor of 1000 [*3,10,36-38*]. Organic contaminants may be physically entrapped into micro pores, or sorbed very solidly to high-affinity carbonaceous geosorbents like soot, kerogens, active coal, etc, and therefore not be able to desorb. Although the term carbonaceous geosorbents [*9,11*] is more correct, within this thesis the term black carbon will be used. Desorption of HOCs from sediments has been recognized to occur in three kinetically defined stages: a 'fast', 'slow', and a 'very slow' desorption stage. HOC fractions that desorb during these stages have typical desorption half lives of about 10 hours, 100 hours, and 10,000 hours, respectively [*39*]. Increased contact time between contaminants and sediments or suspended solids (often referred to as aging) decreases the fast desorbing fraction, probably because the compound sequesters into the sediment due to retarded diffusion in either micro pores or organic matter [*29,40*]. Thus, in the field, due to aging and sorption to BC, not all organic contaminants are fully available for partitioning between sediment and water [*9,11*]. This also affects the amount of a compound that can be accumulated by biota.

Bioavailability of a hydrophobic organic compound in sediment or soil is often considered to depend on the way the chemical is sorbed to the sediment [*5,8,31,40*]. Bioavailability is defined here as the fraction of a compound that can be taken up by biota within relevant time frames through all relevant uptake routes, where the relevant time frame relates to the life span (months or years) of the organism which is exposed to the contaminant. Within relevant time frames for bioaccumulation, the very slow desorbing fraction can be assumed to be unavailable for uptake by organisms, whereas especially the fast desorbing fraction is generally assumed to be the bioavailable one [*2,4,5*]. This explains why actual risk of a compound in sediment may depend primarily on its bioavailable concentration rather than on its total concentration.

Measuring bioavailability

Because risk assessment for sediments involves more than just measuring total contaminant concentrations [*4,5,41*], there is a great demand for adequate methods to determine bioavailable concentrations. Measuring bioavailability should be done, if possible, by measuring uptake rates in biota [*42*]. However, this is often not feasible due to financial and practical reasons. To assess exposure of organisms to sediment-bound contaminants without using biota, various chemical techniques have been developed.

An overview of numerous passive accumulation devices is given by Stuer-Lauridsen, 2005 {*43*]. Many of these techniques are very laborious. Some passive samplers can deplete the surroundings, and provide primarily kinetic information. The most widely used depletive passive samplers are semi-permeable membrane devices (SPMDs) [*6,44*], Tenax beads [*7,30*], empore disks with C_{18} resin [*45*] and XAD resins [*46*]. Mild solvent extractions [*47*] and Supercritical Fluid Extraction (SFE, [*46,*48]) are also methods that can be used to assess bioavailability. For all of these methods good correlations with accumulated concentrations in biota have been reported.

It is also possible to estimate the freely dissolved concentration in (pore) water (C_W in Figure 1.2). Depletion with these techniques is negligible, and it does not affect partitioning within the system. A SPME fiber (Solid Phase Micro Extraction; [*49-51*]) or POM strip (Polyoxymethylene; [*52*]) is then placed in the water column or within the sediment layer. After certain time equilibrium is reached between strip or fiber and the water phase, and then the amount sorbed to this material is analyzed. If the distribution coefficient between water and the SPME or POM is known, the freely dissolved concentration can be calculated. However, this method only works if the sediment-water equilibrium is not disturbed when SPME fibers or POM strips are added, and thus the freely dissolved concentration in the water phase will not change significantly.

A recently developed and validated method to mimick uptake by biota is that of extracting contaminants from sediment using Tenax beads [*7,8,30,53*]. These are small polymer beads, with a large sorption capacity. When they are shaken together with sediment in water, the contaminant will desorb from the sediment and sorb to the Tenax beads. Which fraction of the contaminant will desorb depends on the extraction time, in this case the duration of shaking. To accurately determine full desorption curves for a particular sediment, covering the 'fast', 'slow' and 'very slow' desorbing fraction, Tenax beads are added and removed at various time steps. An

easier approach, which yields reasonable estimates for the fast desorbing fraction only, is to use a single-time point Tenax extraction after 6 or 24 hours of shaking [*7*].

Bioaccumulation of organic chemicals

Organic pollutants can be very persistent and can also be characterized as very hydrophobic. This means that these compounds can accumulate to a great extent in the lipid phase of biota and are often transferred from lower trophic levels to the predators in higher trophic levels.

Bioaccumulation in biota can be expressed using a biota-to-sediment-accumulation factor (BSAF), with [*54*]:

$$BSAF = \frac{C_{biota}/f_{lip}}{C_{sed}/f_{oc}} \quad (4)$$

With C_{biota} the concentration in biota and f_{lip} the fraction lipid in biota. If only partitioning plays a role ánd equilibrium exists, then BSAF = K_{lip}/K_{OC}, with Klip the lipid/water partitioning coefficient. According to the equilibrium partitioning theory, when equilibrium exists and a compound has equal affinities for the lipid and organic carbon phase, the BSAF value should be between 1-2. Many researchers have already shown that BSAFs are often lower than 1 however (e.g., when a compound is metabolized within the biota or when its bioavailability is reduced due to sorption to BC) or higher than 1 (e.g., in case of biomagnification) [*55,56*].

Thus, accumulation of chemicals in biota is not as straightforward as the use of a general value of 1 for BSAFs implies. Various uptake and loss processes, many of which depend on chemical characteristics and the biotic species itself, influence accumulation of organic chemicals. These processes include biomagnification, biotransformation, and growth dilution [*57,58*]. Highest BSAFs are generally measured for compounds with a log K_{OW} between 5.5 and 7.5 [*57,59,60*]. Compounds with a log K_{OW} lower than 5.5 are less hydrophobic and more easily excreted; compounds with a high log K_{OW} are often relatively large and may not pass cell membranes as easily as compounds with lower log K_{OW} values [*60*] and are thus more easily biomagnified in higher trophic levels.

Modeling bioaccumulation

Models for bioaccumulation have been reviewed by Mackay and Fraser, 2000 [*60*], Koelmans et al., 2001 [*21*], Barber, 2003 [*62*] and Arnot and Gobas, 2004 {*63*]. Bioaccumulation models have developed from simple Log K_{OW} - log BCF regression models to very extensive food web models. In the 70s, two compartment (organism and water) models were developed, soon followed by fugacity-based models [*64,65*]. During the 80s and 90s, these models became more and more sophisticated, including kinetic processes, both dietary and gill uptake, and incorporating complete food webs.

At present, models for bioaccumulation usually comprise a combination of two models: an exposure model based on partitioning, which is the input for a model in which uptake and loss of a chemical in biota is described. Uptake processes are absorption from water and assimilation from invertebrate food. Loss processes are excretion into water, egestion through food, internal processes like growth dilution and metabolic transformation, and loss due to reproduction (spawning). Thus, the amount of a chemical that is taken up or excreted in time, can be described as [*57,58,66*]:

$$\frac{dC_{biota}}{dt} = k_{abs,in}C_w + k_{ass,in}C_{food} - (k_{excr,out} + k_{eges,out} + k_{grdil,out} + k_{metab})C_{biota} \quad (5)$$

With t time; C_{biota} the concentration in biota; $k_{abs,in}$ the rate constant for absorption from water; $k_{ass,in}$ the rate constant for assimilation from food; C_{food} the concentration in food; $k_{exr,out}$ the rate constant for excretion to water, $k_{eges,out}$ the rate constant for egestion through the gut, $k_{grdil,out}$ the rate constant for growth dilution; and k_{metab} the rate constant for metabolic transformation.

Assuming steady state, $dC_{biota}/dt = 0$, which results in:

$$C_{biota} = \frac{k_{abs,in}C_w + k_{ass,in}C_{food}}{k_{excr,out} + k_{eges,out} + k_{grdil,out} + k_{metab}} \quad (6)$$

This generic model is used widely, although estimation of rate constants varies among applications. Uptake through food can be modeled using just one type of food, but can also be extended to include detailed diet characteristics, if necessary composed of different compartments of the food web. This food web can (1) be linear (e.g. phytoplankton is consumed by zooplankton, which is consumed by fish, which is consumed by a top predator) [*57*], (2) include benthivorous interactions and uptake

of sediment organic matter [*57,58,67*], and (3) consist of numerous interactions, which can be described in a matrix form [*68,69*]. Rate parameters can be estimated using measurements or using empirical relationships, which may be based on weight correlations (allometric relationships) [*57,68,70*].

Exposure of organisms to organic contaminants is generally assumed to be through the water phase and through food, which in turn has also been exposed through the water phase. If no measured freely dissolved water concentrations are available, water concentrations are calculated from sediment concentrations using equation 1. Especially for PAHs in situ however, various model studies have shown that water concentrations (and thus exposure) may be overestimated by this exposure model [*3,10,36-38*].

Ecosystem structure and interactions with contaminants

Many, sometimes counteractive, processes play a role in the interactions between food webs and contaminants [*17-19,21,71-74*]. Food web structure depends on many factors such as lake trophic state, size, depth, river connectivity, pH and salinity. There are three main ways for interaction between contaminants and food webs: (1) contaminant fate is closely linked to the carbon cycle, since organic contaminants are mainly bound to organic carbon phases (2) nutrients may influence food quality and thus accumulation through food uptake (3) contaminants can change food web structures due to toxicity.

In eutrophic systems, carbon pools are very dynamic. During summer, algal growth increases fresh organic matter inputs to the upper layer of the sediment. Sedimentation rates of suspended particles are higher in eutrophic systems [*75*]. These particles are supposed to scavenge organic contaminants from the water column [*76*]. Microbial breakdown of the organic phase concentrates the organic contaminants in the remaining settling material even further [*75*]. In oligotrophic systems this happens in the water column, but in eutrophic systems due to the higher sedimentation rates this happens mainly at the sediment surface. Extra nutrient availability in eutrophic systems further increase bacterial activity and thus microbial breakdown of organic matter [*77*]. These findings are supported by Gobas and MacLean, 2003 [*38*], who used a model to show that the increase of contaminant concentrations from plankton to suspended solids to bottom sediments can be explained by organic carbon mineralization throughout the process of sediment diagenesis.

Furthermore, high growth rates in eutrophic systems may also cause 'growth dilution': the total pool of contaminants in an organism stays constant, but the steady state concentration within the organism is reduced due to growth [*78,79*]. 'Biomass dilution' may occur when chemical concentrations in biota are decreased due to dilution into a higher amount of biomass [*15,19*], which may occur especially in planktonic groups [*80*]. Combined with changes in species composition and lipid content, this may also affect contaminant concentrations within planktonic compartments [*81*].

Positive relationships between bioaccumulation and food supply have also been reported. For instance, for benthic invertebrates, increased benthic feeding activity and respiration, may lead to increased toxicity [*74*]. For some species a high food quality and availability can completely counteract toxicity effects. Some species thrive very well on sediments with high food availability despite sub-lethal toxic effects. This is the case when their predators and competitiors are affected more severely by toxicants and thus the more tolerant species do not suffer from predation and competition anymore [*82*].

Microcosm experiments suggested that community nutrient status at least affects the types and magnitude of indirect effects of insecticides [*83*]. Trophic status may influence exposure due to the processes mentioned above, but nutrient status also affects the susceptibility of organisms to different types of stress. For instance, at sublethal concentrations of toxicants, well-fed organisms may be less susceptible than organisms that are starving [*83*].

Floodplain sediments in the Netherlands generally are rich in nutrients and floodplain lake ecosystems range from mesotrophic to very eutrophic states [*25,26*]. Usually they are categorized into two main ecological structures: clear or turbid. The clear lakes typically are dominated by macrophytes and are less eutrophic than the turbid lakes, which are either dominated by algal growth or benthivorous fish. These benthivorous fish increase organic and inorganic turbidity when they resuspend the sediment looking for prey. Turbid lakes are usually more dynamic, with large variations in algal densities and species composition. This also causes the carbon cycle to be more dynamic than in less eutrophic macrophyte-dominated systems. However, these conditions may change due to inundation and floodings. Especially in these shallow lakes, ecosystem structures may shift regularly from clear to turbid and back [*27,28*]. Considering the afore-mentioned mechanisms, this means that in flood plain lakes such a change in ecosystem structure may cause significant changes in the cycling, bioavailability and effects of contaminants in the benthic-pelagic food web.

Study area and compounds

This research was part of the Stimulation Programme System-oriented Ecotoxicological Research (SSEO), funded by the Dutch Organization for Scientific Research (NWO). Within this programme, three research sites were selected, one of which was the floodplain of the Afferdense en Deestsche Waarden (ADW). The ADW are part of the floodplains of the river Waal, which is the southern branch of the river Rhine. In Figure 1.3 our sample locations are identified. The most important sample locations were located in ADW, but some other (reference) locations were situated elsewhere along the river Waal. The ADW floodplain is about 3 km^2, comprises agricultural fields, extensively grazed grasslands and a number of lakes, and is flooded frequently. At the moment, the ADW floodplain is being lowered and redeveloped into a nature reserve, to provide more river storage capacity during floodings. As described in the previous section, dynamic lakes such as those in the ADW, provide good possibilities to study availability, cycling and accumulation of HOCs.

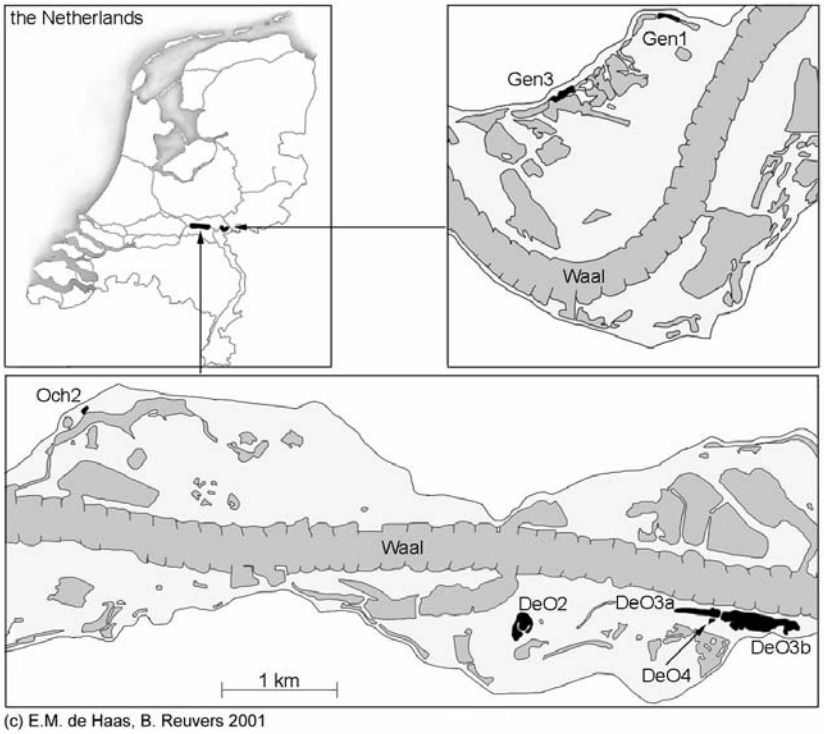

Figure 1.3. *Sample locations in the Afferdensche and Deestsche Waarden (DeO2, DeO3a, DeO3b, DeO4) and the floodplains near Ochten (Och2) and Gendt (Gen1, Gen3).*

Contaminants in these floodplain lake sediments include heavy metals, hydrophobic organic pollutants, pesticides, and pharmaceuticals. Because of the number of different chemicals, it is not possible to measure them all in routine monitoring programs. Many of them are still unknown, and cannot even be measured. Therefore, this thesis focuses on two groups of contaminants that can be measured very well, are known to be present in floodplain sediments, and are well described with regard to chemical characteristics: polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs).

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Chapter 2

Uptake of sediment-bound bioavailable polychlorobiphenyls by benthivorous carp (Cyprinus carpio)

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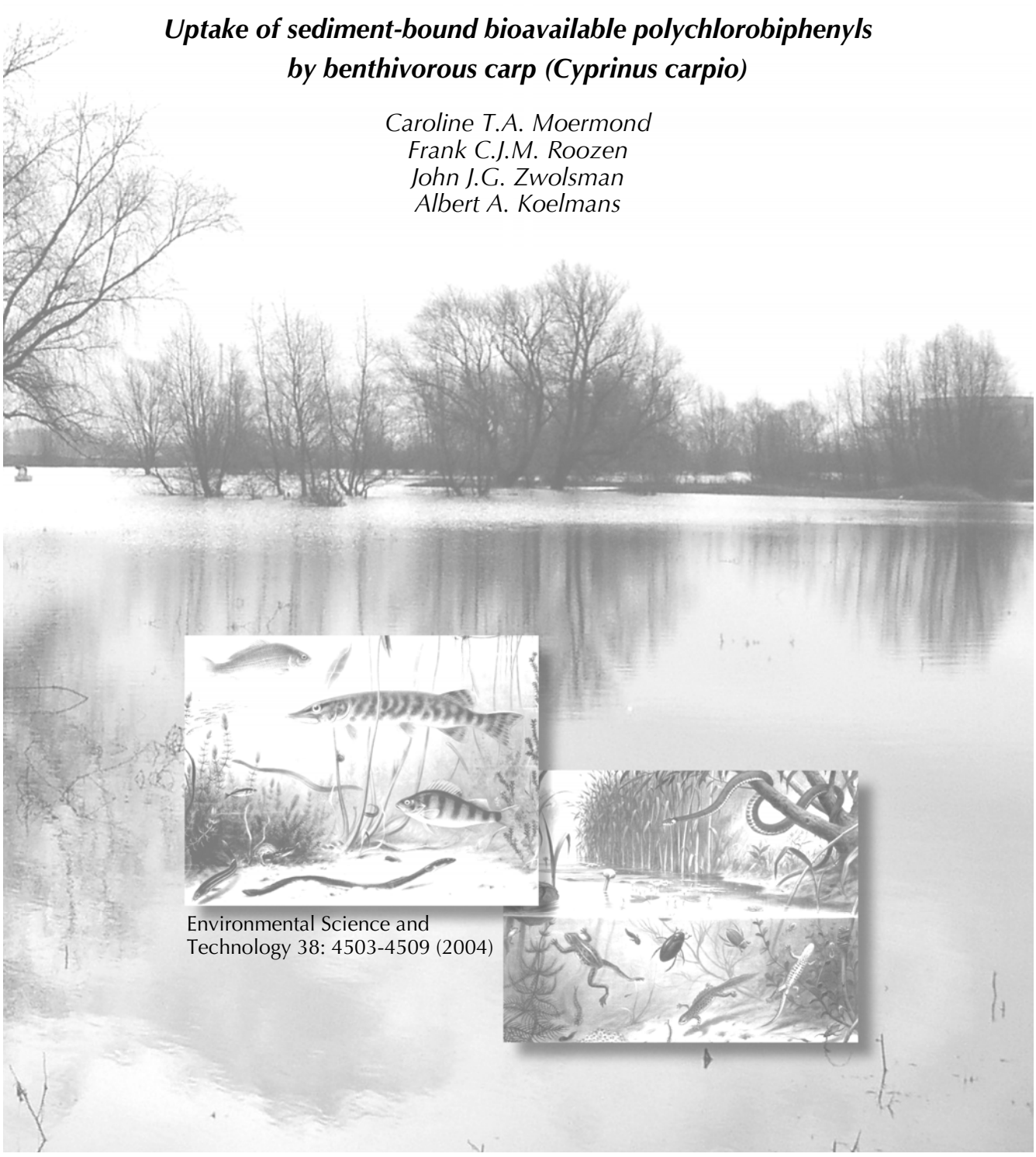

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Abstract

It is unclear whether accumulation of sediment-bound chemicals in benthivorous fish depends on the degree of sequestration in the sediment like it does for invertebrates. Here, we report on the potential of slow and fast desorbing sediment-bound polychlorobiphenyl (PCB) fractions for accumulation in carp (*Cyprinus carpio*) in lake enclosures treated with different nutrient doses. Routes of PCB uptake were quantitatively evaluated for 15 PCBs (log Kow range 5.6-7.8) using model analysis. Fast-desorbing PCB fractions in the sediment were defined as the ratio of 6-h Tenax-extractable to (total) Soxhlet-extractable concentrations. These fractions varied between 4 and 22% and did not show a clear trend with log Kow. However, bioaccumulation of PCBs in carp correlated much better with Tenax-extractable concentrations than with totalextractable concentrations. Nutrient additions in the enclosures had a positive effect on PCB accumulation. Model results show that PCB uptake in carp can be explained from (1) uptake through invertebrate food, (2) uptake from fast-desorbing fractions in ingested sediments, and (3) uptake from water, where PCBs are in partitioning equilibrium with fast-desorbing fractions. The main implication of this research is that fast-desorbing PCB fractions in sediments have great predictive potential for bioaccumulation in benthivorous fish.

Introduction

As a result of decreased contaminant loadings, many sediments throughout the world have changed from sinks to possible sources for hydrophobic contaminants. As nutrient loadings also change, for example due to a decrease in eutrophication, food web structures and thus growth and biomass of biota may be affected [*1-4*]. In turn, this may influence fate and bioavailability of contaminants. Remobilization of aged, sediment-bound contaminants into the aquatic ecosystem is an important issue in risk assessment of polluted sediments, especially in shallow systems such as floodplain lakes. Many floodplain lakes in The Netherlands are dominated by benthivorous cyprinid fish [*5*]. These benthivorous fish are exposed to sediments through their feeding behavior. When feeding, they not only resuspend sediments (6) but also ingest considerable amounts of sediments [*7,8*]. As this direct sediment uptake route is generally not taken into account (e.g., refs [*9,10*]), this implies that current models for contaminant uptake by fish may be less suitable for benthivorous fish.

For benthic invertebrates, sediment ingestion is an important uptake route for hydrophobic contaminants [*11-13*], although considerable differences exist among species and even among individuals of a species [*14*]. Bioavailability of contaminants such as polychlorobiphenyls (PCBs) to sediment-inhabiting organisms may be limited by the presence of a very-slow-desorbing fraction in the sediment [*15-18*]. In contrast, the fast-desorbing (labile) fraction is supposed to be exchangeable with water and biota within relevant time frames, and is as such often considered to be a better measure for bioavailability than total concentrations. When sediment ages, bioavailability decreases [*19-21*], which is generally attributed to a decrease in fast-desorbing fractions [*22*]. Hence, aging and the subsequent decrease in fast-desorbing fractions may affect contaminant transfer within aquatic food chains.

Measured fast-desorbing PCB fractions correlate well with benthic invertebrate PCB accumulation [*17*]. For higher trophic levels such as benthivorous fish however, it is still unclear whether the magnitude of fast-desorbing sediment-bound PCBs influences PCB uptake. We hypothesize that PCB levels in benthivorous fish also correlate better with fast-desorbing PCB fractions in sediments than with total PCB fractions.

The primary objective of this research was therefore to evaluate the role of fast-desorbing, sediment-bound PCBs for accumulation in benthivorous fish. The second objective was to evaluate the effect of nutrient additions on accumulation, and the third objective was to evaluate different exposure routes using a modeling approach, with uptake through ingested sediments as a new feature.

Accumulation of PCBs by carp (*Cyprinus carpio*) was measured in enclosures in a floodplain lake along the lower river Rhine in The Netherlands to which no, medium, or high amounts of nutrients were added. Fast-desorbing PCB fractions were distinguished from slow-desorbing fractions using a Tenax extraction technique modified from Cornelissen et al. [*23*]. A simple model based on first-order processes [*9,10*] was expanded with PCB uptake through sediment ingestion to evaluate different exposure routes. Dissolved PCB concentrations and bioavailable concentrations in the sediment were estimated using measured 6-h Tenax-extractable fractions.

Materials and methods

Experimental setup

The experiment was carried out from August 15 through October 20, 2000.

Study area. Enclosures were placed in a floodplain lake on the south side of the lower river Rhine in The Netherlands. The lake is a turbid, man-made clay pit of about 2 ha with a mean depth of 1 m, which was formed around 1930. It is separated from the main river channel by a summer dike and is inundated between 50 and 150 days a year, which did not happen during the experiment. The upper layer of the sediment consists of clay and silt, and aquatic vegetation is absent. The fish population has been monitored from 1997 through 1999 and was dominated by cyprinid bream (*Abramis brama*), with biomasses up to 440 kg ha^{-1} [*5*].

Enclosure setup. Six transparent Perspex cylinders 1.35m high and 1.05 m in diameter were installed at a water depth of about 0.9 m, penetrating 10 cm into the sediment. During installation, each enclosure was lowered carefully to the lake bottom to minimize disturbance of sediments. Each enclosure was covered with a metal frame with a 1-cm mesh size to prevent predation of fish by birds and to prevent fish from jumping in or out during the experiment. Light measurements indicated no negative effect of the cover on light irradiance in the water column. At the start of the experiment, dissolved nutrient concentrations (n = 12) were 0.013 ± 0.003 mg/L NH_4^+-N, 0.051 ± 0.017 mg/L NO_3^--N, and 0.053 ± 0.011 mg/L PO_4^{3-}-P. To assess the effect of nutrient additions on PCB accumulation, a nutrient solution was gently added to the enclosures.Two enclosures received no nutrients (treatment 0), two enclosures received 1 mg/L NO_3^--N and 0.1 mg/L PO_4^{3-}-P (treatment 1), and two enclosures received 3 mg/L NO_3^--N and 0.3 mg/L PO_4^{3-}-P (treatment 2). Treatments were randomly assigned to the enclosures. Carp (*Cyprinus carpio*) was chosen as test species due to availability and because their feeding behavior is similar to that of native bream.

Procedure. In each enclosure one carp (of equal size; obtained from a commercial fish farm) was added, resulting in a fish density of approximately 1100 kg/ha. Another carp was immediately frozen at -20 °C to be analyzed as a blank for PCBs. Because the available benthic invertebrates in the enclosures were an important food source for carp, these invertebrates could not be sacrificed for PCB analysis. Instead, one month after the experiment started benthic invertebrates were sampled just outside the enclosures, assuming identical PCB concentrations. Ten 15 x 15 cm samples were taken with an Ekman grab, sieved over a 500-µm sieve, separated from the

debris by hand, and pooled. After the samples were freeze-dried, they were stored at -20 °C in a glass jar. Two months after the experiment started, each fish was caught using a fish net, and three sediment samples were taken in each enclosure using a core sampler with a 5-cm diameter. Samples were transported immediately to the laboratory. In the laboratory, length and weight of each fish were measured, after which each fish was cut into small pieces, freeze-dried, pulverized, and stored at -20 °C in a glass jar. The upper 5 cm of each sediment core was carefully removed, homogenized, freeze-dried, and stored at -20 °C in a glass jar.

Fish and benthic invertebrate samples were analyzed for PCB and lipid contents. Sediment samples were analyzed for organic matter, organic carbon, and total and 6-h Tenax-extractable PCB concentrations, as described below.

Analytical procedures

General characteristics. Dry to wet weight ratios were measured by weighing each sediment and fish sample before and after freeze-drying. Organic matter content of each sediment was measured in triplicate as weight loss after combustion at 550 °C until constant weight. Sediment organic carbon was analyzed, after removal of carbonates with HCl, with an elemental analyzer (Fisons Instruments EA 1108 CHN-O analyzer, CE Instruments, Milan, Italy). Sediment grain size was measured after decalcification with 1 M HCl and removal of organic matter with 30% H_2O_2, using laser diffraction on a Coulter 230 (Beckman-Coulter, Coulter Corporation, Scientific Instruments, Miami, FL) at 10% obscuration of the laser beam. The amount of lipid in each fish was measured gravimetrically in triplicate after Soxhlet extraction for 5 h in a hexane/acetone 3:1 v/v mixture. Invertebrate samples did not contain enough material for gravimetrical lipid analysis, so invertebrate lipids were extracted according to Bligh and Dyer [*24*] and quantified photometrically according to Zöllner and Kirsch [*25*] on a Beckman DU-64 spectrophotometer (Beckman Instruments, Fullerton, CA).

Chemicals for PCB analysis. PCB congeners (IUPAC numbers) 18, 20, 28, 31, 44, 52, 101, 105, 118, 138, 143, 149, 153, 170, 180, and 194 were purchased from Promochem (Wesel, Germany). Other chemicals used were acetone and hexane (picograde; Promochem), isooctane (analytical grade; Acros, Geel, Belgium), ethanol (99.8%; Merck, Darmstadt, Germany), Barnstead Nanopure water (Sybron-Barnstead, Dubuque, IA), sodium azide (NaN_3; 99%; Sigma-Aldrich, Steinheim, Germany), aluminum oxide-Super I (ICN Biomedicals, Eschwege, Germany), silica gel 60 (63-200 mesh; Merck), Cu powder (99.7%, Merck), and Tenax beads (60-80 mesh;

Chrompack, Middelburg, The Netherlands) Prior to use, silica gel was activated overnight at 180 °C, aluminum oxide was deactivated with 10% (w/w) Nanopure water, Cu powder was Soxhlet-extracted with hexane for 4 h, and Tenax beads were Soxhlet-extracted with acetone and hexane (2 h each) and dried overnight at 75 °C.

Total PCB extraction and cleanup. All glassware was prerinsed with acetone. Samples were extracted during 16 h using a Soxhlet-apparatus with a hexane/acetone mixture (3:1 v/v). The solution was concentrated using a modified Kuderna-Danish apparatus followed by evaporation to 1 mL under a gentle flow of nitrogen. Subsequently the sample was eluted with 30 mL of hexane over a column with 4 g (sediments and invertebrates) or 7 g (fish) of aluminum oxide. Samples were reduced to 1 mL as described above, eluted with 30 mL of hexane over a column with 2 g of silica gel, reduced again, and desulfurized using Cu powder. Hexane was then exchanged to isooctane and PCB143 was added as an internal standard. With every 10 samples, one blank and one sample to determine cleanup recoveries were included. Recoveries ranged from 70 ± 13% (PCB18) to 96 ± 6% (PCB194). Additional reference samples were analyzed; results were always within error limits.

Tenax PCB extraction. The labile fraction was determined using a 6-h Tenax extraction modified from Cornelissen et al. [*23*]. Modifications to this method were that we (1) prewashed the Tenax beads, (2) used a glass column to elute Tenax with hexane and ethanol instead of shaking Tenax with hexane in a separation funnel, and (3) applied a full cleanup to the extract. In short, the method is as follows. A mixture of 0.6 g of Tenax, 1 g of dry sediment, 7.5 mg of NaN_3 (to reduce microbial activity), and 150 mL of Nanopure water was constantly shaken in a 250-ml separation funnel for 6 h in a 20 °C climate chamber. After separation from the sediment, Tenax beads were transferred to a glass column using a small amount of Nanopure water, eluted with 15 mL of ethanol and eluted two times with 25 mL of hexane. After a volume reduction to 1 mL (techniques as described above), 20 mLof hexane was added and the extract was again reduced to 1 mL. This last step was repeated once, to make sure that all ethanol was replaced by hexane. Cleanup and analytical procedures were equal to those of total PCB analysis. With every 10 samples, one blank (Tenax shaken with Nanopure water and NaN_3) and one sample to determine cleanup recoveries were included.

GC analysis. PCBs were analyzed on a Hewlett-Packard 5890 II gas chromatograph (Hewlett-Packard, Little Falls, Wilmington, DE) equipped with a HP7673A autosampler, two ^{63}Ni electron capture detectors, and two capillary fused silica columns (CP Sil-8 CB and CP Sil-5 CB, Varian, Bergen op Zoom, The Netherlands).

GC responses were corrected for blanks and cleanup recoveries. The typical relative standard deviation for replicated samples was 8%.

Statistical analysis. In total there were six experimental units (fish in enclosures) with 15 observations (PCB concentrations) each. Regression coefficients of fish concentrations against sediment concentrations were calculated. The significance of the regressions' improvement when using the Tenax-extractable concentration as independent variable was calculated using an F-test. Homogeneity of regression slopes among different nutrient treatments was also tested (F-test).

Results and discussion

PCB uptake in fish from sediment

Fish, benthic invertebrate, and sediment characteristics are given in Table 2.1. All enclosure sediments showed a similar composition, except for one enclosure without nutrient additions (0b). Sediment from this enclosure had a higher percentage of grainsizes larger than 63 ím than the other enclosures ($P < 0.01$; Dixon's test for outliers [*26*]), and contained less organic material and PCBs ($P < 0.1$; Dixon's test for outliers [*26*]). Furthermore, standard deviations for this enclosure were much higher, indicating larger heterogeneity than the other enclosures (Table 2.1). Also, the fish from this enclosure had gained more weight than the other fish, resulting in a higher weight/length ratio. Because of the statistics and because selective feeding of fish on organically rich parts of sediments may have occurred, this disqualifies this enclosure as a reliable blank.

∑PCB concentrations in fish were 30.5 µg/kg dry weight (blank fish) at the start of the experiment and on average 386 ± 67 µg/kg dry weight at the end of the experiment. Lipid contents at the end of the experiment varied between 5.2 and 18.8% (on a dry weight basis). However, since the fish grew quite well, we do not assume the fish were food-limited. The fish PCB concentration at the end of the experiment was four times less than the concentration of 1470 µg ∑PCBs/kg dry weight found in 0+ bream (*Abramis brama*; containing about twice as much lipids), caught in the same lake in the same period (unpublished results). As feeding behavior of bream and carp is very similar, this suggests that steady state between carp and sediments was probably not reached within the duration of the experiment.

Table 2.1. *General characteristics and PCB contents of carp, benthic invertebrates and sediments. Standard deviations (n=3) are given between brackets.*

Invertebrates/Carp	length (cm)	weight (g ww)	fraction dw (of ww)	% lipids (of dw)	ΣPCB[a)] (µg/kg dw)
Inv			0.25	24.0	188
C-B	18.0	88	0.26	17.9 (0.6)	30.5
C-0a	21.4	115	0.26	18.8 (1.0)	350
C-0b	21.7	157	0.23	10.0 (1.0)	422
C-1a	21	123	0.23	5.8 (0.6)	318
C-1b	20.7	128	0.22	7.1 (0.8)	318
C-2a	21.8	120	0.17	5.2 (0.4)	483
C-2b	18.8	90	0.21	7.2 (0.3)	423

Sediment	OC (% of dw)	%<2µm	%<63 µm	ΣPCB[a)] (µg/kg dw)	ΣPCB_{Tenax}[a)] (µg/kg dw)
0a	4.3 (0.1)	26 (0)	92 (2)	160 (7)	20 (0)
0b	3.7 (0.7)	14 (4)	69 (16)	133 (22)	13 (2)
1a	4.3 (0.3)	22 (1)	94 (2)	158 (7)	18 (1)
1b	4.7 (0.5)	21 (1)	92 (1)	157 (12)	18 (1)
2a	4.0 (0.6)	20 (1)	92 (1)	176 (21)	19 (2)
2b	4.2 (0.2)	19 (0)	92 (1)	181 (14)	16 (1)

Inv = invertebrates; C = carp; C-B = blank carp (t = 0); ww = wet weight; dw = dry weight; OC = organic carbon. Treatments 0a, 0b = blank enclosure with respect to nutrient additions; 1a, 1b = low nutrient additions; 2a, 2b: high nutrient additions

[a)] ΣPCB is the sum of concentrations of PCBs 18, 20, 28, 31, 44, 52, 101, 105, 118, 138, 149, 153, 170, 180 and 194 after two months exposure

To assess the fast-desorbing, bioavailable fraction of sediment-bound PCBs, 6-h Tenax-extractable fractions were measured. The percentage of PCBs that is desorbed from the particles within 6h varied between 4 and 22 % of total (Soxhlet extractable) concentration, and did not show a clear trend with log K_{OW} of the PCB congeners (See Figure 2.1). When concentrations of individual PCB congeners in carp in enclosure 1b are plotted against individual PCB concentrations in sediment obtained through total extraction (Figure 2.2A) and 6-h Tenax extraction (Figure 2.2B), it is clear that the latter greatly improved the regression's correlation (R^2 from 0.77 to 0.95) and significance levels (P from 2.0×10^{-5} to 1.2×10^{-9}). An overview of similar statistics for all enclosures is given in Table 2.2. In this table is also given the significance of the regressions' improvement (calculated using an F-test on residual squares). Remarkably, the improvement when using 6-h Tenax-extractable concentrations is highly significant in five of the six cases. For the remaining enclosure, the regression did improve, but the regression was already highly significant for total concentrations in the first place.

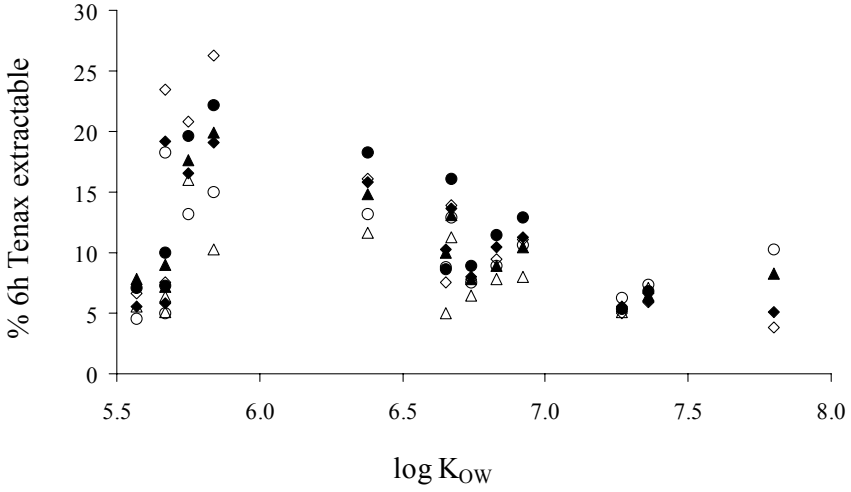

Figure 2.1. *6-h Tenax-extractable sediment concentrations as a percentage of total (Soxhlet extractable) sediment concentrations against log* K_{OW}. ● = *0a and* ○ = *0b (no nutrient additions);* ◆ = *1a and* ◇ = *1b (medium nutrient additions;* ▲ = *2a and* △ = *2b (high nutrient additions).*

Table 2.2. *Correlation coefficients* R^2 *with significance levels P for regressions of PCB concentrations in carp against total PCB concentrations in sediments or 6h TENAX extractable PCB concentrations in sediments. In the last column the significance of the model improvement (F-test on residual squares) is given.*

	Total PCBs		6-h TENAX-extractable PCBs		P (6-h better than total)
	R^2	P	R^2	P	
0a[a]	0.73	5.5×10^{-5}	0.93	2.1×10^{-8}	6.7×10^{-3}
0b	0.83	2.3×10^{-6}	0.93	5.4×10^{-9}	5.5×10^{-2}
1a	0.80	6.0×10^{-6}	0.95	6.4×10^{-10}	8.7×10^{-3}
1b	0.77	2.0×10^{-5}	0.95	1.2×10^{-9}	5.9×10^{-3}
2a	0.84	1.4×10^{-6}	0.95	4.7×10^{-10}	1.8×10^{-2}
2b	0.91	4.9×10^{-7}	0.94	7.1×10^{-8}	0.47

[a] Treatments: 0a, 0b = blank enclosure with respect to nutrient additions; 1a, 1b = low nutrient additions; 2a, 2b: high nutrient additions.

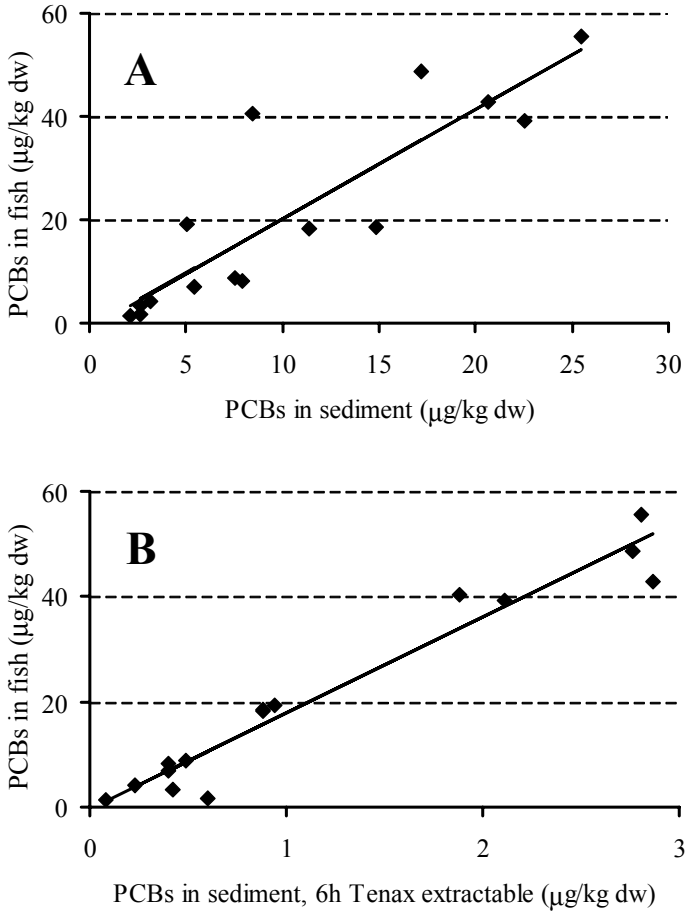

Figure 2.2. *Levels of individual PCB congeners in carp against total (A) and 6h-Tenax (B) extractable sediment concentrations for enclosure 1b (low nutrient additions).*

These results suggest that the 6-h Tenax-extraction method is a better estimator of bioavailability than the Soxhlet-extraction method, not only for benthic invertebrates [*17,27*], but also for higher trophic levels in the food chain such as benthivorous fish. The correlations' improvement may be explained from the proportionality of PCBs in fish with bioavailable, fastdesorbing PCB fractions, through three alternative uptake routes: (1) absorption from water, (2) assimilation from invertebrate food, and (3) assimilation from ingested sediment. These three uptake routes are discussed below.

(1) Absorption from water. Dissolved PCB concentrations in (pore-)water are governed by rapid equilibrium with the fast desorbing fraction, regardless of the degree of sequestration or aging [*28*]. Especially for less hydrophobic PCBs, absorption from water can be the dominant exposure route. For more hydrophobic PCBs however, other uptake routes may be more important.

(2) Assimilation from invertebrate food. PCB concentrations in invertebrates also equilibrate rapidly with fast desorbing fractions [*17,27*]. In our case, a rough calculation with invertebrate and fish data (Table 2.1) indicates that invertebrate PCB concentrations were insufficient to explain all PCBs accumulated by the fish. From the weight and % dry weight data in Table 2.1, it can be calculated that in two months the fish grew on average 4 g dry weight and accumulated 9.6 µg ΣPCBs. Assuming all fish weight gain is derived from ingestion of benthic invertebrates, and using a conservative invertebrate assimilation efficiency of only 50% where usually 80% is reported [*29*], then 8 g of invertebrates would have been consumed. This invertebrate biomass contained 188 µg/kg ΣPCBs (Table 2.1). With a maximum chemical assimilation efficiency of 100%, this still accounts for only 8×10^{-3} kg x 188 µg/kg = 1.5 µg of the accumulated 9.6 µg ΣPCBs.

(3) Assimilation from ingested sediment. Fish in general are assumed to acquire PCBs and other persistent pollutants through absorption from water and assimilation from invertebrate food [*9,10*]. Benthivorous fish, however, may also be exposed directly to sediment-bound contaminants through sediment ingestion. Recently, contaminant uptake through sediment ingestion by benthic invertebrates has been shown to be considerable [*11-14*]. Furthermore, Russell et al. [*30*] found that benthic feeding fish appear consistently more contaminated than pelagic feeding fish, despite the fact that pelagic fish are piscivorous and higher in the food chain. They suggest that this is caused by uptake of PCBs through sediment ingestion. The observed improved correlation of PCB concentrations in benthivorous fish with 6-h Tenax-extractable concentrations can also be explained by direct uptake through sediment ingestion being an important uptake route, especially for the more hydrophobic PCBs. Direct uptake through sediment ingestion is governed by the fraction of PCBs that can be desorbed from the sediments during gut passage. Weston and Mayer [*11*] showed that invertebrates do not absorb all PAHs present in sediment, but only the fraction that can be solubilized by digestive fluids. They consider this fraction a measure for bioavailability. We suggest that slow fractions probably are resistant to gut fluids at relevant time scales, so that the fraction that can be solubilized by digestive fluids may very well be comparable to the fast desorbing fraction. In summary, we conclude that, because 6-h Tenax-extractable concentrations correlate better with PCB concentrations in benthivorous fish than total-extractable

concentrations, part of the PCBs present in the sediment are unavailable for uptake. This unavailable part is assumed to be the (very) slow-desorbing fraction [*15-18*].

Nutrient effects

The effect of nutrient additions on PCB accumulation in benthivorous fish is shown in Figure 2.3, where levels of individual PCB congeners in carp are plotted against 6-h Tenax-extractable concentrations for all enclosures except 0b. Enclosure 0b is omitted due to statistically significant deviating sediment and fish characteristics, as mentioned earlier. The hypothesis that the five groups of data were sampled from populations of equal slopes was tested following an analysis of variance procedure described by Sokal and Rohlf [*26*]. The difference among slopes appeared to be significant at $P = 9.709 \times 10^{-11}$. Differences between slopes of the replicas were not significant ($P > 0.5$). However, low-dose treatments 1a and 1b differed significantly ($P < 0.005$) from high-dose treatments 2a and 2b. Treatment 0a differed significantly ($P < 0.001$) from 2a and 2b, but not from 1a and 1b.

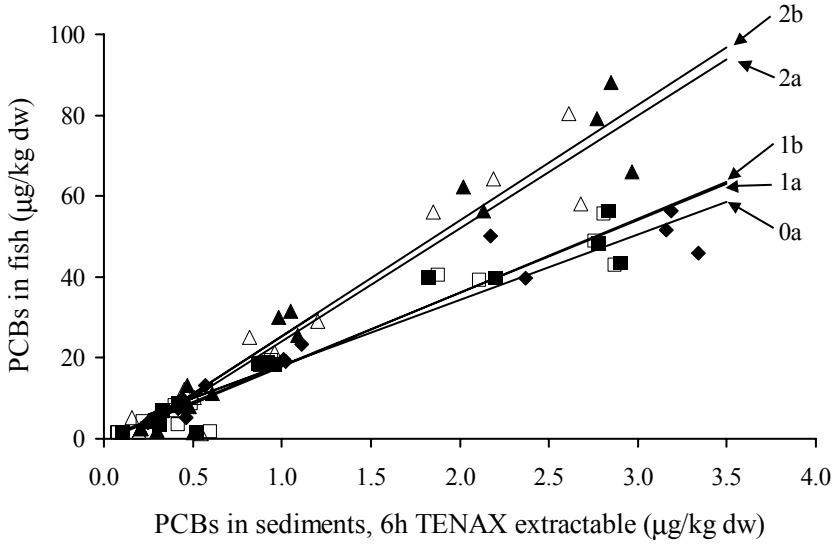

Figure 2.3. *Levels of individual PCB congeners in carp against 6-h Tenax-extractable sediment concentrations.* ● *= 0a and (no nutrient additions);* ◆ *= 1a and* ◇ *= 1b (medium nutrient additions;* ▲ *= 2a and* △ *= 2b (high nutrient additions). Treatment 0b (no nutrient additions) is left out of the graph due to deviating sediment and fish characteristics (see Table 2.1).*

In summary, we conclude that enclosures differ in their accumulation response to Tenax-extractable PCBs, depending on enclosure treatment. These limited but significant observations indicate that when more nutrients are added, fish seem to take up more PCBs, despite lower lipid contents. For pelagic fish, it is often assumed that in eutrophicated waters fish accumulate less PCBs, either due to growth dilution or a higher sedimentation rate of particles to which the pollutants are adsorbed [*1,3*]. For benthivorous fish, however, it can be hypothesized that eutrophication can cause increased PCB uptake, which is in line with results of Gunnarsson et al. [*2*] for benthic invertebrates. After all, nutrient loadings may increase sedimentation of algae [*1*], and thus the amount and quality of organic matter in sediments. For benthivorous organisms this may result in increased feeding on sediment material and thus exposure through sediment ingestion [*2*].

Accumulation model for benthivorous fish

To evaluate the relative importance of uptake routes, a simple model using first-order processes to describe PCB uptake in benthivorous fish was constructed based on equations provided by Thomann et al. [*9*] and Hendriks et al. [*10*]. Uptake processes are (1) absorption from water and (2) assimilation from invertebrate food.The model was expanded with (3) PCB uptake through sediment ingestion, to evaluate different exposure routes. Loss processes are excretion into water, egestion through food, and internal processes such as growth dilution. Metabolic transformation was assumed negligible for PCBs [*31*].

PCB uptake by benthivorous fish can then be estimated using

$$\frac{dC_{fish}}{dt} = k_{abs,in}C_w + k_{ass1,in}C_{food} + k_{ass2,in}C_{sedfast} - (k_{excr,out} + k_{eges,out} + k_{grdil,out})C_{fish} \qquad (1)$$

with C_w the dissolved PCB concentration in water (µg/L), C_{fish} the PCB concentration in fish (µg/kg), C_{food} the PCB concentration in invertebrate food (µg/kg), and $C_{sedfast}$ the fast-desorbing PCB concentration in sediment (µg/kg).

Rate constants $k_{abs,in}$ (absorption rate constant from water; (µg x kg^{-1} wet wt)/(µg x L^{-1} x d)), $k_{ass1,in}$ (assimilation rate from invertebrate food; (µg x kg^{-1} wet wt)/(µg x kg^{-1} wet wt x d)), $k_{ass2,in}$ (assimilation rate from sediment; (µg x kg^{-1} wet wt)/(µg x kg^{-1} wet wt x d)), $k_{excr,out}$ (excretion rate into water; d^{-1}), $k_{eges,out}$ (egestion rate with food; d^{-1}), and $k_{grdil,out}$ (growth dilution rate constant; d^{-1}) are dependent on K_{OW} and species weight and are estimated independently using allometric relationships ([*10*]; see appendix).

$k_{ass2,in}$ is the assimilation rate from sediment ((μg x kg^{-1} wet wt)/(μg x kg^{-1} wet wt x d^{-1})) and depends on the food ingestion rate constant k_{ing} (kg x kg^{-1} x d^{-1})

$$k_{ass2,in} = k_{ing} DW_{sed} \quad (2)$$

with DW_{sed} the dry to wet weight ratio (0.34 ± 0.04) of the sediment. For our modeling purposes, we assume that benthivorous fish take up the complete fast-desorbing fraction during gut passage of sediment, but not the slow-desorbing fraction. For PCBs, Cornelissen et al. [*23*] found a ratio for the fast desorbing fraction to the 6-h Tenax-extractable fraction of 0.95. Furthermore, benthivorous fish appear to ingest as much sediment as invertebrate food (results not shown) [*7,8*]. Thus,whenusing the food ingestion rate constant to calculate sediment ingestion, it should only be corrected for the dry to wet weight ratio of the sediment. The food ingestion rate constant king for cold-blooded animals can be estimated as [*10*]

$$k_{ing} = \gamma_1 w^{-\kappa} \quad (3)$$

with γ_1 being the food ingestion coefficient (kg^{κ} /d; 0.01), κ being the rate exponent (0.25), and w being the species weight (kg wet weight). The dissolved concentration in water (C_w) was not measured. Many examples of regressions exist for the relationship between the concentration in water and sediment (e.g., refs [*32,33*]). However, these do not distinguish between fast- and slow-desorbing fractions. It can be assumed that only fast-desorbing fractions play a role in the partitioning process, hence an estimation is needed using the concentration in the labile fraction and a K_{OC} for that fraction, assuming equilibrium in the closed systems. Recently, Kraaij et al. [*28*] measured the relationship between the organic carbon-water partition coefficient for the fast desorbing fraction ($K_{OC,fast}$; L/kg) and K_{OW}. Based on their data for PCBs and lower-weight PAHs, the following regression (R^2 = 0.88; P = 2.25 x 10^{-6}) was calculated:

$$\log K_{OC,fast} = 0.59 \log K_{OW} + 1.67 \quad (4)$$

To obtain the dissolved concentration in water, we used

$$K_P = K_{OC} f_{OC} \quad (5)$$

and

$$C_w = \frac{C_{sedfast}}{K_p} \quad (6)$$

with K_P the sediment-water partition coefficient (L/kg) and f_{OC} the fraction organic carbon in the sediment (g/g).

Other measured input values to the model were fish weight, fish invertebrate lipid contents, PCB concentrations in fish and invertebrates, and 6-h Tenax-extractable PCB concentrations and the fraction organic carbon in sediment (Table 2.3). As fish lipid contents varied (Table 2.1), the model was run with the lipid content of the blank fish at t = 0, linearly decreasing to the average lipid content of the other fish at t = 60. Log K_{OW} values were taken from Hawker and Connell [*34*]. Total simulation time was 60 days with a time step of 0.01 day. Fish data at t = 0 are measured blank values. Modeled results were compared to measured fish data at t = 60 days, which were obtained by averaging data from all experimental fish.

Table 2.3. *Model input values and calculated time at which 50% of the calculated steady state concentration in fish is reached (SS_{50}). All fish and prey concentrations are calculated into wet weight concentrations. Fish values are averages from all six enclosures.*

PCB	log K_{ow}	$C_{sed,6h}$ (µg/kg)	$C_{fish,\ t=0}$ (µg/kg)	$C_{fish\ ,\ t=60}$ (µg/kg)	C_{prey} (µg/kg)	SS_{50} (days)
18	5.24	0.43	0.15	0.57	0.43[2)]	10
20	5.57	0.40	0.05	0.39	0.27[2)]	18
28	5.67	0.49	0.36	2.06	0.51[2)]	13
31	5.67	0.37	0.22	1.54	0.36[2)]	15
44	5.75	0.93	0.17	4.15	0.93[2)]	27
52	5.84	1.72	0.49	9.05	2.32[2)]	33
101	6.38	2.57	0.80	11.0	4.00	132
105	6.65	0.35	0.18	0.93	1.17[2)]	246
118	6.74	0.89	0.75	4.28	1.05	274
138	6.83	1.99	1.28	9.14	8.50	358
149	6.67	2.80	0.60	9.81	6.75	261
153	6.92	2.86	2.10	13.0	11.2	419
170	7.27	0.42	0.18	1.9	2.75	770
180	7.36	0.99	0.56	4.55	6.25	858
194	7.80	0.30	0.04	0.38	0.47[2)]	1281

[1)] From Hawker and Connell [*34*].

[2)] Original values below detection limits due to insufficient sample material. Value shown is seasonal average from samples taken at the same location (unpublished results).

Simulation results were used without optimization of parameters and show that model results do not systematically over- or underestimate the individual observed concentrations (Figure 2.4). To calculate the time at which 50% of the steady state concentration is reached, simulation times were increased (Table 2.3). After 60 days of simulation time (the duration of the experiment), steady state was only reached by PCB18. This lack of steady state for all other congeners is confirmed by the fact that measured PCB concentrations in native benthivorous fish caught in the field were

about four times (two times when based on lipid contents) higher than those in the carp at the end of the experiment. Increasing simulation time showed that more hydrophobic PCBs (log Kow > 6) are much further away from steady state than less hydrophobic PCBs (log Kow < 6). This can be explained by the fact that for less hydrophobic PCBs assimilation from water is more important, which is governed by equilibrium rather than kinetic processes. For the more hydrophobic PCBs however, other uptake routes that are governed more by kinetic processes, are more important. This limits the applicability of steady-state models for more hydrophobic PCBs.

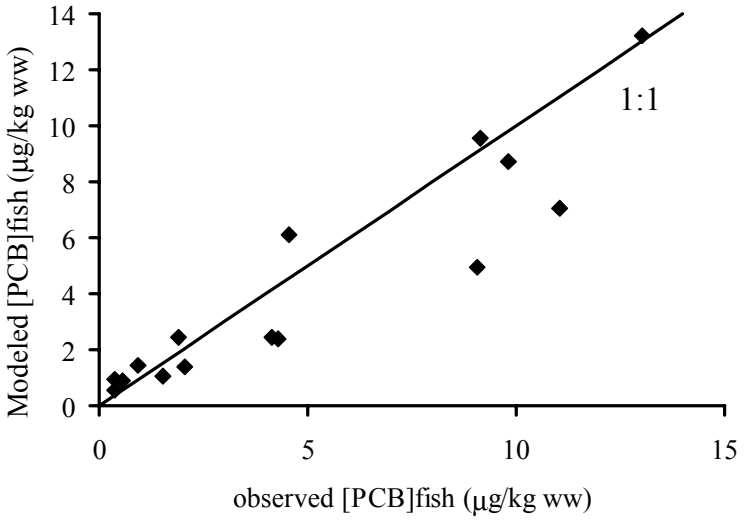

Figure 2.4. *Observed versus calculated model results for PCB concentrations in fish.*

The dependence of model results on log Kow is further detailed in Figure 2.5, where the modeled contribution of water, invertebrate food, and sediment ingestion to total PCB uptake after 60 days are given as a function of log Kow. At high log Kow values, PCB accumulation from invertebrate food is more important, whereas absorption from water is more important at lower log Kow values. This also confirms the rough calculation (see above) that food intake alone cannot explain total bioaccumulation. The contribution of sediment uptake ranges from 5% to 20% and shows no clear trend with log Kow. This can be explained by the fact that also the Tenax-extractable fractions show no clear trend with log Kow (Figure 2.1). Therefore, PCB uptake, especially for the more hydrophobic PCBs, may depend largely on invertebrate food availability and sediment organic matter quality, which in turn depends on ecosystem

structure or nutrient status. The model results are independent of fish density, which means that the percentages in Figure 2.5 are also valid outside the enclosures where densities were approximately two times lower.

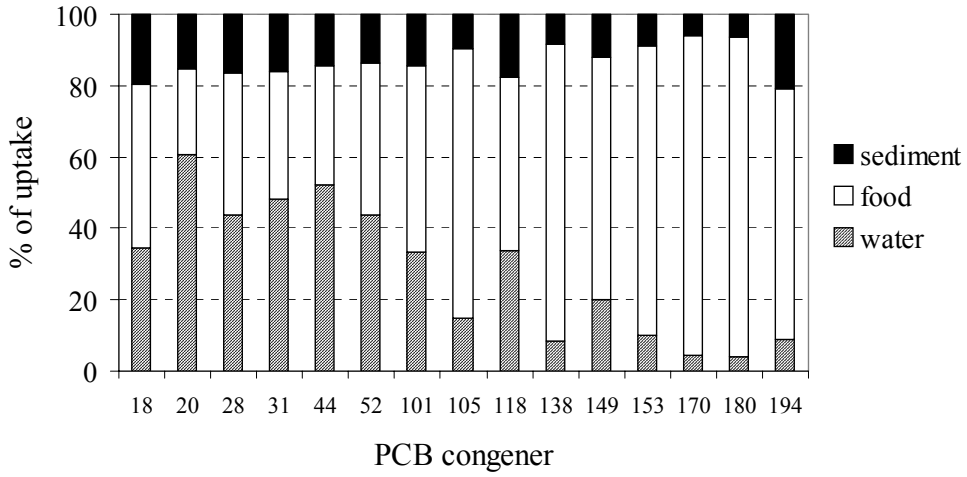

Figure 2.5. *Modeled contribution of water, invertebrate food and sediment to total PCB uptake, depending on log* K_{OW}.

The main implications of this research are that (1) fast desorbing PCB fractions in sediments have great predictive potential for bioaccumulation in benthivorous fish, and (2) accounting for fast-desorbing PCB fractions and sediment ingestion is an important conceptual improvement in food chain accumulation modeling for benthivorous fish. Effects of nutrients on accumulation of hydrophobic organic chemicals in fish need further exploration.

Acknowledgements

We thank John Beijer, Fred Bransen, Gerdine Gaikhorst, Frits Gillissen, and Ronald Gylstra for analytical assistance and Michiel Jonker and Jan Hendriks for helpful suggestions.

Appendix

Allometric rate constants [*10*] are dependent on species weight w, which can be calculated from species weight at t = 0 using

$$w(t) = w(t - dt) + (\gamma_2 \times w(t - dt)^{-\kappa})dt$$

Uptake from water:

$$k_{abs,\,in} = \frac{w^{-\kappa}}{\rho_{H_2O,0} + \frac{\rho_{CH2}}{K_{OW}} + \frac{1}{\gamma_0}}$$

Assimilation from invertebrate food:

$$k_{ass1,in} = \frac{p_1}{1-p_1} \times \frac{1}{p_{CH2,1} \times (K_{OW} - 1) + 1} \times \frac{w^{-\kappa}}{\rho_{H2O,1} + \frac{\rho_{CH2}}{K_{OW}} + \frac{1}{p_{CH2,1} \times K_{OW} \times (1-p_1) \times \gamma_1}}$$

Excretion rate:

$$k_{excr,out} = \frac{1}{p_{CH2,2} \times (K_{OW} - 1) + 1} \times \frac{w^{-\kappa}}{\rho_{H2O,0} + \frac{\rho_{CH2}}{K_{OW}} + \frac{1}{\gamma_0}}$$

Egestion rate:

$$k_{eges,out} = \frac{1}{p_{CH2,2} \times (K_{OW} - 1) + 1} \times \frac{w^{-\kappa}}{\rho_{H2O,1} + \frac{\rho_{CH2}}{K_{OW}} + \frac{1}{p_{CH2,1} \times K_{OW} \times (1-p_1) \times \gamma_1}}$$

Growth dilution rate:

$$k_{grdil,out} = \gamma_2 \times w^{-\kappa}$$

Used factors, with standard values for fish feeding on benthic invertebrates

$k_{abs,in}$	absorption rate constant from water (µg x kg^{-1} wet wt)/(µg x L^{-1} x d)
$k_{ass1,in}$	assimilation rate from invertebrate food (µg x kg^{-1} wet wt)/(µg x kg^{-1} wet wt x d)
$k_{excr,out}$	excretion rate into water (d^{-1})
$k_{eges,out}$	egestion rate with food (d^{-1})
$k_{grdil,out}$	growth dilution rate constant (d^{-1})
γ_0	water absorption-excretion coefficient (kg^{κ} x d^{-1}; 200)
γ_1	invertebrate food ingestion coefficient (kg^{κ} x d^{-1}; 0.01)
γ_2	biomass production coefficient (kg^{κ} x d^{-1}; 0.0006)
K_{OW}	octanol-water partition ratio (unitless)
κ	rate exponent (unitless; 0.25)
p_1	fraction of ingested invertebrate food assimilated (unitless; 0.8)
$p_{CH2,i}$	lipid fraction of invertebrate food (1) or fish (2)
$\rho_{H2O,j}$	water layer diffusion resistance (d x $kg^{-\kappa}$; 2.8×10^{-3} if j = 0; 1.1×10^{-5} if j = 1)
ρ_{CH2}	lipid layer permeation resistance (d x $kg^{-\kappa}$; 68)
t	time (days)
w	species weight (kg)

References

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Chapter 3

Black carbon and ecological factors affect in situ biota to sediment accumulation factors for hydrophobic organic compounds in flood plain lakes

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Abstract

Ecological factors may play an important role in the bioaccumulation of polychlorobiphenyls (PCBs) and polyaromatic hydrocarbons (PAHs). Geochemical and bioaccumulation behavior of these chemicals also appears to be related to the presence of black carbon (BC) in sediment. In situ PCB and PAH biota to sediment accumulation factors (BSAF) for benthic invertebrates, as well as 6-h Tenax-extractable (fast-desorbing) concentrations and lake characteristics (including BC in sediment), were determined for different seasons in chemically similar but ecologically different lakes (fish-dominated turbid, algae-dominated turbid, and macrophyte-dominated). BSAFs could be explained with a model including a term for Freundlich sorption to BC and a term for uptake from fast-desorbing concentrations in ingested sediments. Freundlich coefficients for in situ sorption to BC (K_F) were calculated from slow desorbing fractions and BC contents and agreed well with literature values for K_F. Furthermore, in contrast to BSAFs based on total extracted concentrations, Tenax-based BSAF showed a strong positive correlation with log K_{OW}. We therefore argue that BC caused slow desorption and limited BSAFs in these lakes. Seasonal and lake effects on BSAFs were detected, while the differences between oligochaetes and other invertebrates were small for PCBs and within a factor of 10 for PAHs. BSAFs for pyrogenic PAHs were much lower than for PCBs, which was explained by stronger sorption to BC and lesser uptake from ingested sediment.

Introduction

Biota to sediment accumulation factors (BSAFs) are often used as a tool to predict accumulation of hydrophobic organic chemicals (HOCs) in biota in the field. Usually, BSAFs are calculated on an organic carbon and lipid normalized basis [*1*]:

$$BSAF = \frac{C_{biota}/f_{lip}}{C_{sed}/f_{oc}} \quad (1)$$

with C_{biota} the concentration in biota (micrograms per kilogram), C_{sed} the concentration in sediment (micrograms per kilogram), f_{lip} the lipid fraction in biota, and f_{oc} the total organic carbon fraction in sediment. If only aqueous equilibrium partitioning processes play a role, $C_{biota}/f_{lip} = C_w K_{lip}$ and $C_{sed}/f_{oc} = C_w K_{OC}$, with C_w the concentration in water (micrograms per liter), K_{lip} the lipid-water partition coefficient (liters per kilogram), and K_{OC} the organic carbon to water partition coefficient (liters per kilogram). By use of these relationships, eq 1 reduces to the ratio of the lipid and

organic carbon to water partition coefficient (K_{lip}/K_{OC}). When HOCs have similar affinities for lipids and organic carbon ($K_{lip} \approx K_{OC}$), BSAFs are assumed to approach a value of 1. However, in field situations BSAFs as low as 0.05 [*1*] and 0.07 [*2*] have been reported, so apparently other factors also affect BSAFs. As eq 1 contains an organism term as well as a sediment term, ecological characteristics as well as sediment characteristics may explain these deviations.

Ecological characteristics may influence BSAFs through processes such as biomagnification, sediment ingestion, elimination, and metabolic transformation [*3-6*]. These processes may be influenced by the trophic structure of a lake, which affects (feeding) behavior and growth of biota [*7,8*]. Shallow flood plain lakes in lowland river catchments are highly dynamic and can be categorized in two main trophic structures: dominated by macrophytes, or turbid through resuspension of sediments by bottom-feeding fish and algal or cyanobacterial blooms [*9,10*]. Sediments in these lakes may contain many persistent contaminants that were deposited during past river floods. As the present suspended solids quality of river water has improved, these aged sediment-bound contaminants may be remobilized into the water column. To date, it is unclear whether lake ecosystem structure affects remobilization of sediment-bound contaminants and in situ BSAFs.

Sediment characteristics may influence availability of HOCs and thus BSAFs through physicochemical mechanisms. Recently, it was demonstrated that bioavailability of sediment-bound contaminants to benthic organisms depends on the fast-desorbing fraction of HOCs in the sediment [*6,11,12*]. Until now, this idea has been evaluated mainly in laboratory settings [*11,12*]. Also recently, much focus has been on the role of so-called high affinity carbonaceous geosorbents, such as black carbon, coal, and kerogen, in sediments [*1,13-15*]. In this paper, we will refer to this condensed organic matter as black carbon (BC). BC may influence bioavailability as it binds polychlorobiphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) to a much greater extent than amorphous organic matter, which is mainly biological in origin [*1,13,14*]. If the presence of BC in the field can be coupled to in situ bioaccumulation or BSAF patterns, BC would be an important parameter to consider when bioavailability of sediment-bound contaminants is quantified.

In this study, a field survey was designed to measure in situ BSAFs of PCBs and PAHs for benthic invertebrates. Objectives were to (1) evaluate the effect of lake ecosystem structure (both temporal and spatial) on bioavailability of sediment-bound HOCs to benthic invertebrates and (2) evaluate the effects of fast-desorbing HOC fractions and BC on BSAFs. To this end, flood plain lakes were selected that differed in trophic structure. General water and sediment quality parameters, biomasses and species

composition of invertebrates, and PCB andPAH concentrations in sediment and invertebrates were monitored over time. As benthic invertebrate communities can be very diverse, oligochaetes were selected for separate analysis, since they were present in sufficient amounts in all samples. The in situ BSAFs of oligochaetes versus the composite of remaining invertebrates (referred to as mixed invertebrates in the rest of this paper) were interpreted in terms of fast-desorbing fractions (by use of a Tenax extraction technique [*16*]) and fractions of BC (measured after controlled chemothermal oxidation at 375 °C [*13*]) through a simple modeling framework.

Experimental section

Study area

The studied lakes were situated on the south side of the lower River Rhine in The Netherlands. The lakes are located within the same flooding area and adjoin each other with only a few meters of land between them, so variation between the lakes with respect to external influences can be assumed to be minimal. The three lakes consisted of a plankton-dominated, turbid lake with regular cyanobacterial blooms during thesummer(DeO3A), a fish-dominated, turbid lake, where the bottom-feeding cyprinid bream (*Abramis brama*) is the dominant species (DeO3B; [*17*]), and a small lake that shifted from macrophyte-dominated to algae-dominated during our survey (DeO4). A more detailed description of these lakes can be found in refs [*10*] and [*18*].

Sampling

Samples were taken at six times, at three locations per lake, from September 2000 through March 2002. During this period, flooding events occurred in January, February, March, April, and December 2001 and January, February, and March 2002. In March 2001 and May 2001, samples could be taken only in the algae-dominated lake. As it was only possible to sample one lake per day and flooding could take place very rapidly, some flooding events interfered with our sampling. At every sampling location, general surface water characteristics such as pH, temperature, oxygen, conductivity, turbidity, and secchi depth were measured. Samples were transported immediately to the laboratory and most samples were processed for storage on the day of sampling. Only macroinvertebrates were processed within 2 days of sampling. Storage materials were prerinsed with acetone (Promochem, Wesel, Germany).

Sediment samples were taken with a Jenkins core sampler (Ø 5 cm). At each location three sediment (sub)samples were taken. In the laboratory, the upper 5 cm of each sediment core was carefully removed, after which the subsamples per location were combined, homogenized, freeze-dried, and stored at -20 °C in a brown glass jar until further analysis for organic carbon and black carbon content, grain size fractions, and PAH/PCB concentrations.

Per location, 10 benthic invertebrate samples (15 × 15 cm sediment, at least 5 cm deep) were taken with an Ekman sampler. Samples were sieved over a 500 µm sieve and transferred to 500 mL plastic containers. In September 2000 only four samples per location were taken. In the laboratory, invertebrate samples were again sieved over a 500 µm sieve, after which the living invertebrates were sorted out of the debris and species composition was identified according to available keys. The 10 samples from each sampling location were combined, after which the animals were kept overnight in aerated glass containers with filtered field water in a 6 °C dark climate room for gut clearance. Spilled gut contents were removed and invertebrates were rinsed with Barnstead Nanopure water (Sybron-Barnstead, Dubuque, IA), transferred to glass containers, freeze-dried, and stored at -20 °C until analysis of lipid content and PAH/PCB concentrations.

Analytical procedures

General characteristics. Dry to wet weight ratios of sediments and benthic invertebrates were measured by weighing each sample before and after freezedrying. Suspended solids dry weight was measured in triplicate by weighing samples before and after drying at 105 °C. To determine black carbon contents, sediment was combusted at 375 °C for 24 h [*13*]. After removal of carbonates with HCl, BC and total organic carbon in 375 °C and noncombusted samples respectively, were detected with a CHN-O elemental analyzer (Fisons Instruments EA 1108, CE Instruments, Milan, Italy). Sediment grain size was measured after decalcification with 1 M HCl and removal of organic matter with 30% H_2O_2, by laser diffraction on a Coulter 230 (Beckman-Coulter, Coulter Corp. Scientific Instruments, Miami, FL) at 10% obscuration of the laser beam. Macroinvertebrate lipids were extracted with chloroform/methanol according to Folch et al. [*19*] and quantified photometrically by use of phosphovanillin reagent [*20*] on a Beckman DU-64 spectrophotometer (Beckman Instruments, Fullerton, CA). Chemicals for PCB and PAH Analysis. PAHs [anthracene (Ant), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[e]pyrene (BeP), benzo-[k]fluoranthene (BkF), benzo[ghi]perylene (BghiPe), chrysene (Chr), dibenzo[ah]anthracene (DahA),

indeno[123]pyrene (Ind123Pyr), phenanthrene (Phen), fluoranthene (Fla), pyrene (Pyr), and 2-methylchrysene] were obtained from Sigma Aldrich (Zwijndrecht, The Netherlands). PCBs (IUPAC numbers 18, 20, 28, 31, 44, 52, 101, 105, 118, 138, 143, 149, 153, 170, 180, and 194), were purchased from Promochem (Wesel, Germany). Other chemicals used were acetone and hexane (picograde; Promochem, Wesel, Germany), acetonitrile (HPLC grade; Lab-Scan, Dublin, Ireland), isooctane (for pesticide analysis; Acros, Geel, Belgium), ethanol (99.8%; Merck, Darmstadt, Germany), sodium azide (99%; Sigma-Aldrich, Steinheim, Germany), aluminum oxide Super I (ICN Biomedicals, Eschwege, Germany), silica gel 60 (63-200 mesh; Merck),Cupowder (99.7%, Merck), and Tenax-TA beads (60-80 mesh; Chrompack, Middelburg, The Netherlands). Prior to use, silica gel was activated overnight at 180 °C, aluminum oxide was deactivated with 10% (w/w) Nanopure water, Cu powder was Soxhlet-extracted with hexane for 4 h, and Tenax beads were Soxhlet-extracted with acetone and hexane (2 h each) and dried overnight at 75 °C.

Total PCB and PAH extraction and cleanup. All glassware was prerinsed with nanograde acetone. To prevent photolytic breakdown of PAHs, brown glassware was used for PAH extraction, cleanup, and analysis. The procedure was performed according to ref [*21*]. In short, sediment as well as biota samples were extracted during 16 h on a Soxhlet apparatus with a hexane/acetone mixture (3:1 v/v). The solution was concentrated on a modified Kuderna-Danish apparatus followed by evaporation to 1 mL under a gentle flow of nitrogen. Subsequently the sample was eluted with 30 mL of hexane over a column with 4 g of aluminum oxide. After reduction to(4 mL, the sample was split gravimetrically into a part for PCB and a part for PAH analysis. PAH samples were exchanged to acetonitrile, after which 2-methylchrysene was added as an internal standard. PCBs amples were reduced to 1 mL, eluted with 30 mL of hexane over a column with 2 g of silica gel, reduced again, and desulfurized with Cu powder. Hexane was then exchanged to isooctane and PCB143 was added as an internal standard.

Tenax extractions. Fast-desorbing PCB and PAH fractions were determined according to earlier reports [*16,22*]. In short: a mixture of Tenax (0.6 g), sediment (1.0 g dry weight), NaN_3 (biocide), and Nanopure water was shaken in a separation funnel for 6 h. After separation from the sediment, Tenax beads were transferred to a glass column and eluted with ethanol and hexane. After the ethanol was replaced with hexane, cleanup and analytical procedures were similar to those of total PCB and PAH analysis. Microscopic inspection of Tenax beads shaken with sediments showed that no soot or sediment particles were adsorbed to the Tenax beads

GC/LC analysis. PCBs were analyzed on a Hewlett-Packard 5890 II gas chromatograph (Hewlett-Packard, Little Falls, Wilmington, DE) equipped with a HP7673A auto sampler, two 63Ni electron capture detectors, and two 50-m capillary fused silica columns (CP Sil-8CBandCPSil-5/C18 CB, Varian, Bergen op Zoom, The Netherlands). PAHs were analyzed on a Hewlett-Packard 1100 HPLC equipped with 250 × 4.6mm Vydac guard analytical reverse-phase C18 columns (201GD54T and 201TP54), with methanol/water as mobile phase. After each run, the columns were rinsed with acetonitrile. PAHs were detected on an HP 1100 multiwavelength fluorescence detector.

Quality assurance. With every 10 samples, one sample to determine cleanup recoveries was included. This sample consisted of all PCBs in acetone and hexane and was extracted and cleaned up together with the other samples. Cleanup recoveries for 24 Soxhlet-extracted samples averaged 91% ± 3% for PAHs and90% ± 8%for PCBs. For five Tenax-extracted samples, cleanup recoveries averaged 96% ± 4% for PAHs and 102% ± 8% for PCBs. For determination of reproducibility, reference samples were analyzed. Analytes in reference samples were typically within error limits of reported values. Analytical quality was further assured by including multiple blanks. (For Tenax extraction: Tenax-TA was shaken with Nanopure water and NaN_3). All samples were corrected for cleanup recoveries and blanks.

Results

Lake characteristics

The algae-dominated lake had no macrophytes and little or no fish-caused disturbance of the sediments. Turbidity was mainly caused by algae and cyanobacterial blooms. The benthic invertebrate community of this lake (Table 3.1) consisted of many oligochaetes and midge larvae (Diptera), as well as snails and molluscs in smaller amounts. The fish-dominated lake also had no macrophytes but had higher turbidity and suspended solids concentration. In contrast to the algae-dominated lake, this turbidity was mainly caused by sediment resuspension by fish, which follows from the lower chlorophyll a concentrations and the lower organic matter content of the suspended solids (data not shown). The numbers of individuals of the different benthic invertebrate taxa were comparable to those from the algae-dominated lake, except for the smaller number of molluscs. The macrophyte-dominated lake changed from macrophyte to algae domination during 2001. This type of change in trophic structure is an often-occurring process in these lakes [*9,10*].

This macrophyte-dominated lake mostly had more oligochaetes and midge larvae than the other two lakes. Organic carbon was 3-4% in the lakes and significant amounts of BC were detected, contributing 8-10% to the total organic carbon pool (Table 3.2).

Table 3.1. *Composition of benthic invertebrate fauna*[a].

		Olig	Dipt	Arth	Moll	Mega	Hiru	Cole
DeO3A	Sept '00	28722	5895					
	March '01	9358	1114		170			
	May '01	9710	323		188			
	July '01	4329	327	61	303			
	Sept. '01	3921	1144		158			
	Jan/feb '02	5041	474		170			
DeO3B	Sept '00	3574	877					
	March '01	No sampling possible						
	May '01	No sampling possible						
	July '01	5371	443	87	62			
	Sept. '01	4221	274		74			
	Jan/feb '02	4925	462		90			
DeO4	Sept '00	6320	622		614	192	133	89
	March '01	No sampling possible						
	May '01	No sampling possible						
	July '01	6673	810		111			
	Sept. '01	7391	3759		188			
	Jan/feb '02	7418	814					

[a]Results are given as number of individuals per m^2. All data lower than 1% of the total are not reported. Taxa that were always present in numbers lower than 1% of the total were Plathelminthes (flatworms), Ephemeroptera (mayflies), Trichoptera (caddisflies), Hemiptera (true bugs) and Crustacea (crustaceans). Olig = Oligochaetes (worms), Dipt = Diptera (midge/fly larvae), Arth = Arthropoda (mites), Moll = Mollusca (snails/molluscs), Mega = Megaloptera (dobsonflies), Hiru = Hirudinea (leeches), Cole = Coleoptera (beetles).

Table 3.2. *Ecological and chemical characteristics of floodplain lakes. (Averages with range between brackets)*

	Algae-dominated	Fish-dominated	Macrophyte-dominated
General characteristics			
Surface area (ha)	2.0	8.0	0.2
Depth (m)	1.5 (0.5-2.6)	1.0 (0.6-1.4)	1.0 (0.4-2.3)
Turbidity (NTU[a])	33 (7-107)	47 (18-66)	30 (14-47)
Biota characteristics			
Oligochaetes (g DW/m^2)	1.9 (0.7-3.3)	0.7 (0.5-0.9)	2.0 (1.6-2.3)
Oligochaetes (% lipids of DW)	27 (16-39)	32 (26-37)	34 (27-44)
Mixed macro-invertebrates (g DW/m2)	1.7 (0.9-3.0)	1.0 (0.5-1.5)	2.9 (1.3-5.8)
Mixed macro-invertebrates (% lipids of DW)	14 (2.2-26)	24 (18-29)	24 (22-26)
Sediment characteristics			
Organic carbon (% of DW)	3.3 (3.0-3.9)	3.9 (2.7-4.7)	3.8 (3.2-4.1)
Black carbon (% of DW)	0.32 (0.25-0.43)	0.31 (0.29-0.33)	0.36 (0.35-0.37)
% Grain size < 2 µm	20 (15-25)	21 (9-25)	17 (13-19)
Sum PCBs (µg/kg)	96 (84-104)	150(124-180)	128(115-147)
Sum PCBs Tenax (µg/kg)	12 (10-15)	18 (16-23)	16 (12-23)
Sum PAHs (mg/kg)	5.3 (4.5-5.9)	6.0 (5.6-6.7)	7.5 (6.1-10.5)
Sum PAHs Tenax (mg/kg)	0.30 (0.25-0.38)	0.38 (0.33-0.47)	0.40 (0.30-0.47)
PAH ratios for source identification[b]			
Ant/(Ant + Phen)	0.29	0.26	0.28
Fla/(Fla + Pyr)	0.56	0.57	0.86
BaA/(BaA + Chr)	0.50	0.49	0.51
Ind123Pyr/(Ind123Pyr + BghiPe)	1.30	1.30	1.46

[a] NTU = Nephelometric Turbidity Units

[b]Ratios with average PAH values, according to Yunker et al. [*40*] to determine source (petrogenic/pyrogenic) of PAHs. PAHs can be assumed to have a pyrogenic origin when Ant/(Ant + Phe) > 0.1; Fla/(Fla + Pyr) > 0.5; BaA/(BaA + Chr) > 0.35; Ind123Pyr/(Ind123Pyr + BghiPe) > 0.5.

PCB and PAH concentrations

Sum PAH and PCB concentrations in sediments (Table 3.2) show that differences among the lakes were small, though significant for most individual congeners (ANOVA, $p < 0.05$). Both PAH and PCB concentrations were lowest in the algae dominated lake sediments. Sediment PCB concentrations were highest in the fish-dominated lake, while PAH concentrations were slightly higher in the macrophyte-dominated lake. In contrast, differences in sediment concentrations between seasons were not significant for sum PAHs and sum PCBs and for individual PAHs and PCBs, except PCB 52 (different at $p < 0.001$).

Six-hour Tenax-extractable PCB/PAH concentrations as fractions of total (Soxhlet) extractable concentrations for different lakes and seasons are plotted versus log K_{OW} [*22, 23*] in Figure 3.1. These fractions can be converted to estimates of fast-desorbing fractions, which are considered to be a measure for bioavailability of PCBs and PAHs to benthic invertebrates [*11,12*] and fish [*16*]. At lower log K_{OW} values, our results show considerable variation in Tenax-extractable fractions up to log K_{OW} = 5.2 (PCBs) and 6 (PAHs). Once above these K_{OW}s, a decrease in Tenax-extractable PCBs and PAHs is visible with much less variation.

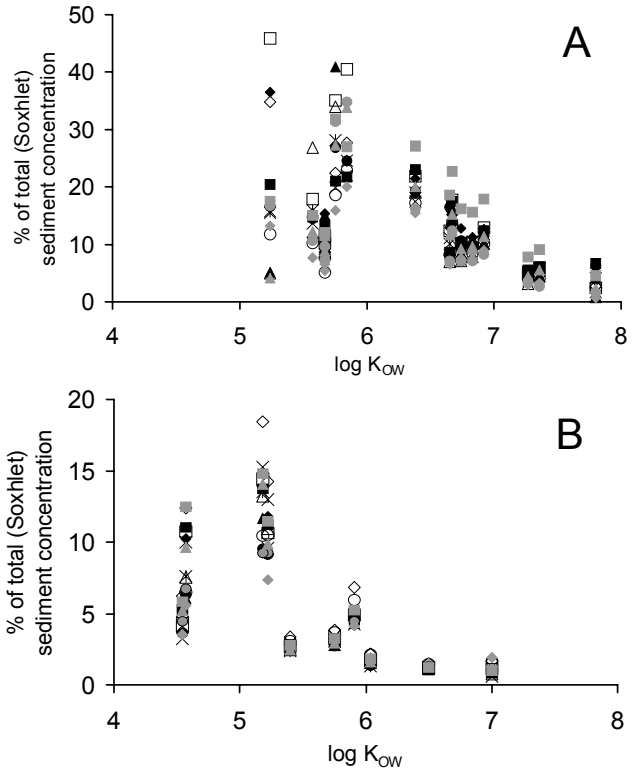

Figure 3.1. *Percent Tenax extractability for PCBs (A) and PAHs (B). Log K_{OW} values taken from [46] for PCBs and [47] for PAHs. Black markers = algae dominated lake; white markers = fish dominated lake; grey markers = macrophyte dominated lake; ◇ = September 2000; ∗ = March 2001 (algae dominated lake only); × = May 2001 (algae dominated lake only); ○ = July 2001; □ = September 2001; △ = January/February 2002.*

Biota to sediment accumulation factors

BSAFs for PCBs in oligochaetes were on average 0.39 (range 0.01-1.6) and are plotted versus log Kow in Figure 3.2A. Because the BSAF variation between lakes was generally smaller than between seasons (also for PAHs, see later sections), we decided to present the lake averages per season. This was legitimized by ANOVA on BSAF values from the three lakes for three seasons (July 2001, September 2001, and winter 2002; see Table 3.3). In September 2000, toomanyvalues were below detection limits due to insufficient sample amounts, and in March and May 2001 only the algae-dominated lake was sampled.

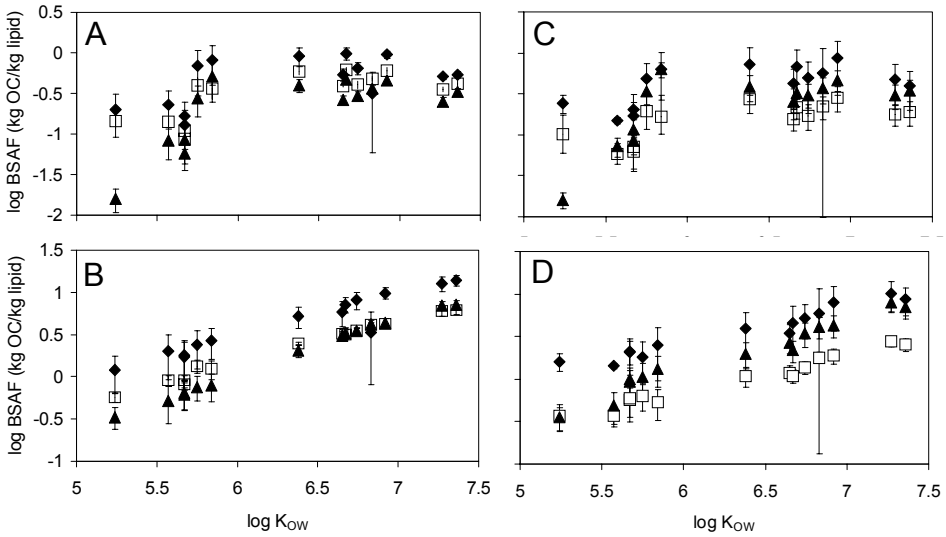

Figure 3.2. *PCB log BSAFs for oligochaetes based on Soxhlet- (A) and Tenax- extracted concentrations (B) and for mixed invertebrates based on Soxhlet- (C) and Tenax-extracted concentrations (D). Values are averaged over lakes, and standard errors are shown.* ◆ *= July 2001;* □ *= September 2001;* ▲ *= January/March 2002.*

Table 3.3. *ANOVA results on differences in BSAFs for seasons and lakes.*

	Species	Seasons		Lakes	
		Significance p	Low → high values[1]	Significance p	Low → high values[2]
PCBs	Oligochaetes	0.002	Winter < Sept < July	0.03	Fish < Algae < Mf
	Mixed invertebrates	0.001	Sept < Winter < July	6.3*10-4	Fish < Mf < Algae
PAHs	Oligochaetes	0.002	Sept ≈ Winter < July	0.46	Fish ≈ Mf < Algae
	Mixed invertebrates	1.4 *10-11	Sept ≈Winter < July	7.9*10-4	Fish ≈ Mf < Algae

[1] Winter = Samples taken in January (algae dominated lake); February (fish dominated lake) or March (Macrophyte dominated lake)

[2] Fish = fish dominated lake; Algae = algae dominated lake; Mf = Macrophyte dominated lake

Statistics show that, for PCB BSAFs, differences between lakes were very small but significant (fish- < algae- < macrophytedominated) and that differences between seasons were also not very large, although significant. Figure 3.2A shows that BSAFs were highest in July, followed by September, and then January/March. Furthermore, it appears that log BSAF values increase up to log K_{OW} = 6, with much variation between congeners. In Figure 3.2B we present Tenax-based BSAFs, which are still based on eq 1, but where C_{sed} is estimated by bioavailable (6-h Tenax-extractable) concentrations instead of the total (Soxhlet-extractable) concentrations [*12*]. In contrast to BSAFs basedonSoxhlet-extracted concentrations, these Tenax-based BSAFs do show a clear positive correlation with log K_{OW} (R^2 > 0.90 for all three seasons). PCB BSAFs for mixed invertebrates (all sampled invertebrates without oligochaetes) were very similar to those for oligochaetes with an average of 0.32 (range 0.01 - 1.9), and show the same trends (Figure 3.2C,D). For mixed invertebrates, ANOVA calculations (Table 3.3) also showed a small but significant season effect and a similarly significant lake effect (fish- < macrophyte- < algae-dominated). The clearest difference with oligochaete BSAFs is that, for mixed invertebrates, samples taken in September 2001 had lower BSAFs than samples taken during the winter of 2002.

Log BSAFs for PAHs are shown in Figure 3.3, similar to the PCB log BSAFs. We observed 1 order of magnitude lower BSAFs for PAHs than for PCBs (see above). The all-data average PAH BSAFs for oligochaetes were 0.03 (range 0.004- 0.12) and for mixed invertebrates 0.02 (range 0.002 - 0.16). Similar to the PCB BSAFs, there was a small and significant seasonal effect with highest BSAFs in July and lower values in September and January/March.

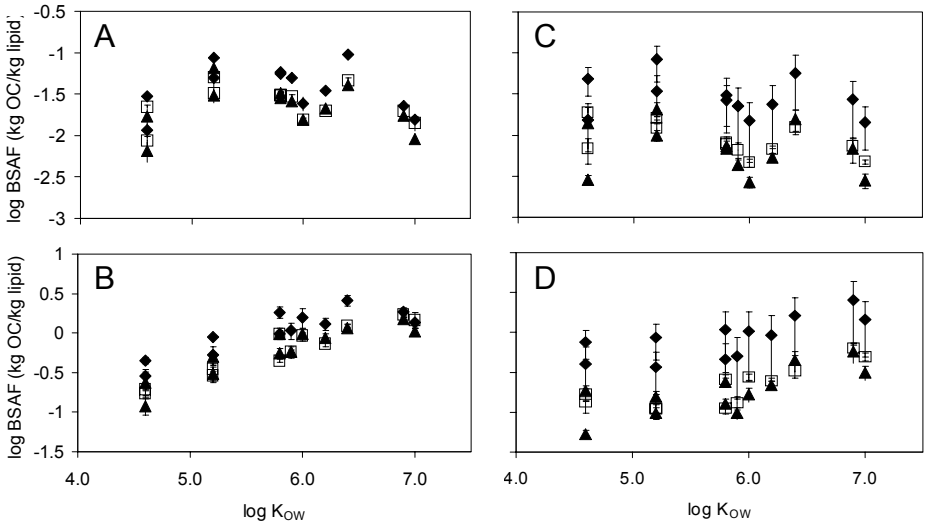

Figure 3.3. *PAH log BSAFs for oligochaetes based on Soxhlet- (A) and Tenax- extracted concentrations (B) and for mixed invertebrates based on Soxhlet- (C) and Tenax-extracted concentrations (D). Values are averaged over lakes, and standard errors are shown.* ◆ *= July 2001;* □ *= September 2001;* ▲ *= January/March 2002.*

Differences between lakes were insignificant (fish- ≈ macrophyte- < algae-dominated). Like for PCBs, BSAFs based on Soxhlet-extracted concentrations show no clear trend with log K_{OW} (Figure 3.3A), but for Tenax-based BSAFs a positive linear trend with log K_{OW} is shown in Figure 3.3B ($0.71 < R^2 < 0.92$). The use of Tenax-based BSAFs also reduces the observed difference between PAH and PCB BSAF values by about a factor of 3. Like for PCBs, the shape of the graphs of PAH BSAFs was similar for mixed invertebrates and oligochaetes. ANOVA (Table 3.3) showed a significant lake effect (fish- ≈ macrophyte- < algaedominated) as well as a significant season effect. PAH BSAFs for mixed invertebrates are also highest in July. However, PAH BSAF values in the macrophyte- and fish-dominated lakes were about a factor of 5 lower for mixed invertebrates than for oligochaetes, while BSAF values in the algaedominated lake were similar to the values for oligochaetes.

Discussion

Tenax-extractable fractions

Our results (Figure 3.1) show scattered Tenax-extractable fractions upto logK_{OW} = 6 (PCBs) and log K_{OW} = 5.2 (PAHs) and after that a decrease, which agrees with earlier results [*12*]. The same scatter was also measured in our reference material and may be due to the fact that less hydrophobic, fast-desorbing substances redistribute faster and thus are more susceptible to analytical error and to seasonal and interlake differences. Tenax-extractable fractions have been found to depend on log K_{OW}, planarity of the congeners, sorbent-sorbate interactions due to van der Waals forces [*23*], and slow sorption to high-affinity sorption sites within organic matter. These slow sorption sites may be provided by the large surface area of BC [*13,24,25*], which is present in our field sediments (Table 3.2). The decrease of the fraction of HOCs that is Tenax-extractable at higher log K_{OW}s indicates that at these higher log K_{OW} values relatively small portions of the total sorbed HOCs desorb within time frames of hours. This is consistent with ref [*22*] and can be explained by the fact that hydrophobic chemicals have lower molecular diffusion rates, a higher affinity for black carbon [*14,15,25-27*] or organic matter, and thus overall a slower effective diffusion into micropores [*28*]. Van Noort et al. [*23*] report slower desorption rates and smaller fast-desorbing fractions for planar HOCs compared to nonplanar HOCs with similar log KOWs, and they conclude that sites for slow-desorbing HOCs are sensitive for sorbate planarity. However, no clear confirmation of planarity effects is found in our data set.

Tenax-extractable fractions for PAHs are generally lower than Tenax-extractable fractions for PCBs. This means that within the 6-h time frame, PAHs desorb less than PCBs and are probably less bioavailable. On the basis of recent literature [*13-15,26,27*], we suppose that the reason for this is strong sorption of PAHs to BC in the sediments, as BC contributes 8-10% of total organic carbon in all three lakes (Table 3.2).

For fish [*16*] and invertebrates [*11,12*], Tenax-extractable PCBconcentrations in sediment have been shown to correlate better with tissue concentrations than total extractable PCB concentrations. In this study, correlations with PCB andPAH Tenax-extractable concentrations were not consistently better or worse than with total (Soxhlet) extractable concentrations (data not shown). An explanation for this dissimilarity is that the research in refs [*11*], [*12*], and [*16*] was primarily conducted under controlled conditions (field enclosures and laboratory experiments), while the present research is performed on a field scale, where sediment concentrations,

foraging patterns, and microhabitats are much less homogeneous. These findings are important and highlight the limitations of Tenax based extractions alone for assessing bioavailability of sediment-bound contaminants in site-specific, real-world contexts.

K_{OW} dependence of BSAFs

Up to log K_{OW} = 6, usually constant or increasing BSAF values are reported; at log K_{OW} values higher than 6 or 7, however, BSAF values tend to decrease (3-5, 29, 30). Our data indeed roughly follow such a trend (Figures 3.2A,C and 3.3A,C), although random variation remains, especially for PAHs. Earlier reports explain the curvilinear relationship through biomagnification, variations in congener lipid solubility, and slow desorption [*3-5*] or from overestimation of bioavailable water concentrations, effect of molecular size (and thus reduced membrane passage of the larger molecules), inaccurate KOW values, and elimination into feces [*30*].

In contrast, Tenax-based BSAFs reduce the random variation with log K_{OW} and show a striking linear increase with log K_{OW} (Figures 3.2B,D and 3.3B,D) for PCBs and PAHs in different seasons and lakes, and for oligochaetes as well as a seasonally varying mixture of invertebrates. Note that a correction factor should be applied to estimate fast-desorbing (bioavailable) fractions from Tenax-extractable fractions [*22*]. The fact that expressing BSAFs by use of Tenax-based concentrations reduces the random variation with log K_{OW}, implies that the variation in our BSAF values basedonSoxhletextracted concentrations can be attributed in large part to chemical processes such as differences in bioavailability and sorption behavior. After all, Tenax-based BSAFs exclude the slow-desorbing HOC fractions that are unavailable for partitioning to biota. Assuming chemical equilibrium partitioning of the remaining labile HOCs between water, lipids, and fast sorption domains, Figures 3.2B,D and 3B,D theoretically should show a horizontal line. Instead, a clear proportionality to log K_{OW} is left, which appears rather constant among lakes and can be explained by biological processes. These processes may include slower elimination, biomagnification, and gastrointestinal magnification [*31,32*].

Differences in BSAFs between seasons, lakes, and species

BSAFs were calculated for oligochaetes as well as for mixed invertebrates. Mixed invertebrates differed in species composition among lakes and seasons, while the oligochaete composition can be considered to be more constant. Generally, seasonal differences were more significant than interlake differences, with July having the

highest BSAF values. This may be explained by the fact that algal blooms during the summer season increase fresh organic matter inputs to the upper layer of the sediment. This fresh OM has 2-5 times lower K_{OC} values than mineralized organic matter [*33*] and also dilutes the BC present in the sediment (lower f_{bc}). During our survey the lowest BC fractions were indeed found in the summer (not shown).

Among lakes, lowest BSAFs were generally detected in the fish-dominated lake, where suspended solids mainly originate from the sediment and not from algal growth. Despite the statistical significance of these ecological effects on BSAFs, the ecological differences between the BSAF values for individual compounds (typically a factor of 3-5) are small compared to differences between compounds (up to a factor of 400). BSAFs for oligochaetes appeared very similar to BSAF values for mixed invertebrates, and the same effect of log K_{OW} and Tenax normalization on BSAFs was shown (Figures 3.2 and 3.3). For PAHs only, in two of the three lakes BSAF values were about a factor of 5 lower for mixed invertebrates than for oligochaetes. This limited variation in BSAFs is especially striking, since these mixed invertebrates consisted of highly variable groups of species (Table 3.1), with obvious temporal and spatial differences in densities, organism size, growth rate, metabolism, and feeding strategies. This implies that, for modeling and risk assessment purposes, benthic invertebrates may be considered as one functional group. Therefore, in the following sections average BSAFs over all lakes and seasons are discussed.

Differences in BSAFs between PCBs and PAHs

The all-data averages of our BSAF values for PCBs were 0.39 for oligochaetes and 0.32 for mixed invertebrates (the composite of invertebrates without oligochaetes). This is slightly lower than other values reported in the literature [*2,12,29,34*]. Generally, such small differences may originate from methodological differences in HOC, lipid, or OC determinations. For PAHs, however, all-data average BSAFs are 0.03 for oligochaetes and 0.02 for mixed invertebrates, which belong, to our knowledge, to the lowest values ever reported and are much lower than the theoretical BSAF value of 1 and usually reported values [*12,35,36*]. In fact, PAHs in these lakes seem hardly bioavailable. Still, our data are in line with field-based PAH BSAFs of 0.07 for oligochaetes [*2*] and 0.05 for bivalves [*1*]. Low PAH BSAFs for invertebrates might be attributed to metabolic transformation and/or depuration of PAHs (35). Although some biotransformation of pyrene and benzo[a]- pyrene in Lumbriculus variegatus has been reported [*37*], most reports argue that oligochaetes do not metabolize PAHs [*2,6,38*]. Theoretically, this should make PAH accumulation

for oligochaetes comparable to PCB accumulation, since PCBs are also assumed not to be metabolized or depurated [*39*]. However, our field-based BSAFs show a large difference between PCB and PAH values at comparable log K_{OW}s. We hypothesize that the lower BSAFs for PAHs are mainly caused by limitations in bioavailability of PAHs, which is very relevant in field situations where strong sorption to BC is found [*1,13-15*]. PAHs from pyrogenic sources have been observed to have especially low field BSAFs [*1*]. To determine whether our PAHs indeed have a pyrogenic rather than a petrogenic origin, ratios between specific PAHs can be calculated and compared to certain transition values for these ratios as reported by Yunker et al. [*40*]. These calculated ratios can be found in Table 3.2 and show a pyrogenic origin for PAHs at all locations. Thus, the observed differences between PCB and pyrogenic PAH BSAFs may be caused by the presence of BC (Table 3.2). As BC concentrations in the three lakes are very similar, this also explains why PAH BSAFs were almost identical between the lakes.

Our hypothesis that the difference in BSAF values between PCBs and PAHs is mainly due to bioavailability is further confirmed by the aforementioned comparison of BSAFs based on Soxhlet-extracted concentrations with Tenax-based BSAFs. As Tenax-based BSAFs reduced the difference between PAH and PCB BSAFs by more than a factor of 3 when compared to Soxhlet-based BSAFs (Figures 3.2 and 3.3), this indicates that bioavailability of PAHs can be very limited in field situations.

BSAF model including BC

To further elucidate the effect of BC on BSAFs, we evaluated a steady-state BSAF model that quantitatively accounts for sorption to black carbon. Following Accardi-Dey and Gschwend [*27*] and Thorson et al. [*1*], we assume that HOC distribution between sediment and water is determined by only two sediment fractions, BC and amorphous organic carbon (the rest). When linear equilibrium partitioning to amorphous carbon is quantified byanorganic carbon-water distribution coefficient K_{OC} (liters per kilogram) and sorption to black carbon is governed by a Freundlich isotherm [*26,27*], the concentration in sediment (C_{sed}) in eq 1 is

$$C_{sed} = \left(f_{oc} - f_{bc}\right) K_{oc} C_w + f_{bc} K_{F,bc} C_w^n \qquad (2)$$

with f_{bc} the black carbon fraction in sediment, K_F the Freundlich coefficient (micrograms per kilogram$_{bc}$)/(micrograms per liter)^n, n the Freundlich exponent, and C_w the concentration in water (micrograms per liter). Following Thomann et al. [*3*], the steady-state lipid normalized concentration in biota (C_{biota}/f_{lip} in eq 1) can be

related to C_w through a lipid/water partition coefficient (K_{lip}), accounting for water exposure, and a second term accounting for uptake from ingested sediment organic matter:

$$\frac{C_{biota}}{f_{lip}} = K_{lip}C_w + gK_{oc}C_w \quad (3)$$

with g, a food-chain multiplier, defined as the ratio of uptake to excretion and growth rate constants [3]. For simplification, it is assumed that sediment and water are in equilibrium and that no growth dilution and no selective feeding occur (and thus that black carbon and organic carbon are taken up in the same ratio in which they are present in the sediment). Equation 3 also assumes that the concentration in ingested organic matter (C_{sed}/f_{oc}) equals $K_{OC}C_w$ and is fully available for uptake. However, this is not consistent with eq 2, which states that part of the HOCs are bound to BC, as quantified by the Freundlich term. This problem is solved by assuming that primarily fast-desorbing HOC fractions, bound to amorphous carbon (f_{oc} - f_{bc}), are bioavailable [*6,11,12*]. Consequently, the available concentration is approximated by the first term in eq 2, so that $C_{sed}/f_{oc}) = (1 - f_{bc}/f_{oc})K_{OC}C_w$. By use of this and by substitution of eqs 2 and 3 in eq 1, an equation for a BC-inclusive steady-state BSAF model is obtained that also accounts for additional uptake from ingested sediment:

$$BSAF = \frac{K_{lip} + g\left(1 - \frac{f_{bc}}{f_{oc}}\right)K_{oc}}{\left(1 - \frac{f_{bc}}{f_{oc}}\right)K_{oc} + \frac{f_{bc}}{f_{oc}}K_F C_w^{n-1}} \quad (4)$$

Note that if f_{bc} equals zero and $K_{lip} \approx K_{OC}$, this equation reduces to BSAF = 1 + g (eq 23 in ref [*3*]).

We used eq 4 to independently estimate BSAFs for PAHs and PCBs without any fitting, using measured or literature based variables and parameters. For f_{bc} and f_{oc}, measured values were used. K_{lip} and K_{OC} are assumed to be equal to K_{OW} [*3,41*]. The sediment ingestion term g was modeled as $\alpha I/K_e$ [*42*] with α the chemical assimilation efficiency (micrograms per kilogram/micrograms per kilogram), I the specific consumption of organic carbon by invertebrates ($g_{oc}g_{lipid}^{-1}$ per day) and K_e the overall loss rate (per day) of the chemical from the invertebrates. Estimates for these three variables were obtained following refs [*3*], [*42*], and [*43*] and are detailed in the Appendix to this chapter. Equation 4 further predicts that BSAFs depend on C_w and K_F, which were not directly measured. Assuming that the first term in eq 2 matches

the fast-desorbing concentration, this term can be divided by the measured C_{sed} to yield an estimate of the fast-desorbing fraction f_{rap}:

$$f_{rap} = \frac{(f_{oc} - f_{bc}) K_{oc} C_w}{C_{sed}} \quad (5)$$

Hence, C_w was calculated from eq 5. Values for f_{rap} were estimated from the measured 6-h Tenax-extractable fractions with correction factors provided by Cornelissen et al. [*22*] for sediments from the same river basin. For PCBs, the average correction factor of 0.95 was used (thus, $f_{rap} = 0.95\ f_{6\text{-}hTenax}$). For PAH compounds, specific correction factors were available except for Ant, BeP, BghiPe, DahA, and Ind123Pyr, for which the average PAH correction factor of 3.85 was used [*22*]. K_F can be estimated from the second term in eq 2 with the assumption that this term comprises slowly desorbing fraction of HOCs (f_{slow}), with black carbon acting as a superadsorbent with very slow release kinetics [*14,25,44*]:

$$f_{slow} = \frac{f_{bc} K_F C_w^n}{C_{sed}} = 1 - f_{rap} \quad (6)$$

Apart from K_F, the only remaining unknown in eq 6 is n, for which recent reports on Freundlich sorption to BC [*26,27*] provide values between 0.6 and 0.8. We tested whether calculated BSAFs are sensitive to this uncertainty, which appeared not to be the case. Hence, an average value of n = 0.7 was used for the calculation of K_F. These K_F values are thus operationally defined for two reasons. First, they relate to the selected value for n. Second, they relate to the measurement method for BC, as fbc is used to calculate K_F. Recently, similar estimates of K_F were reported for Boston and New York harbor sediments, also with the assumption that n = 0.7 and by the sameBCmeasurement method (CTO-375; [*13*]), by Accardi-Dey and Gschwend [*27*] and Lohmann et al. [*44*], respectively. Consequently, all these indirectly derived in situ K_F values have units of (micrograms/kilogram$_{bc}$)/(micrograms per liter)$^{0.7}$, which allows their direct comparison in Figure 3.4. Error bars relating to seasonal and interlake differences are omitted here as they were smaller than the markers. The comparison shows remarkable agreement between calculated and literature data for PCBs (Figure 3.4A) as well as PAHs (Figure 3.4B). The estimated log K_F values for PCBs were linearly correlated to log K_{OW} (log K_F = 0.980 log K_{OW} + 0.491; R^2 = 0.943, n = 14) and were 1 order of magnitude lower than the analogous log K_F values for PAHs (log K_F = 0.912 log K_{OW} + 1.584; R^2 = 0.982, n = 13), which agrees with reported differences between in situ K_{OC} [*24*] as well as K_F values [*44*] for these compound classes. In summary, the consistency of the present values with those from

earlier studies strongly supports the idea that BC is the adsorbent responsible for the slowly desorbing, nonavailable HOC fractions.

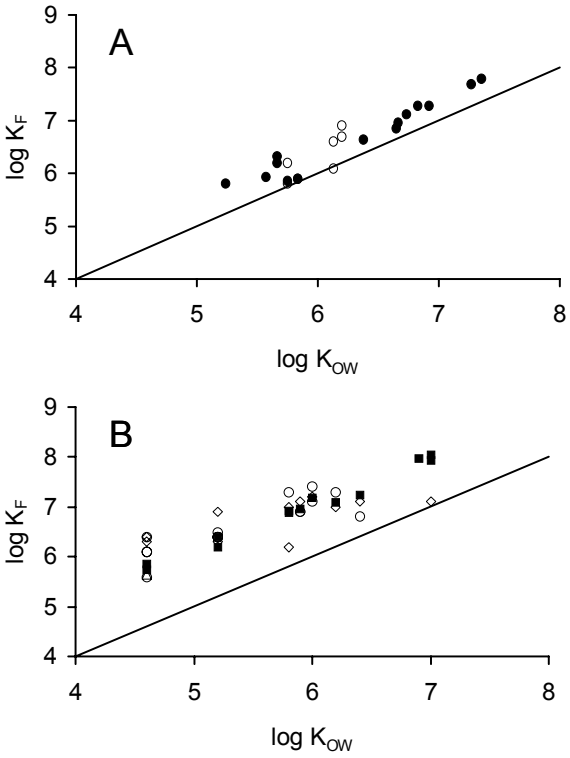

Figure 3.4. *Calculated in situ K_F values [solid symbols, in units of (micrograms/kilogram$_{bc}$)/(micrograms/liter)$^{0.7}$] based on eq 6, for PCBs (A) and PAHs (B), compared with literature values (open symbols). PCB K_F literature values are from ref [44]:* ○. *PAH K_F literature values are from refs [27]:* ◇, *[26]:* △ *(recalculated with n = 0.7), and [44]:* ○. *Error bars were smaller than markers and were omitted from the graphs. The line represents the 1:1 line ($K_F = K_{OW}$).*

Finally, Figure 3.5A shows the model results together with measured values for PCB and PAH BSAFs. Error bars in Figure 3.5 relate to ecological as well as geochemical variation among lakes and seasons, plus the variation regarding analytical and sampling errors, and are relatively small. It appears that the model without any optimization satisfactorily describes PCB BSAFs and explains the often-observed dichotomy between PCBs and PAHs [*15*] but overestimates PAH BSAFs for PAHs with a factor of 9 (lower weight compounds) to 3 (higher weight compounds). The traditional model (BSAF) Kl_{ip}/K_{OC}, without sediment ingestion) reduces to a value of BSAF = 1 when both partition coefficients are assumed to be equal to K_{OW} and is included in Figure 3.5 for comparison.

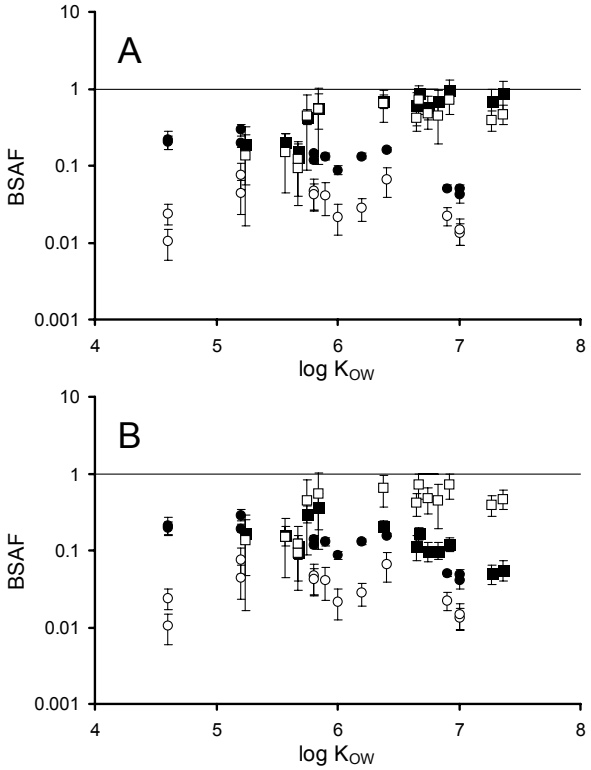

Figure 3.5. *Measured and modeled BSAF values for PCBs (■ /□) and PAHs (●/○). Measured values have open symbols. Model results (solid symbols) were obtained by use of eq 4, with a food ingestion term g (panel A) versus food ingestion set to zero (g) 0; panel B). Results over all lakes and seasons (n = 11) are averaged and standard errors are shown. The solid line represents the conventional BSAF value of 1.*

The superiority of the BC-inclusive model compared to the conventional model was tested by ANOVA and appeared to be highly significant ($p = 8.03 \times 10^{-21}$ for PCBs and $p = 3.75 \times 10^{-84}$ for PAHs) despite the larger number of parameters. It follows from the model that the main difference in BSAF betweenPAHs and PCBs is explained from substantial uptake from ingested particles. If g is set to 0 (food ingestion excluded), estimates for PCBs approach those for the PAHs but do not match the measured PCB BSAF values anymore (Figure 3.5B). Therefore, we conclude that food ingestion should be taken into account and that BC-inclusive BSAF models that omit food ingestion [*1,45*] may have limited general predictive capability for HOC uptake in benthic invertebrates. For PAHs, 50-97% has been reported to be unavailable for partitioning, dependent on the type of BC [*27*]. This is also confirmed in the present study by the low Tenax extractability of PAHs (Figure 3.1B). Furthermore, the available PAHs have higher affinities for BC than PCBs [*26,27,44*], so that biological factors will have only minor effects on PAH BSAFs. The nonextractable (resistant) fractions resemble the fraction (f_{slow}) bound to BC. For PAHs, the BC term in eq 2 accounts for 80-95% of total sorption. For most PCBs, however, the extractability by Tenax or organisms is larger, and BC accounts for 50-95% of total sorption (Figure 3.1A). These differences in sorption explain the remaining difference in Figure 3.5B.

The model shows that significant contributions of sediment ingestion (larger values for g in eq 4) are expected mainly for PCBs between log K_{OW} 5.5 and 7.5 as was shown earlier by Thomann et al. [*3*]. They calculated that PCB BSAFs for amphipods, when sediment ingestion was not included, decreased from 0.3 to 0.01 when log K_{OW} increased from 3 to 8. When sediment ingestion was included, however, this route dominated uptake above log K_{OW} = 5, with a maximum BSAF value of 5 at log K_{OW} = 7, and a good description of their data was obtained. Their model result (Figure 6 in ref [*3*]) is very similar to our Figure 3.5A, albeit our BSAFs are systematically shifted to lower values, due to BC sorption. The final question,why PAH BSAFs are overestimated, cannot be answered conclusively on the basis of our data. One possibility is metabolic transformation, as has been reported for PAHs [*37*], but this is not as such included in the model. Metabolic transformation of lower molecular weight PAHs may be more substantial than that of high molecular weight PAHs, and thus only part of the difference can be explained. Another possibility is an underestimation of the slow desorbing fraction, which was now estimated from 6-h Tenax-extractable concentrations and a correction factor provided by Cornelissen et al. [*22*], which of course may also have introduced uncertainties.

Appendix

Definition of food chain multiplier g.

Definition	Parameter	Dimension	Formula	Value	Ref.
Food chain multiplier	g	$g_{oc}\ g_{lipid}^{-1}$	$g = \frac{\alpha I}{K_e}$		[*42*]
Chemical assimilation efficiency	α	$\mu g\ kg^{-1}/\mu g\ kg^{-1}$	*PCBs:* $4.5 < \log K_{OW} < 6.5$: $\alpha = 0.7$ $\log K_{OW} = 7$: $\alpha = 0.5$ $\log K_{OW} = 7.5$: $\alpha = 0.3$ $\log K_{OW} = 8$: $\alpha = 0.1$ $\log K_{OW} = 8.5$: $\alpha = 0.05$ *PAHs:* $\log \alpha = 1.255 - 0.44 \log K_{OW}$		[*42*] [*43*]
Specific consumption	I	$g_{oc}\ g_{lipid}^{-1}\ d^{-1}$	$I = \frac{G + \rho}{a \cdot a_{wd}} \left(\frac{f_{OC}}{f_L} \right)$		[*42*]
Overall loss rate	K_e	d^{-1}		Figure 7 in [*43*]	
Growth rate of organism lipid	G	d^{-1}		0.035	[*42*]
Respiration rate	ρ	d^{-1}		0.125	[*42*]
Nett energy efficiency	a	-		0.20	[*42*]
Wet to dry weight ratio organism	a_{wd}	-			
Fraction organic carbon in organism	f_{oc}	- (based on wet weight)		0.4[a]	[*48*]
Fraction lipids in organism	f_L	- (based on wet weight)			

[a] 0.4 is based on dry weight, can be recalculated into wet weight by using a_{wd}.

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Chapter 4

Impact of Polychlorinated Biphenyl and Polycyclic Aromatic Hydrocarbon sequestration in sediment on bioaccumulation in aquatic food webs

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Abstract

It is not clear whether sequestration or aging of organic chemicals like polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) limits accumulation in higher levels of aquatic food chains. Therefore, the effect of aging on accumulation was studied in 1-m^3 model ecosystems that mimicked fish-dominated, macrophyte-dominated, and fish- and macrophyte-dominated shallow lakes. Also treatments without fish and macrophytes were included. General characteristics, biomasses, total (Soxhlet-extractable), and labile (6-h Tenax-extractable) PCB and PAH concentrations in sediment and biota were monitored over time. Accumulation data for PCB 28, PCB 149, and fluoranthene (native to the sediment taken from the field) were compared to those for spiked analogues PCB 29, PCB 155, and fluoranthene-d_{10}. Labile fractions for spiked compounds were higher than for their native analogues and decreased over time, suggesting sequestration in the sediment. In the majority of cases, 6-h Tenax-extractable concentrations correlated better with concentrations in biota than Soxhlet-extractable concentrations. Ecosystem structure affected food web accumulation, but replicate variability was too high to detect clear treatment effects. Differences in accumulation between spiked compounds and their native analogues indicated an effect of aging for invertebrates, macrophytes and benthivorous fish. Thus, aging may translate directly into reduced uptake at higher trophic levels.

Introduction

Prolonged contact times between hydrophobic organic chemicals (HOCs) and sediments have been shown to result in a substantial decrease in mobility and bioavailability of these compounds [*1-3*]. This decrease is caused by kinetic and/or diagenetic processes and is often referred to as aging or sequestration [*4-6*]. Desorption of HOCs from sediments has been recognized to occur in three stages: a fast desorption, a slow desorption, and a very slow desorption stage [*7*]. Fractions of HOCs that desorb during these stages have desorption half lives of approximately 10, 100, and 10,000 h, respectively [*7*]. The slow and very slow desorbing fractions can be assumed to be unavailable for uptake by organisms because they do not desorb within timeframes that are relevant for bioaccumulation (e.g., within contact times between organism and sediment or gut and sediment). Hence, only the fast desorbing fraction is generally considered to be bioavailable [*1-3,8-10*]. On larger time scales, however, also the slow desorbing fraction will add to the amount that is available for uptake by biota. Until now, effects of aging on bioavailability have been

demonstrated for benthic invertebrates in single species laboratory experiments [1,3]. For risk management purposes, however, it is necessary to be able to estimate risks for top predators and ultimately humans. Therefore, an important remaining question is whether aging and the subsequent decrease in bioavailability translates into the aquatic food web. To our knowledge, no earlier studies have addressed this question. In addition, there is a great demand for adequate measures to determine bioavailable concentrations. Recent research shows that bioavailable concentrations correlate well with the previously mentioned fast desorbing HOC fraction [*1-3,8-10*]. A recently developed and validated method to extract fast desorbing fractions from sediment suspensions uses Tenax beads as solid phase extractant [*9,11-13*]. For benthivorous fish in floodplain lake enclosures, we have shown that polychlorinated biphenyl (PCB) bioaccumulation in fish correlates better with 6-h Tenax-extractable (TE) fractions than with total, Soxhlet-extractable (SE) PCB fractions [*14*]. Similarly, for invertebrates in the laboratory, bioaccumulation correlated better with the TE fraction for PCBs as well as polycyclic aromatic hydrocarbons (PAHs) [*3,11,13*].

If aging is relevant for food chain accumulation, and Tenax extractions can be used to account for aging, the next question is whether these issues can be influenced by specific ecological conditions. Recent reviews have shown that food web structure might influence fate and bioavailability of contaminants [*15-17*]. First, contaminant fate is closely linked to the carbon cycle, since organic contaminants are bound mainly to organic carbon phases. Second, nutrients may influence food quality and thus accumulation through food uptake. Third, contaminants can change food web structure because of toxicity. In eutrophic systems, sedimentation rates of suspended particles and associated HOCs may be higher than in oligotrophic systems [*15,18,19*], which leads to higher HOC amounts in the sediment [*18*]. Because of the higher settling rates, mineralization may take place at the sediment surface rather than in the water column [*18*]. This leads to a higher proportion of fresh biogenic, less mineralized and less condensed organic matter in the sediment. The affinity of HOCs for this relatively fresh organic matter is lower [*20*], which thus may lead to differences in HOC sediment-water partitioning between eutrophic and oligotrophic systems. For benthic invertebrates, increased food supply in eutrophic lakes may increase benthic bioactivity and respiration, which may lead to increased uptake and subsequent toxicity [*15*]. Finally, eutrophication may lead to higher biomass, also for fish [*18,19,21*].

We hypothesize that food chain accumulation of HOCs is influenced by the time they have been in contact with sediment and that availability of organic contaminants is affected by ecosystem structure. To test these hypotheses, food chain accumulation of aged and nonaged chemicals was compared in 12 indoor model

ecosystems that represented a wide range of ecological structures. Nonaged HOCs are more mobile than aged chemicals, which makes them more sensitive to ecological differences between the systems. Historically polluted (aged) floodplain lake sediment was brought into these model ecosystems, which were constructed to mimic four ecological structures (each in triplicate): with fish, with macrophytes, with fish and macrophytes, and without fish and macrophytes. The resultant 2 x 2 factorial design was evaluated using analysis of variance (ANOVA). General characteristics, biomasses, Soxhlet-extractable and 6-h Tenax-extractable PCB and PAH concentrations in sediment and biota were monitored during a four-month period. The systems were spiked with PCB 29 (2,4,5-trichlorobiphenyl), PCB 155 (2,2′,4,4′,6,6′-hexachlorobiphenyl), and fluoranthene-d_{10}, and results for these spiked compounds were compared with those for their native analogues PCB 28 (2,4,4′-trichlorobiphenyl), PCB 149 (2,2′,3,4′,5′,6-hexachlorobiphenyl), and fluoranthene (Flu). These analogues were selected to have (almost) identical octanol-water partition coefficients (K_{OW}; see Table 4.1) and/or chlorine substitution patterns (PCB 28 and PCB 29 both have one chlorine atom at the ortho positions and PCB 149 and PCB 155 have three and four Cl atoms at the ortho positions, respectively). A number of other native PCBs and PAHs was monitored to evaluate the effectiveness of 6h Tenax-extractions.

Table 4.1. *Characteristics and concentrations in sediment (with standard errors; n = 12 systems) for spiked and native compounds*

Compound[a]		Flu-d_{10}[b]	Flu	PCB 28	PCB 29[b]	PCB 149	PCB 155[b]
Log K_{OW}		5.22[c]	5.22[c]	5.67[d]	5.60[d]	6.67[d]	6.41[d]
Concentration in sediment[e]							
Before spiking[f]	t = 0	0.01±0.00	1.1 ± 0.3	7.3 ± 1.6	0.25±0.11	20 ± 5	0.45±0.26
After spiking[f]	t = 4	2.9 ± 0.5	1.2 ± 0.3	8.1 ± 2.1	22 ± 4	21 ± 2	23 ± 4
	t = 9	3.1 ± 0.5	1.2 ± 0.3	9.6 ± 1.4	26 ± 4	23 ± 3	26 ± 4
	t = 13	2.5 ± 0.6	1.1 ± 0.2	7.9 ± 2.3	22 ± 4	21 ± 3	22 ± 5
	t = 17	2.8 ± 0.7	1.1 ± 0.2	8.1 ± 1.8	21 ± 6	20 ± 4	22 ± 6
	t = 19	2.6 ± 0.5	1.1 ± 0.3	8.8 ± 1.7	20 ± 5	22 ± 5	26 ± 7

[a] Flu = Fluoranthene; polychlorinated biphenyl (PCB) 28 = 2,4,4′-trichlorobiphenyl; PCB 29 = 2,4,5-trichlorobiphenyl; PCB 149 = 2,2′,3,4′,5′,6-hexachlorobiphenyl; PCB 155 = 2,2′,4,4′,6,6′-hexachlorobiphenyl.

[b] Spiked compound.

[c] Values taken from Mackay et al. [*45*].

[d] Values taken from Hawker and Connell [*46*].

[e] PCBs in µg/kg; fluoranthene in mg/kg.

[f] t = time in weeks after spiking.

Materials and methods

Chemicals

The NH_4NO_3 and KH_2PO_4 (both >99% purity) were obtained from Merck (Darmstadt, Germany). Polycyclic aromatic hydrocarbons (anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[k]fluoranthene, benzo[ghi]perylene, chrysene, dibenz[a,h]anthracene, fluoranthene, indeno[123-cd]pyrene, phenanthrene, pyrene, and 2-methylchrysene) were obtained from Sigma Aldrich (Zwijndrecht, The Netherlands). Fluoranthene-d_{10} was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Polychlorinated biphenyls (International Union of Pure and Applied Chemistry IUPAC numbers 18, 20, 28, 29, 31, 44, 52, 101, 105, 118, 138, 143, 149, 153, 155, 170, 180, 194) were purchased from Promochem (Wesel, Germany). Acetone used for spiking was picograde quality (Promochem). Other chemicals used for extraction and clean-up are described in Moermond et al. [*19*].

Experimental setup

General. Twelve model ecosystems representing floodplain lake ecosystems were constructed in a climate room of 20 °C. The model ecosystems were 110 x 110 x 70 cm (length x width x height) glass aquaria. Sediment was sampled from a floodplain lake along the lower river Rhine, The Netherlands. This lake was created around 1930 and since then served as a sedimentation area for polluted suspended solids. Further characteristics of this lake can be found in Moermond et al. [*19*] (where this lake is coded DeO3B). Ten months prior to the start of the experiment the upper layer of the lake sediment was scraped off with an excavator, transported to the laboratory in a large truck and homogenized. This sediment was added to the model ecosystems in a layer of 10 cm. The room was kept dark until the start of the experiment.

Spiking procedure. Sediments in the model ecosystems were spiked with a cocktail solution of Flu-d_{10}, PCB 29, and PCB 155 in acetone, to obtain concentrations in sediment that were similar (within a factor of two) to concentrations of their native analogues Flu, PCB 28, and PCB 149 (see Table 4.1). In contrast to Flu-d_{10}, PCB 29 and PCB 155 were originally present in the sediment. Their background concentrations were very low, however, and spiked amounts were such that final concentrations were at least 20-fold higher than background concentrations, ensuring that the aged fraction of these PCBs was negligible compared to the nonaged fraction [*20*]. Spiking was performed in the dark to prevent photolytic breakdown of PAHs.

Approximately 20 cm of water, which was pumped from a deep well located at the "Dreijen" area in Wageningen, The Netherlands, was added to the systems. During spiking, the sediment was kept in suspension using a large mechanic stirrer [*21*], with sediment in the corners being mixed manually. One-third of the spike solution (total ~ 0.5 l) was slowly injected below the surface of the slurry using a continuous dosage system. This lasted for approximately 25 min per system, after which stirring proceeded for another 15 min. The next 2 d, the remaining two thirds of spike solution were added in the same way, after which the sediment was allowed to settle for 3 d. Subsequently, the systems were filled to a volume of 600 L using water from the previously mentioned well. Oxygen concentrations were monitored daily and addition of biota was not started before these concentrations exceeded 3 mg/L. In Table 4.1, PCB and PAH concentrations in the sediment before and after spiking are reported.

Setup of model ecosystems. The model ecosystems were designed to contain four different ecosystem structures (n = 3): systems with fish and macrophytes, systems with fish without macrophytes, systems with macrophytes without fish, and systems with neither fish nor macrophytes. These systems were designed to represent Dutch floodplain lakes. When no macrophytes were present, the systems were phytoplankton dominated. Not all biota groups were introduced in the systems at the same time, to allow macrophytes to get rooted before other biota were added and to allow invertebrate communities to adapt before predators were introduced. Four weeks after spiking, the six systems designed to contain macrophytes were seeded with 20 10-cm-long shoots of Elodea nuttallii, obtained from a nonpolluted site in Wageningen, The Netherlands. Five weeks after spiking, all model ecosystems were stocked with an invertebrate and zooplankton community from another unpolluted reference site near Wageningen. Nine weeks after spiking, three 3 cm-sized carp (Cyprinus carpio, obtained from laboratory cultures from the department of Fish Culture and Fisheries at Wageningen University) were added to the model ecosystems designed to contain fish. During the experiment no additional fish food was added, but to enhance phytoplankton growth each system received nutrient dosages of 0.9 mg/L N as NH_4NO_3 and 0.15 mg/L P as KH_2PO_4 on a weekly basis. Also weekly, the water level in the model ecosystems was restored to the initial water level to compensate losses due to evaporation and sampling. The experiment lasted for 19 weeks after spiking, which is sufficiently long to reach ecological maturity in the systems but not so long that macrophytes start to decay [*22*]. Lamps (Philips HPIT 400 Watt; Philips, Eindhoven, The Netherlands) were hung over each model ecosystem, producing an average irradiance at the water level of 140 $\mu E \times m^{-1} \times s^{-1}$ and a 14:10-h light:dark photoperiod.

Sampling

All storage materials for PCB and PAH samples were pre-rinsed with picograde acetone. Samples for PCB and PAH analysis were freeze-dried and stored in brown glass jars at -20 °C until analysis.

Sediment samples were taken just before spiking and every four weeks during the experiment. Five cores were sampled randomly in each system using self-made Perspex tubes (Ø 2.5 cm). The upper 5 cm of these five subsamples per system were pooled and homogenized. Macroinvertebrates, zooplankton, and fish could be sampled only at the end of the experiment to prevent disturbance of the systems. After sampling, the macroinvertebrates were divided into oligochaetes and remaining (mixed) invertebrates. For gut clearance, they were kept overnight (16 h) in aerated glass containers with filtered water from the model ecosystems at 6 °C in a dark climate room. A gut clearance time of 16 h has been calculated to be short enough for elimination losses to be less than 5% [*6*]. Spilled gut contents were removed, and macroinvertebrates were rinsed with Barnstead Nanopure® water (Sybron-Barnstead, Dubuque, IA, USA). Macrophytes were sampled once every four weeks by cutting a few shoots just above the sediment (to prevent disturbance of the system). Invertebrates were removed from the leaves and returned to the systems. Floating algal biomass (FAB) was collected every four weeks (when present) by scooping it from the water surface with a 500 µm sieve. Invertebrates attached to the FAB were manually removed and returned to the systems. Periphyton was mainly present on the walls of the model ecostems. To collect periphyton, every four weeks approximately 2000 cm^2 of wall area was scraped off with an aquarium net, after which the periphyton was immediately transferred into glass containers. At the end of the experiment, fish were caught using a small net and killed using metacaine. All zooplankton remaining in the systems was concentrated by means of a plankton net (Hydrobios, Kiel, Germany; mesh size: 55 µm). In 6 out of 12 systems, insufficient zooplankton and periphyton biomass was present to be able to analyze PAH and PCB concentrations.

Analytical procedures

General characteristics. To determine black carbon (BC) contents, sediment samples were combusted at 375 °C for 24h [*19,23*], after which inorganic carbon was removed with 2M HCl. Total organic carbon (OC) and BC contents in 375°C- and non-combusted samples respectively, were detected with a CHN elemental analyzer

(Fisons Instruments EA 1108, CE Instruments, Milan, Italy). Lipids in biota were extracted with chloroform/methanol [*24*] and quantified gravimetrically.

PCB and PAH analysis. Concentrations of PCBs and PAHs in sediment and biota were determined by means of a 16-h Soxhlet-extraction with hexane:acetone (3:1 v/v) as described before [*14,19,25*]. Tenax extractable concentrations in sediment were determined following previous work [*14,19*]. The PCBs were analyzed on an upgraded Hewlett-Packard 5890 II gas chromatograph (Agilent, Little Falls, Wilmington, DE, USA) equipped with a HP7673A autosampler, two ^{63}Ni electron capture detectors, and two 50m capillary fused silica columns (CP Sil-8 CB and CP Sil-5/C18 CB, Varian, Bergen op Zoom, The Netherlands). The PAHs were analyzed on a Hewlett-Packard 1100 HPLC (Agilent) equipped with a Vydac guard and analytical reverse phase C18 column (201GD54T and 201TP54).

Quality assurance. With every ten samples, one recovery sample (a cocktail solution containing all analyzed HOCs) and one blank sample were included. These were extracted and cleaned up together with the other samples. For selected series of six samples, recoveries and blanks were determined in triplicate. Cleanup recoveries for 48 Soxhlet-extracted samples averaged 94 ± 4% (standard deviation) for PAHs and 97 ± 9 % for PCBs. For 10 6-h Tenax-extracted samples, cleanup recoveries averaged 97 ± 4 % for PAHs and 98 ± 11 % for PCBs. All samples were corrected for cleanup recoveries and blanks. In addition, we used an internal reference sediment (freeze-dried Wadden sea sediment, which is used as a reference sediment in our laboratory) that was analyzed regularly. Results were typically within one standard deviation of previously measured values.

Statistical analysis

Pearson's correlation coefficients between concentrations in sediment and biota were calculated for each individual biota sample, with n = 18 PCBs and n = 14 PAHs, using the Statistical Package for the Social Sciences (SPSS), version 11.5 (SPSS, Chicago, Illinois, USA). Differences between treatments (2×2 factorial design based on macrophyte and fish presence) were analyzed with the statistical software package SAS, version 9.1 (SAS Institute Inc, Cary, North Carolina, USA), using two-way ANOVA tests.

Results and discussion

Soxhlet extractable and Tenax extractable concentrations: evidence for sequestration

In Table 4.1, concentrations in sediment are shown for PCB 28, PCB 149, and Flu (native) and PCB 29, PCB 155, and Flu-d_{10} (spiked). The total concentration of each compound did not change over time, and calculations show that approximately 99.99% of each compound in the model ecosystems was present in the sediment layer. The constant concentrations imply that no substantial degradation occurred for these compounds. Figure 4.1 shows the fraction of SE (total) concentrations that was 6h Tenax-extractable (fast-desorbing), for Flu-d_{10}, Flu, and PCBs 28, 29, 149, and 155, as averaged values over all 12 model ecosystems.

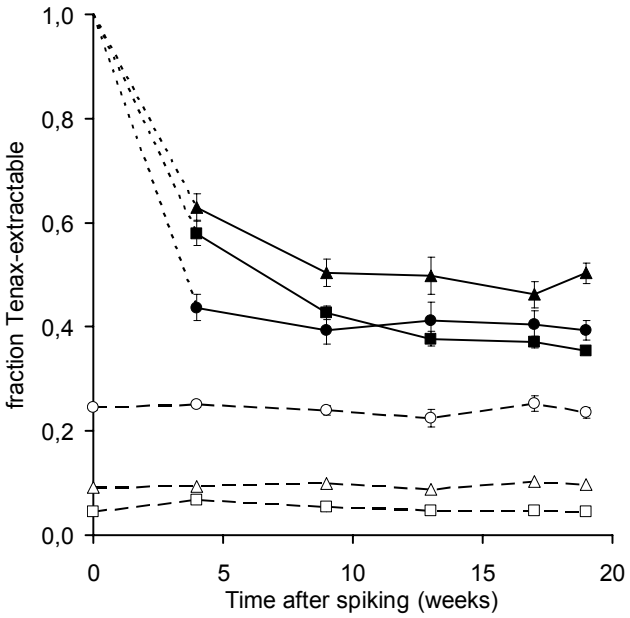

Figure 4.1. *Polychlorinated Biphenyl (PCB) and Polycyclic Aromatic Hydrocarbon (PAH) 6-h Tenax-extractable fraction of total (Soxhlet-extractable) sediment concentrations as a function of time. Samples for native compounds at t = 0 were taken just prior to spiking. Open symbols represent native compounds (□: PCB 28; ○: PCB 149; △: Flu). Closed symbols represent spiked compounds (■: PCB 29; ●: PCB 155; ▲: Flu-d_{10}). Error bars (n=12) for native compounds are mostly smaller than markers. The dashed line in the first weeks for PCB 29, PCB 155, and Flu-d_{10} indicates the drop of the 6-h Tenax-extractable fraction from the intial theoretical value of 1.0 at spiking.*

The small error bars indicate that accuracy was high and that ecosystem structure had imited effects on these concentrations. Ecosystem structure (presence of fish and/or macrophytes) did not significantly affect TE fractions (ANOVA, $p > 0.05$), except for PCB 155 after 13 and 19 weeks. Although statistically significant, these differences for PCB 155 are small.

Our measured TE fractions of native PCBs and PAHs are comparable to results from earlier reports [*11,14,19*], and did not change during the experiment. In contrast, TE fractions of spiked compounds PCB 155, Flu-d_{10}, and especially PCB 29 decreased considerably during the first weeks and then remained fairly constant. For the TE fraction of PCB 155 no statistically significant decrease after week 5 was observed. Because total concentrations of spiked compounds did not change over time, it can be concluded that no depletion or significant breakdown of sediment-bound contaminants occurred. Therefore, the decline of PCB 155, PCB 29, and Flu-d_{10} points to sequestration in the sediment. The TE fractions of hexachlorobiphenyls PCB 155 (spiked) and 149 (native) stayed relatively high, which is consistent with other reports [*11*] where measured TE fractions for hexachlorobiphenyls were also relatively high (up to 40%). Apparently, sequestration is less pronounced for these compounds, which may be explained as follows. The PCBs 149 and 155 are relatively hydrophobic compared to the other test compounds and are relatively bulky with three and four chlorine atoms at the ortho positions, respectively. This means that their adsorption rates may be lower and thus that they reside at the outer regions of the organic matrix for a longer time and their fast desorbing fractions may decrease more slowly than for other compounds [*7,8*].

Tenax-extractable fractions as a measure of bioavailability

The fast desorbing fraction of a chemical is generally assumed to be the bioavailable fraction [*1-3,8-10*]. This fraction is defined here as the fraction of a chemical's concentration in sediment that is available for uptake by biota within relevant timeframes through all relevant uptake routes (e.g., skin, gills, gut). It has been reported that this fast desorbing fraction correlates well with a single time point (6 h) Tenax extraction [*9,12,13*]. Consequently, concentrations in biota should show stronger correlations with TE concentrations than with SE concentrations. Indeed, this was recently demonstrated for PCBs in fish in field enclosures [14] and for PCBs and PAHs in invertebrates in laboratory tests [*3,11,13*]. For PCBs and PAHs in invertebrates in the field, however, such an improvement of correlations was not observed [*19*], which may be explained by the fact that different taxa were all combined in this group and by the fact that the research was performed on a field

scale, where sediment concentrations, foraging patterns, and microhabitats are heterogeneous.

To further investigate this matter, we correlated the present TE and SE concentrations in sediment with concentrations in biota. This was done for each individual biological sample (126 samples in total), with all measured PAHs (n = 14) and PCBs (n = 18). For the PCBs, SE-based correlations were significant ($p < 0.05$) in more than 98% of the cases, and 6-h TE-based correlations were significant in 91% of the cases. For PAHs in fish, both types of correlations were never significant. For PAHs in all other biota samples, SE-based correlations were significant in 97% of the cases and TE-based correlations in 100% of the cases. Table 4.2 shows the percentage of correlations for which the correlation coefficient R^2 and the significance level improved when TE concentrations were used instead of SE concentrations. In this table, it is also indicated how many of these improvements were significant (F test on the mean sum of squares of the regressions; $p < 0.05$). For those compartments for which time-integrated sampling has been performed (macrophytes, periphyton, floating algal biomass), no effect of time on the improvement of the correlations was observed. In addition, ecosystem structure (treatment) did not seem to affect the number of correlations that improved. The number of improved correlations differed among compartments and compounds, sometimes in a counterintuitive way. For PCBs, we expected to see an improvement using TE-based correlations. However, an improvement was observed in only 10 to 33% of the cases for FAB, zooplankton, and fish, while for oligochaetes and mixed invertebrates an improvement occurred in 50% of the cases. Only for macrophytes and periphyton, PCB concentrations generally correlated better with TE concentrations. In contrast, we expected less improvement for PAHs, since body burdens for PAHs may not reflect uptake only, because of biotransformation. Surprisingly, the improvement was significant for PAHs in most cases in all compartments except fish and zooplankton.

Many factors may influence strength and significance (R^2, p) of correlations between concentrations in sediment and in biota: differences in equilibration state among individual compounds, physiology of the organism, trophic position of the organism, compound-specific characteristics, unsufficient taxon resolution, and uncertainties in the relationship between TE and the true fast desorbing fraction. These factors will be discussed below. The first factor relates to the possible influence of a lack of steady state. The quality of the correlations, however, did not change over time for the compartments where time-integrated sampling was possible. Therefore, it seems that the correlation between the concentration of PCBs and PAHs in biota and the TE concentration is relatively insensitive to the state of equilibrium.

Table 4.2. *Percentage of the correlations between concentrations in biota and concentrations in sediment that improved (higher r^2) using 6-h Tenax-extractable sediment concentrations instead of Soxhlet-extractable sediment concentrations*

	# of samples	% improved[a]	
		PCBs[b]	PAHs[b]
Macrophytes	24	83 (58)	100 (100)
Periphyton	22	77 (55)	100 (100)
Floating algal biomass	31	10 (7)	87 (87)
Zooplankton	12	33 (8)	50 (33)
Oligochaetes	12	50 (8)	92 (83)
Mixed invertebrates	12	50 (33)	75 (67)
Fish	13	31 (0)	46 (0)

[a] Correlation coefficients were calculated for each sampled biological compartment, with all measured PAHs (n = 14) and with all measured PCBs (n = 18). The percentage of correlations where this improvement was not only absolute (higher r^2) but also significant (F test, $p < 0.05$) is given between brackets.

[b] PCBs = polychlorinated biphenyls; PAHs = polycyclic aromatic hydrocarbons

Still, even if compartments are at steady state, the amount of a chemical in biota does not necessarily reflect the amount that is bioavailable from sediment. After all, species-specific physiological factors such as biotransformation, growth dilution, and biomagnification through the food chain play a role in bioaccumulation. For macrophytes and periphyton, uptake and depuration of organic compounds is controlled mainly by diffusion, and biotransformation is not likely [*26*]. This is supported by the finding that the majority of correlations for macrophytes and periphyton was better for TE than for SE concentrations, for both PCBs and PAHs (see Table 4.2). In contrast, biomass and species composition of phytoplankton can be very dynamic, and when growth rates exceed elimination rates, growth dilution may significantly decrease total cell concentrations [*27*], which is especially the case for larger algal cells or clusters, such as filamentous algae [*28*]. This may explain the fact that correlation coefficients for PCBs in FAB were generally low and not better for TE concentrations.

Remarkably, for PCBs in fish also no significant improvement was obtained by correlating with TE instead of SE concentrations. An explanation for this may be biomagnification (i.e., elevated tissue concentrations due to ingestion of contaminated prey [*28-30*]), particularly in those cases where concentrations in prey also do not correlate with TE concentrations either, as is the case in our model ecosystems. Possibly, because the fish grew from 3 ± 0.3 cm (0.5 ± 0.13 grams) in week 9 to 6.7 ± 0.7 cm (4.2 ± 1.4 grams) in week 19, growth dilution may have contributed to this lack of correlation for fish as well.

Chemical differences between compounds also influence the quality of the correlations. For PAHs, biotransformation may decrease the bioaccumulated amount. While reports on the ability of oligochaetes and other invertebrates to metabolize PAHs are not conclusive [*31-33*], biotransformation of PAHs in fish has often been demonstrated [*34,35*]. Therefore, body burdens of parent PAHs in fish may not accurately reflect exposure levels. In our study, PAH concentrations in fish were much lower than PCB concentrations of similar hydrophobicity (see next section), and much lower than PAH concentrations in other biological compartments (e.g., invertebrates). In addition to reduced bioavailability due to chemical behavior of PAHs (e.g., sorption to black carbon), this suggests that biotransformation occurred in these fish. Finally, a 6-h Tenax-extraction does not necessarily extract the exact fast desorbing fraction, as the ratio between the actual fast desorbing fraction and the TE fraction may vary among compounds and sediments [*9,12*]. Note that variability among sediments plays no role in our data because all systems contained the same sediment. For any remaining variation, ideally a full desorption curve should be measured to accurately determine the real fast fraction. However, as stated before, a single fixed-time Tenax-extraction is still useful to obtain a reasonable and time-efficient indication of bioavailability [*11-14*]. In summary, TE concentrations work well to predict concentrations in macrophytes and periphyton and partly in other biota but do not universally explain bioaccumulation.

Effect of ecosystem structure on biota to sediment accumulation factors

Biota-to-Sediment Accumulation Factors (BSAFs) were calculated using [*36*]:

$$BSAF = \frac{C_{biota}/f_{lip}}{C_{sed}/f_{oc}} \quad (1)$$

with C_{biota} the concentration in biota (µg/kg), C_{sed} the concentration in sediment (µg/kg), f_{lip} the lipid fraction in biota, and f_{OC} the total organic carbon fraction in sediment. For FAB and phytoplankton, an organic carbon normalization may be more accurate than a lipid normalization, since lipid normalization has been reported to yield some bias [*27,37*]. Still, we decided to report BSAFs on a lipid basis to facilitate comparison among biological compartments. Lipid contents in biota were measured to be on average 4.0% for macrophytes, 4.3% for FAB, 4.2% for periphyton, 12.6% for fish, 6.8% for zooplankton, 5.6% for oligochaetes, and 4.0% for rest invertebrates (all on a dry-wt basis).

Figure 4.2 shows BSAFs for spiked compounds and their native analogues for each of the four ecological structures (n = 3) at the final sampling time. In six out of 12

systems, insufficient zooplankton and periphyton biomass was present to analyze PAH and PCB concentrations (see Materials and methods section), so BSAFs for these biota were not included in the graph. Also, not enough material was present to separate invertebrates into more groups than oligochaetes and rest invertebrates. This mixed group of rest invertebrates often had higher BSAFs than oligochaetes, but the overall picture is largely the same. High variabilities in the results for these invertebrates could be caused by the fact that the composition of this biota group varied among treatments, with differences in, for example, feeding strategies and lipid contents among individual species.

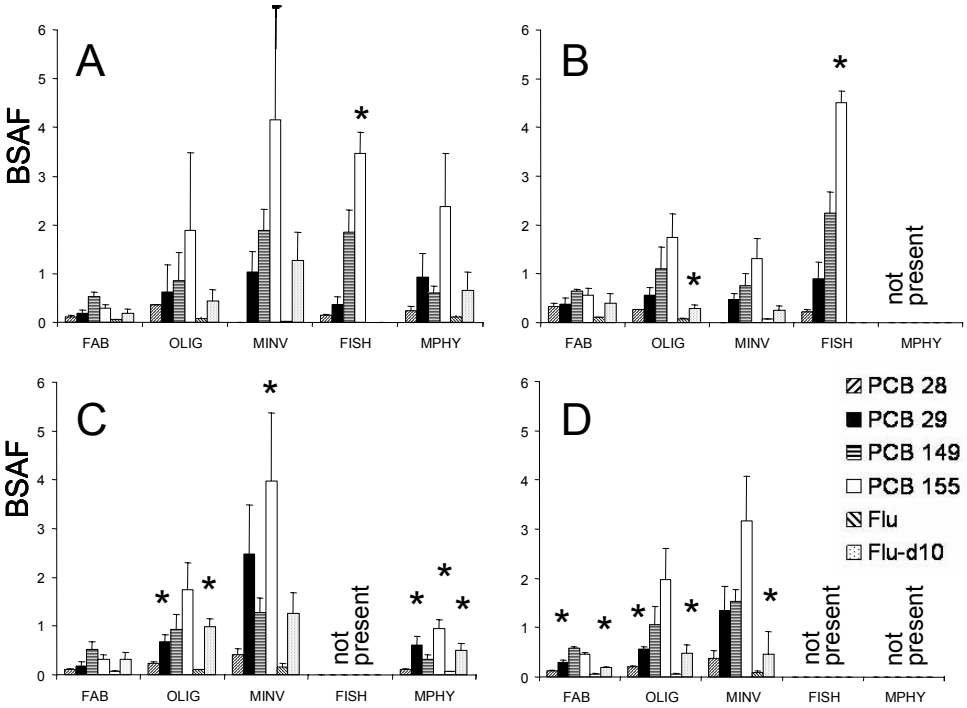

Figure 4.2. *Biota to Sediment Accumulation Factors (BSAFs) for spiked compounds (Polychlorinated Biphenyl [PCB] 29, PCB 155, and Fluoranthene-d_{10} [Flu-d_{10}]) and their native analogues (PCB 28, PCB 149, and Flu) at the final sampling time for all compartments in systems with fish and macrophytes (A), fish without macrophytes (B), macrophytes without fish (C), and without both fish and macrophytes (D). FAB = floating algal biomass; OLIG = oligochaetes; MINV = mixed invertebrates; FISH = fish; MPHY = macrophytes. An asterisk indicates that the BSAF for the spiked compounds differs significantly from the BSAF for the native compounds (t test, $p<0.05$).*

The ecological structure and trophic state of an aquatic ecosystem affect species composition, (feeding) behavior, and growth of biota and thereby influence processes such as biomagnification, sediment ingestion, elimination, and biotransformation [*15-17*]. We hypothesized that bioaccumulation of organic chemicals would also be influenced by ecosystem structure. Variation between the twelve individual systems indeed was considerable. Two-way ANOVA ($p<0.05$) calculations showed that for this particular subset of compounds, differences in BSAFs between treatments (ecosystem structures with fish and/or macrophytes or neither) were only significant for PCB 155 in periphyton. This is mainly because the variation in BSAFs among replicate systems was relatively large. Also, PCB 155 is the most hydrophobic compound spiked in this study. Thus, for almost all compounds and species analyzed in this study (except for PCB155 in periphyton), effects of ecosystem structure could not be detected on the treatment level. Accordingly, for clarity reasons in the rest of the present paper we will discuss averaged values over all systems ($n = 12$).

BSAFs: Deviations from Equilibrium Partitioning Theory

Figure 4.2 reveals large differences in BSAFs among biological compartments and compounds. Differences among compartments were larger than differences among compounds, except for fish. According to Equilibrium Partitioning Theory (EPT), BSAFs should measure 1 to 2 under steady-state conditions [*36*]. This theory assumes that uptake through diffusion is the main route of accumulation and that loss processes other than passive excretion into the water column do not play a role. In this experiment, however, PAH and PCB BSAFs for benthic invertebrates and PCB BSAFs for fish were usually higher than 1, especially for spiked compounds. For both invertebrates and fish, uptake from food and/or sediment may have increased BSAFs relative to EPT expectations [*28-30*]. The difference between spiked and native compounds might be the result of sequestration (see the following discussion).

On the other hand, also in contrast to EPT predictions, our measured BSAFs for FAB and macrophytes were lower than 1. An exception was PCB 155, which is the most hydrophobic spiked compound. Various literature sources suggest that lipid levels for these species are 0.05 to 0.2% on a wet-weight basis [*38,39*], which is below our measured values of 0.4% (wet wt) for macrophytes, but not below the measured 0.1% lipids (wet wt) for FAB. This suggests that lower BSAFs for macrophytes may be caused by our high, possibly biased lipid values. However, these low BSAFs also indicate decreased availability, possibly due to the presence of black carbon [19,40,41]. Black carbon contents in our sediments averaged 0.3% (16% of total

organic carbon). Recent data [*19*] and model simulations [*19,40,41*] show reduced bioaccumulation at these black carbon levels.

BSAFs: Differences between compound classes

Bioaccumulation differed clearly among less hydrophobic PCBs (represented by PCB 28 and PCB 29), very hydrophobic PCBs (PCB 149 and PCB 153), and PAHs (Flu and Flu-d_{10}). For example, fish BSAFs averaged 2.4 for very hydrophobic PCBs 149 and 153, 0.3 for less hydrophobic PCBs 28 and 29, and 0.003 for PAHs. The PCB results suggest a dependence on hydrophobicity; that is, very hydrophobic compounds show additional uptake through feeding and/or slower elimination rates [*28-30*]. For all compartments except fish, BSAFs for Flu(-d_{10}) are often similar to BSAFs for PCB 28 and PCB 29. This seems evident because these chemicals have similar log K_{OW}'s and are not degraded by other biota besides fish. However, stronger sorption to BC may cause lower BSAFs for PAHs than for PCBs [*40,41*]. Furthermore, photolytic breakdown of dissolved PAHs may cause decreased uptake. In the present study, however, reduced BSAFs for PAHs relative to PCBs with similar hydrophobicity are detected only for fish. Any additional effect of BC or photolytic breakdown should have been manifested in other compartments like invertebrates too. As this is not the case, the extremely low BSAFs of Flu(-d_{10}) for fish were most probably caused by biotransformation [*34,35*]. For invertebrates, biotransformation does not seem to play an important role, as BSAFs are higher than BSAFs for fish.

Effect of aging on BSAFs

Biota to sediment accumulation factors for spiked compounds were generally higher than BSAFs for their native analogues (Fig. 4.2). Differences between spiked and native compounds were often (11 out of 21 pairs) significant (t test, $p < 0.05$) in systems without fish but not in systems where fish were present (only 1 out of 21 pairs). The presence of fish caused resuspension of sediments in our systems (visual observation) and changed the invertebrate community composition (data not shown), and thus influenced overall ecosystem functioning. In systems with fish, variation among replicate systems was higher than in systems without fish, which consequently influenced the outcome of the statistics. The fact that differences are often significant in systems without fish, illustrates how interactions between organisms and the particulate phase play a significant role in bioaccumulation.

Due to the prolonged contact time between particles and sediment, condensation of organic matter, and encapsulation of molecules due to diagenetic processes, aging increases apparent sediment-water distribution coefficients [*42,43*]. Hence, aqueous concentrations and uptake through diffusion are reduced. For higher trophic levels, aging will influence uptake not only through reduced passive diffusion but also indirectly through reduced dietary uptake of lower bioaccumulated amounts from lower trophic levels.

We assessed the effect of aging for all biological compartments by comparing BSAFs for spiked versus native compounds. An elegant way to do this is by defining the ratio of the BSAF of a spiked compound over the BSAF of its native analogue (following Rust et al. [*44*]). If this $BSAF_{spiked}/BSAF_{native}$ ratio is larger than 1, this indicates that the spiked compound bioaccumulated more than its native analogue. In Figure 4.3, these $BSAF_{spiked}/BSAF_{native}$ ratios are presented as averaged values (n = 12) for the final sampling time. Periphyton and zooplankton (n = 6 instead of 12) are also included in the graph. Clearly, standard errors are much lower than in Figure 4.2.

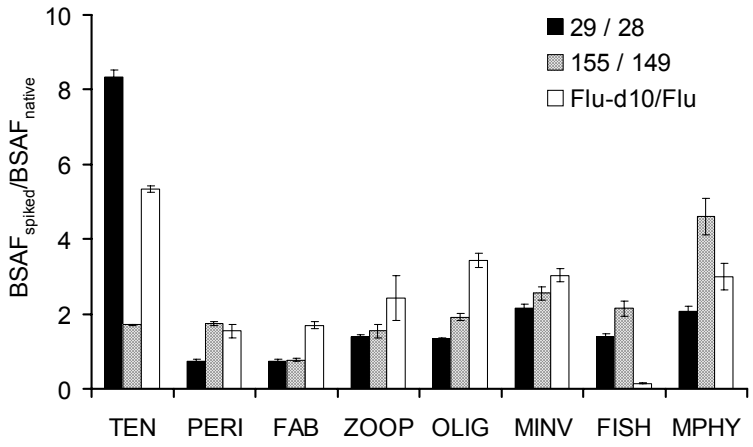

Figure 4.3. *Averaged Biota-to-Sediment Accumulation Factor (BSAF) ratios ($BSAF_{spiked}/BSAF_{native}$; n = 12 systems) for couples of spiked compounds and their native analogues at the final sampling time. TEN = $TENAX_{spiked}/TENAX_{native}$: the ratio of 6-h Tenax extractable concentrations of spiked and native compounds divided by the ratio of total concentrations in sediment; PERI = periphyton; FAB = floating algal biomass; ZOOP = zooplankton; OLIG = oligochaetes; MINV = mixed invertebrates; MPHY = macrophytes. A ratio higher than 1 indicates a higher accumulation of the spiked compound, a ratio lower than 1 indicates a higher accumulation of the native compound.*

In addition to the BSAF ratios, the ratio of TE concentrations to total concentrations in sediment was calculated for each couple of compounds. This $TENAX_{spiked}/TENAX_{native}$ ratio is included as a reference value, although it is formally not a BSAF ratio. Assuming that bioavailability of a compound is directly reflected in the TE concentration, a $TENAX_{spiked}/TENAX_{native}$ ratio larger than 1 indicates a larger bioavailability of the spiked compound. The use of these ratios can be explained as follows. If sediment-water-lipid equilibrium partitioning determines bioaccumulation and all other uptake processes are negligible, a $TENAX_{spiked}/TENAX_{native}$ ratio of 2 will yield a $BSAF_{spiked}/BSAF_{native}$ ratio of 2. When the $BSAF_{spiked}/BSAF_{native}$ ratio deviates from the $TENAX_{spiked}/TENAX_{native}$ ratio, however, the TE concentration does not accurately represent the bioavailable fraction in the same way for spiked and native compounds. After all, biological processes such as biotransformation or growth dilution can not explain this deviation, since spiked and native analogues in these ratios have similar physico-chemical properties.

For PCB 29 and PCB 28, the $TENAX_{spiked}/TENAX_{native}$ ratio of approximately 8 is much higher than the $BSAF_{spiked}/BSAF_{native}$ ratio observed for all biological compartments, i.e., 1.5 to 2 for zooplankton, oligochaetes, invertebrates, fish, and macrophytes, and approximately 1 for periphyton and FAB. Likewise, $TENAX_{spiked}/TENAX_{native}$ for the PAHs Flu-d_{10}/Flu (~ 5) is also higher than $BSAF_{spiked}/BSAF_{native}$, which for the PAHs is highly compartment specific. In contrast, the $TENAX_{spiked}/TENAX_{native}$ ratios for PCB 155 and 149 are comparable to the $BSAF_{spiked}/BSAF_{native}$ ratios (around 2), except for the macrophyte $BSAF_{spiked}/BSAF_{native}$ ratio, which is approximately 4. From these ratios it can be concluded that PCB 29 has accumulated less than proportionally to its TE concentration, PCB 155 has accumulated more or less proportionally, and for Flu-d_{10}, accumulation was less than proportional, but also more compartment specific due to processes like metabolic transformation [*34,35*].

Conclusion

Six-hour Tenax-extractable fractions for spiked compounds were higher than for their native analogues that aged for decades. Furthermore, they decreased over time, which means they sequestered in the sediment. In the majority of cases, 6-h Tenax-extractable concentrations correlated better with concentrations in biota than Soxhlet-extractable concentrations, but there was no uniform improvement among all biota. Ecosystem structure did affect BSAFs, but the effects could not be detected on the treatment level because ofvariability among replicate systems. Only for accumulation of spiked PCB155 in periphyton, a significant effect was found. Measured BSAFs were often lower than EPT predictions (except for PCB 155), which

may be caused by limited bioavailability due to BC (PCBs, PAHs) or biotransformation (PAHs). Differences in accumulation between spiked compounds and their native analogues indicated an effect of aging for invertebrates, macrophytes, and benthivorous fish. Therefore, aging may translate directly into reduced uptake at higher trophic levels.

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Chapter 5

Impact of macrophytes and fish on partitioning of sediment-originating PCBs and PAHs in freshwater model ecosystems

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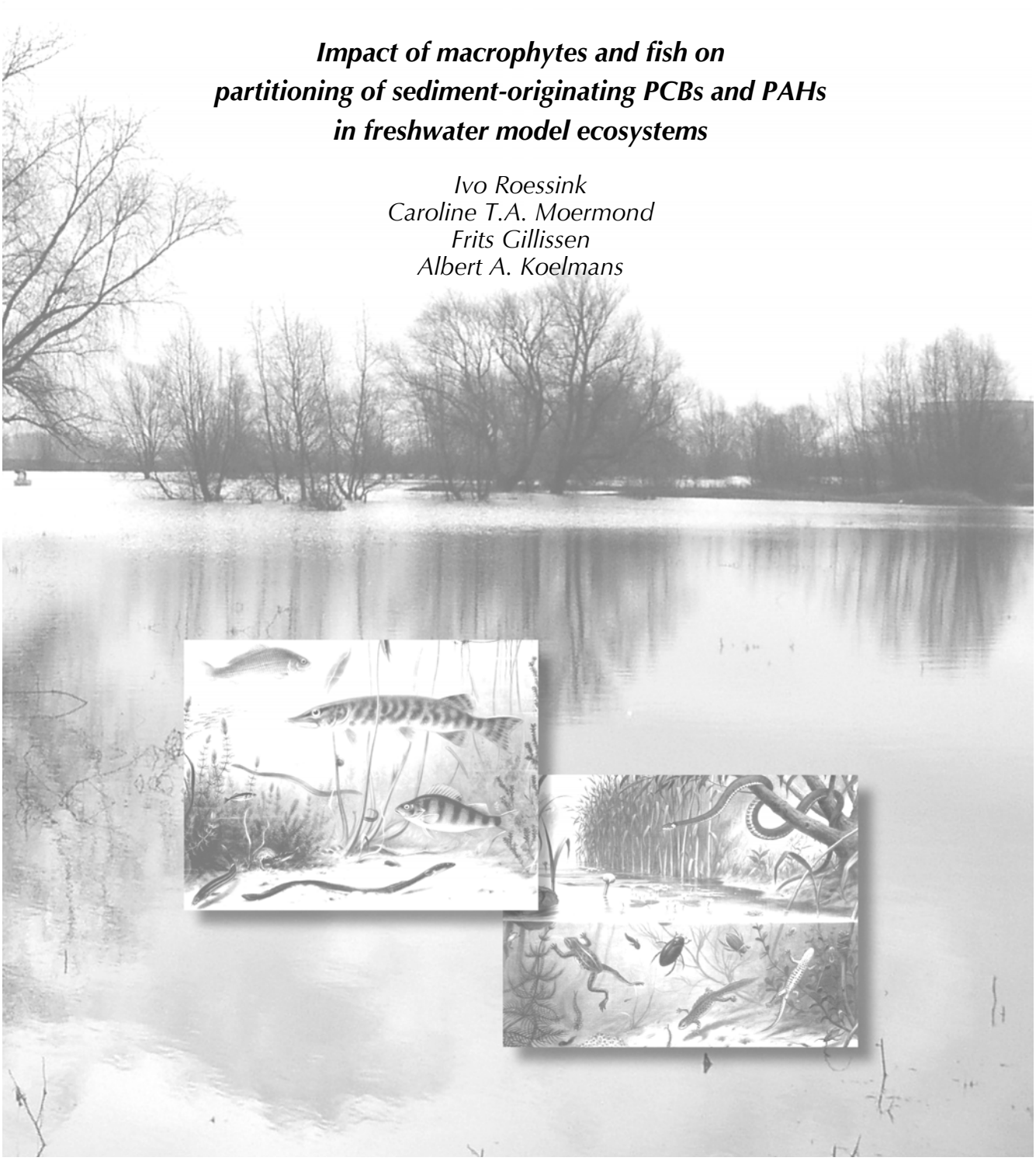

Abstract

Ecosystem structure may significantly affect partitioning of sediment-originating Hydrophobic Organic Compounds (HOCs). We studied effects of macrophyte and benthivorous carp additions on polychlorinated biphenyl (PCB) and polycyclic aromatic hydrocarbon (PAH) (native versus freshly spiked) mass distribution and lipid-normalized concentrations in sediment (Soxhlet- and 6-h Tenax-extractable), suspended solids, macrophytes, periphyton, floating algae biomass, zooplankton, oligochaetes, other invertebrates and carp in replicated 1-m^2 model-ecosystems. Freshly spiked compounds were more mobile in the system than their more sequestered native counterparts. Macrophytes represented the largest amount of non-sediment (bio)mass in the systems and were capable of depleting up to 26 (PCB) and 31 (PAH) percent of the mobile, fast desorbing HOC sediment fraction in the 7 cms of sediment. However, the presence of macrophytes did not have a significant diluting effect on lipid-normalized HOC concentrations in fish. The major biological impact of carp on the test systems was their structuring of invertebrate communities through predation. The chemical impact of carp was increased partitioning of HOCs to other system compartments caused by resuspension of the sediment. and consequently caused increased partitioning of HOCs to other system compartments. For less hydrophobic HOCs, no increased partitioning occurred to floating algae biomass and periphyton.

Introduction

At present, many sediments still contain high concentrations of xenobiotic compounds [*1*]. These sediments may not only act as sink but also as a source of a wide range of chemical substances, for instance Hydrophobic Organic Compound (HOCs) such as polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) [*2*]. As such, they can pose a threat to the ecological status of aquatic systems [*3*]. Numerous studies address behavior and effects of HOCs in the marine environment [*4,5*], rivers [*3,6*], or US great lakes [*7,8*]. Relatively few studies focus on smaller, shallow floodplain lakes, which are abundant in deltas around the world, including the Rhine-Meuse delta in The Netherlands [*9*]. Due to their limited depth, shallow lakes have an intense water-sediment interaction as well as a potentially large impact of aquatic vegetation. This causes their functioning to be different from deep lakes [*10*]. Several factors may affect the ecological structure of shallow lakes, such as climate, nutrient loadings, hydrology, anthropogenic stressors and invasive species.

Besides experiencing gradual changes in ecosystem structure, shallow lakes can switch abruptly from a vegetated state with clear water to a turbid situation with high concentrations of phytoplankton and other suspended solids, and vice versa. Such catastrophic regime shifts can be triggered by seasonality, grazing on macrophytes, inundation, eutrophication, benthivorous fish, toxic shocks and temperature [*11*]. Such changes in ecological structure, and its accompanying food web, can influence transport, partitioning, bioavailability and effects of HOCs in these systems [*7,12-17*].

Unfortunately, the precise nature and mechanisms of these interactions are hard to disentangle. For instance, in several water bodies a negative relationship between lake trophic status and contaminant concentrations in biota has been observed [*16-18*], while in others positive relationships between bioaccumulation and lake trophy for benthic invertebrates was reported [*13*]. Part of this discrepancy may be explained from the fact that originate from comparing lakes with different volumes, areas, geography, food webs, sampling times, or species compositions are compared. The present study aims at systematically investigating how system trophic status and ecological structure affect partitioning, bioaccumulation and implications for risks of sediment-bound contaminants in model ecosystems mimicking floodplain lakes.

The presence of macrophytes can be an important structuring factor in shallow aquatic systems. They can reach biomass densities up to 1 kg dry weight.m^{-2} [*19*], thus representing a significant part of the total system biomass [*20*]. We hypothesize that macrophytes will act as a sink for HOCs and consequently may decrease the amount of HOCs in other compartments of the system. Fish are another important part of the aquatic food web. Shallow lakes are often dominated by benthivorous fish (e.g., bream - *Abramis brama*) which rework sediments while foraging [*21,22*]. Since 100 g bream.m^{-2} may resuspend 46 g sediment.m^{-2}.day^{-1} [*23*] it is hypothesized that the presence of benthivorous fish will mobilize more HOCs from the sediment and results in a higher amount of HOCs in other system compartments. Additionally, predation by fish will structure the invertebrate community hence influencing HOC distributions in zooplankton and other invertebrate fauna compartments.

To test these hypotheses, historically polluted lake sediment was transferred to indoor model ecosystems. Impacts of ecology on partitioning of HOCs may differ for historically sequestered versus recently spiked chemicals, because the latter can be assumed to be more mobile [*24,25*]. Therefore, sequestered as well as freshly spiked HOCs were studied. Trophic status of the systems was characterized by presence of macrophytes (representing a macrophyte-dominated mesotrophic state) and absence of macrophytes (representing a phytoplankton-dominated eutrophic state). Addition of fish resulting in a 2 × 2 factorial design of four different ecological structures: with

fish, with macrophytes, with fish and macrophytes, and without fish and macrophytes (Figure 5.1). General characteristics, macrophyte and invertebrate numbers and biomasses were monitored over a four-month period. To be able to distinguish between total and bioavailable (fast desorbing) HOC fractions in the sediment, Soxhlet-extractable (referred to as total sediment and 6-h Tenax-extractable (referred to as TENAX) PCB and PAH concentrations [*26-28*] in sediment and biota were monitored. Results will be discussed along two angles: HOC mass distribution to address transport and partitioning issues and HOC lipid normalized concentrations in biota to address bioaccumulation.

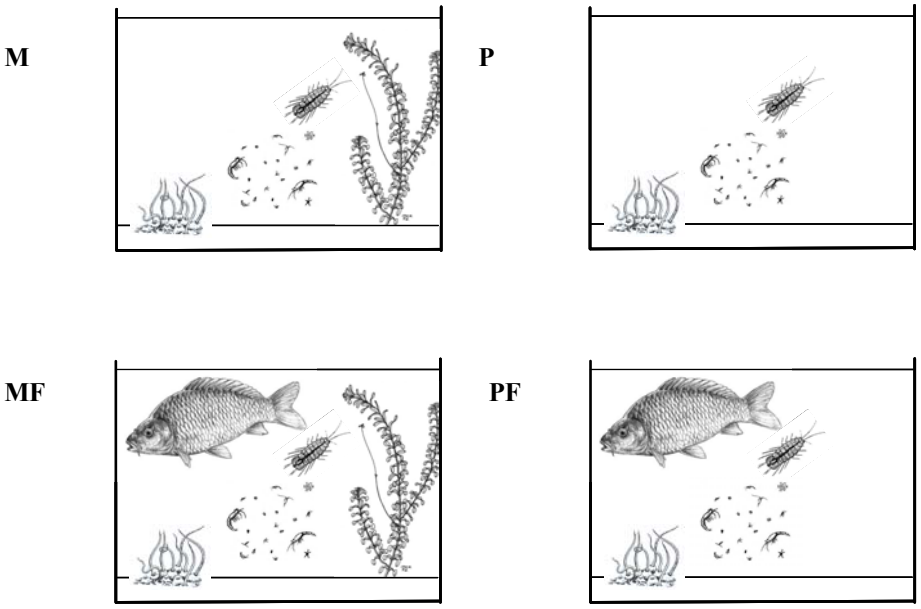

Figure 5.1. *Schematic overview of the ecological structure of the four different treatments. With fish (PF), with macrophytes (M), with fish and macrophytes (MF), and without fish and macrophytes (P).*

Materials and Methods

Experimental set-up

The model ecosystems consisted of glass aquaria (110 cm length, 110 cm width, 70 cm height, depth sediment layer 7 cm, height water column 50 cm) and were designed to contain four different ecosystem structures (each in triplicate): systems with fish and macrophytes (MF), systems with fish without macrophytes (PF), systems with macrophytes without fish (M), and systems with neither (P). When no macrophytes were present (P & PF), systems became phytoplankton-dominated.

Sediments in the model ecosystems were spiked with a cocktail of Fluoranthene-d_{10} (Flu-d_{10}), PCB 29, and PCB 155 in acetone. These chemicals could be analytically distinguished from their respective 'native' counterparts fluoranthene (Flu), PCB 28 and PCB 149, respectively. These chemical couples are assumed to differ only in time of accumulation in the sediment (years to decades for native compounds versus four months for spiked compounds), not in other properties. Concentrations of spiked compounds were also similar in magnitude to concentrations measured in the sediment for their native counterparts. Spiking was performed in approximately 20 cm of water with 7 cm of sediment under dark conditions preventing photolytic PAH breakdown. During spiking, the sediment was kept in suspension by using a large mechanic stirrer [*21*], while sediment in corners of the model ecosystem was suspended manually. In twenty-five minutes one-third of the spike solution (total volume of 0.5L) was slowly injected in the slurry using a continuous dosage system, after which stirring proceeded for another fifteen minutes. Over the next two days, the remaining two-thirds of the spike solution were added in the same way, after which the sediment was allowed to settle for three days. After spiking, the systems were filled to a volume of approximately 600L using clean water from a deep well located at the 'Dreijen' area, Wageningen, The Netherlands.

Six systems were seeded with twenty 10 cm long shoots of *Elodea nuttallii*, obtained from a non-polluted site near Wageningen, The Netherlands. One week later, all model ecosystems were stocked with an invertebrate and zooplankton community from another unpolluted reference site near Wageningen. The added macroinvertebrate community (approximately 75 g wet weight) consisted mainly of *Lymnaea*, *Planorbidae*, *Asellidae*, *Gammaridae*, and *Hirudinea*. Five weeks after macrophyte insertion, three 3 cm-sized carp (*Cyprinus carpio*; obtained from laboratory cultures from the department of Fish Culture and Fisheries at Wageningen University) were added to the model ecosystems which were designed to contain fish. Carp (*Cyprinus carpio*) was chosen as model species for benthivorous fish

typical for shallow lakes. Uncontaminated carp could easily be obtained from a controlled laboratory culture. During the experiment no additional fish food was added.

To enable phytoplankton growth each system received nutrient dosages of 0.9 mg/L N and 0.15 mg/L P on a weekly basis. Also weekly, water levels in the model ecosystems were restored to their initial level to compensate losses due to evaporation and sampling. The experiment lasted for 15 weeks after macrophyte insertion, which is sufficiently long to reach maturity in the systems, but not so long that macrophytes start to decay [*29*]. Lamps were suspended over each model ecosystem, producing an average irradiance at the water surface of 140 $\mu E.m^{-1}.s^{-1}$ and a 14:10 h light: dark photoperiod.

Sampling

Sampling occurred four months after start of the experiment. Suspended solids samples were obtained by filtering depth-integrated water samples over 0.8 µm filters (NC45, Schleicher and Schuell). Sediment was sampled randomly using five Perspex tubes (Ø 2.5 cm). The upper 5 cm of these samples were pooled and homogenized per system for analysis.

When present, floating algal biomass (FAB) was collected by scooping it from the water surface using a 500 µm sieve. All present macrophyte biomass was harvested, weighed and a representative portion was used for PCB/PAH analysis. Periphyton was mainly present on the walls of the model ecosystems. To collect periphyton, about 2000 cm^2 of wall area was scraped off with an aquarium net, after which periphyton was immediately transferred into glass containers. Fish were caught using a small net and killed using metacaine. Macroinvertebrates were sampled by means of core and net samples. Core sampling occurred with a plastic core (29 cm length, 29 cm width, 100 cm height), which was pressed into the sediment after which the enclosed sediment layer was removed and sieved (mesh size: 500 µm) to extract sediment-burrowing taxa, mainly oligochaetes. Two core samples per model ecosystem were taken and numbers and biomass of invertebrates were corrected for the total sediment surface. After sampling, the macroinvertebrates were counted and identified to the highest possible level of taxonomic resolution. Subsequently, macroinvertebrates were divided into oligochaetes and remaining invertebrates (further referred to as mixed fauna). For gut clearance they were kept overnight in aerated glass containers with filtered water from the model ecosystems in a 6°C dark climate room. Spilled gut contents were removed and macroinvertebrates were rinsed

with Barnstead Nanopure® water (Sybron-Barnstead, Dubuque, IA, USA). Zooplankton was sampled using a Perspex tube (length: 0.4 m; volume: 0.8 L). Sub samples were collected until a representative 5L sample had been obtained. The 5L sample was concentrated by means of a plankton net (Hydrobios, Kiel, Germany; mesh size: 55 µm) and was preserved with formalin (final volume: 4%). Cladocera and copepods were counted and identified using a binocular microscope, while rotifers were counted and identified using an inverted microscope. Abundances were adjusted to numbers of organisms per liter. For zooplankton PCB and PAH analysis the remaining model ecosystem volume (about 400L) was filtered over the same net. All storage materials for PCB/PAH samples were pre-rinsed with picograde acetone. All samples for PCB/PAH analysis were freeze-dried and stored in brown glass jars at – 20 °C until analysis.

Analytical procedures

Chemicals. NH_4NO_3 and KH_2PO_4 (both >99% purity) were obtained from Merck (Darmstadt, Germany). PAHs (anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(k)fluoranthene, benzo(ghi)perylene, chrysene, dibenzo(ah)anthracene, indeno(123)pyrene, phenantrene, fluoranthene, pyrene and 2-methylchrysene) were obtained from Sigma Aldrich (Zwijndrecht, The Netherlands). PCBs (IUPAC numbers 18, 20, 28, 31, 44, 52, 101, 105, 118, 138, 143, 149, 153, 170, 180, 194, and HCB) were purchased from Promochem (Wesel, Germany). Acetone used for spiking was picograde quality (Promochem). Other chemicals used for extraction and cleanup are described in [*28*].

Samples used for quantitative analyses (in triplicate) were dried at 105 °C and ashed at 550 °C until constant weight to obtain dry weight and organic matter content. Total PCB and PAH concentrations were determined through a 16-h Soxhlet-extraction with hexane:aceton (3:1 v:v) followed by detection with GC-ECD, as described in [*26,30*]. 6-h Tenax-extractable concentrations in sediment were determined according to [*26*]. With every ten samples, one sample to determine clean up recoveries was included. Cleanup recoveries for 48 Soxhlet-extracted samples averaged 94 ± 4 (s.d.) % for PAHs and 97 ± 9 % for PCBs and analytes in reference samples were typically within error limits of reported values. All samples were corrected for cleanup recoveries and blanks.

Data analysis

Data analysis addressed sum parameters ΣPCB and ΣPAH and six key parameters. These parameters were PCB 28, PCB 149 and Flu (native), and PCB 29, PCB 155, and Flu-d_{10} (spiked). They were selected to represent lower chlorinated PCBs (PCB28/29), higher chlorinated PCBs (PCB149/155), and PAHs. Since PCBs have a broad range of K_{OW} values, which determines their behavior in the environment, ΣPCB is also divided into lower and higher chlorinated congeners (in our study ΣPCBlow comprised HCB, PCB 18 till PCB 52 and ΣPCBhigh PCB 101, 105, 118, 138, 149, 153, 155, 170, 180, and 194).

Threshold levels for p were 0.05 for all statistical analysis. All PCB and PAH data were log-transformed before analysis. Complex parameters, e.g., sumPCB (ΣPCB), were calculated before being log-transformed. PCB and PAH data below detection limits were replaced by half of the detection limit for that specific congener in that specific sample. The influence of fish and macrophyte presence on PCB and PAH levels in the system compartments (sediment, suspended solids, macrophytes, periphyton, FAB, zooplankton, oligochaetes, mix fauna, and fish) was analyzed using ANOVA (both two-way and one-way analysis) within the statistical software package SAS, version 9.1. Using this ANOVA approach the effect of the presence of fish and/or macrophytes on the HOC levels in the several compartments was analyzed on the congener level. Detailed results of the ANOVA calculations will not be included in this paper, but are available on request.

Statistical tests were applied to water quality variables, species abundance, and HOC data. The distribution of invertebrates over the different types of model ecosystems was analyzed using redundancy analysis ordination technique (RDA), the constrained form of principal component analysis [*31*]. Prior to RDA analysis, macroinvertebrate data were ln(2x+1) and zooplankton data ln(10x+1) transformed, where x is the abundance data (for rationale, see [*32*]), and then grouped together in a new invertebrate data set. RDA was performed using the CANOCO computer program, version 4.02 [*33*]. A Principal Response Curve (PRC) analysis of the HOC data was also performed. For more details on this type of analysis see also [*31,34*]. In the present PRC analysis the treatment containing macrophytes and fish (MF) was regarded as control treatment. In this treatment all compartments, including fish and macrophytes, were present which enables comparison with other treatments. Instead of sampling points in time the present experimental set-up yielded sampling points in different system compartments (e.g., sediment, suspended solids, macrophytes, periphyton, FAB, zooplankton, oligochaetes, mix fauna, and fish), which can be plotted on the x-axis. However, this resulted in an unbalanced design since not all

compartments were present in the analysis. Thus, the compartment fish could only be analyzed in the treatments MF and PF, which contained fish, and logically not in treatments M and P, in contrast to compartment zooplankton, which was present in all four treatment types.

Results and Discussion

General characteristics and ecology

Water quality variables (dissolved oxygen, DO, pH, and conductivity) are presented in Table 5.1. Of these variables, only pH differed significantly between macrophyte and phytoplankton-dominated systems at the end of the experiment ($p < 0.01$; average levels 10.0 and 9.0 respectively). DO was low in the two weeks after spiking but increased rapidly before invertebrates were introduced to the systems. DO levels in phytoplankton-dominated systems (8.0 ±2.0 mg/L) were lower than in macrophyte-dominated systems (8.8 ±1.9 mg/L), but the difference was not significant. This indicates that conditions in all systems were equal, apart from the presence of plants and/or fish and consequently that any differences observed in invertebrate communities between systems were caused by the presence of plants and/or fish. These variables are within normal range for the species present [*35,36*], which suggests sufficient agreement between model ecosystems and natural systems.

Figure 5.2 shows results of the RDA analysis of the invertebrate abundance data. The snail *Lymnaea stagnalis* is plotted in the upper left quadrant of the figure near the treatment code M indicating that in this treatment relatively more *Lymnaea* are present. Taxa like the bivalve *Pisidiidae* in the opposite quadrant (lower right quadrant) are relatively rare in the M treatment. Figure 5.2 therefore indicates that most macroinvertebrate species are found when macrophytes are present but fish are not (M). When fish is present (PF and MF) only robust macroinvertebrate species with shells (*Planorbidae* and *Pisidiidae*) or hard exoskeletons (*Agabus* sp.), which can withstand predation by these fish, are found. In systems containing fish relatively more zooplankton is found, especially rotifers and copepods. These taxa are small, reproduce relatively fast, and are agile which makes them harder to predate and thus enables them to coexist with fish. Without fish (M and P), these taxa are relatively less abundant because in these systems they are out-competed and predated by larger zooplankton and macroinvertebrates. Since these responses are reported earlier [*22,37*] in field systems this illustrates that test systems used in this experiment comprise realistic food webs. Combined with the observed growth (from 3 ± 0.3 cm and 0.5 ± 0.13 grams to 6.7 ± 0.7 cm and 4.2 ± 1.4 grams) of the fish, it can be

concluded that the systems were able to sustain small fish for at least a four-month period. Grift et al. [38] reported approximately 2.1 YOY (young-of-the-year) fish.m^{-2} in 3 shallow floodplain lakes alongside the river Waal, The Netherlands. Copp [*39*] estimates a YOY biomass of 11.7 g.m^{-2} in the Upper Rhône River catchment (in systems that were comparable to our experimental systems). Our test systems were stocked with 2.5 fish.m^{-2} and contained a fish biomass of 10.9 g.m^{-2} (based on wet weight) illustrating a good resemblance between our experiments and field conditions [*38,39*].

Table 5.1. *Water quality variables presented as geometric means per treatment.*

Day	Dissolved Oxygen				pH				Conductivity			
	M	MF	P	PF	M	MF	P	PF	M	MF	P	PF
1	2.3	3.1	2.5	2.7	7.5	7.5	7.5	7.5	413	414	406	410
8	0.5	0.4	0.8	0.8	7.4	7.4	7.4	7.5	407	409	401	405
22	1.0	1.1	0.9	0.9	7.4	7.4	7.5	7.4	389	390	390	452
29	3.8	3.6	3.7	3.9	7.5	7.5	7.5	7.4	369	370	369	370
36	6.2	5.9	4.7	5.4	7.8	7.8	7.7	7.7	379	380	380	379
43	9.8	9.7	9.9	9.7	8.6	8.5	8.6	8.6	376	376	376	380
50	7.2	7	6.9	7.1	8.5	8.4	8.5	8.5	381	378	388	388
57	9.4	9.8	8.4	8.6	8.8	8.6	8.6	8.7	354	354	392	387
64	9.4	9.6	8.7	8.8	8.6	8.7	8.4	8.5	293	282	339	335
71	14	13	13	13	9.2	9.2	8.7	8.8	224	222	277	276
78	11	8.3	9.7	8.4	9.9	8.7	9.2	8.7	205	229	239	267
85	11	9.3	11	9.0	10	9.2	9.5	8.8	214	164	229	274
92	9.3	7.9	8	7.5	10	9.3	9.4	8.8	207	219	224	262
100	8.4	7.7	7	7.1	10	9.5	9.3	8.8	203	216	228	262
106	8.6	7.8	7.3	7.0	10	9.7	9.4	8.9	204	209	228	256
113	7.8	7.5	6.5	6.1	10	9.8	9.3	8.6	204	205	237	262
120	8.1	7.8	7.0	6.4	10	9.8	9.1	8.7	201	196	239	267
127	7.6	6.6	6.2	5.9	10	9.8	9.3	8.7	197	201	242	270

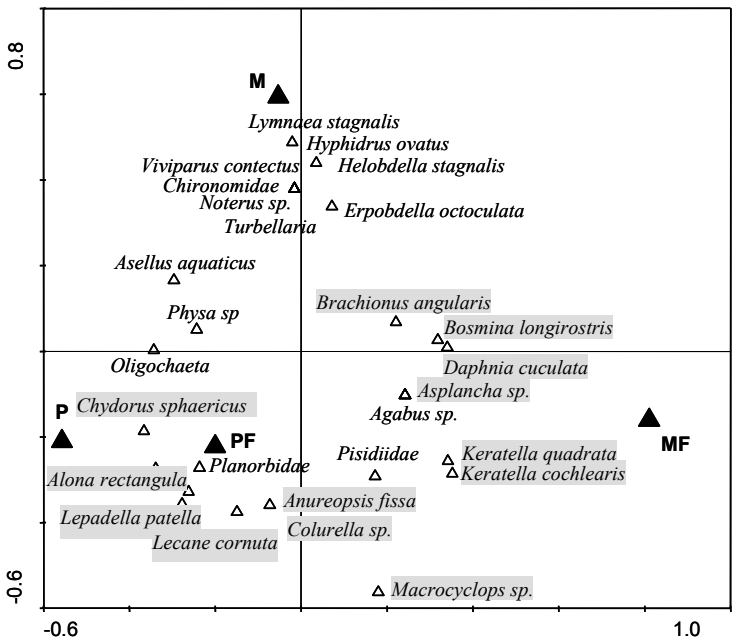

Figure 5.2. *Results of RDA analysis of the invertebrate abundance data. Zooplankton taxa are highlighted in the graph. M = macrophyte-dominated without fish, MF = macrophyte-dominated with fish, P = phytoplankton-dominated without fish, and PF = phytoplankton-dominated with fish. Species plotted close to a treatment type data point, are relatively much present in that treatment.*

HOC mass distribution

On average, sediment pools contained 99.6 (±0.4) % of the total HOC mass in all four system types. The mass distribution of biota, ΣPCBs and ΣPAHs is presented in Table 5.2 and Figure 5.3. In macrophyte-dominated systems, macrophytes represent the main part of biomass (Figure 5.3A). Less macrophyte and more periphyton (algae attached to the model ecosystem wall) biomass are present when fish is present in the macrophyte-dominated systems (M and MF). When no macrophytes are present (P and PF) total biomass in the systems is mainly composed of periphyton. Figures 5.3B and C show how the mass of ΣPAHs and ΣPCBs, which was originally for 100% bound to the sediment, is redistributed amongst different system compartments at the end of the experiment. These figures also indicate that ecological structure strongly affects the amounts of ΣPAHs and ΣPCBs which are mobilized from the sediment.

Table 5.2. *Average and standard deviations of amounts of biomass, **Σ**PCB, and **Σ**PAH measured at the end of the experimental period in the test systems.*

		M[a]		MF		P		PF	
		average	s.d.	average	s.d.	average	s.d.	average	stdev
Biomass	Sediment	6.4×10^4	3.2×10^3	6.4×10^4	4.4×10^3	6.2×10^4	8.7×10^3	6.3×10^4	2.3×10^3
(gr)	Susp. solids	4.3	0.9	6.9	3.7	2.1	0.9	20	14
	Macrophyte	645	52	486	210	n.p.	n.p.	n.p.	n.p.
	Periphyton	n.p.	n.p.	27	44	167	55	33	32
	FAB	2.3	0.9	3.6	0.5	2.2	0.05	1.7	1.8
	Zooplankton	0.32	0.16	0.31	0.01	0.82	0.40	0.61	0.29
	Oligochaetes	8.0	0.6	3.2	2.9	6.4	3.2	3.4	1.5
	Mix fauna	2.1	0.5	1.0	0.01	1.3	1.0	0.65	0.17
	Fish	n.p.[b]	n.p.	2.3	0.3	n.p.	n.p.	3.4	0.84
ΣPCB	Sediment	1.4×10^4	3.5×10^3	1.3×10^4	2.6×10^3	1.5×10^4	1.3×10^3	1.4×10^4	3.8×10^3
(µg)	TENAX	2.1×10^3	1.3×10^2	2.2×10^3	6.4×10^2	2.8×10^3	4.1×10^2	2.8×10^3	1.5×10^2
	Susp. solids	1.9	0.99	3.3	0.8	1.7	0.68	13	9.7
	Macrophyte	52	7.0	67	59	n.p.	n.p.	n.p.	n.p.
	Periphyton	n.p.	n.p.	3.0	5.1	31	10	7.1	6.2
	FAB	0.37	0.15	0.60	0.17	0.37	0.02	0.48	0.44
	Zooplankton	0.28	0.12	0.28	0.08	0.62	0.34	0.99	0.75
	Oligochaetes	2.1	0.80	0.53	0.45	2.5	0.98	1.2	0.75
	Mix fauna	0.77	0.51	0.30	0.20	0.54	0.11	0.13	0.06
	Fish	n.p.	n.p.	3.1	0.52	n.p.	n.p.	5.5	1.3
ΣPAH	Sediment	3.5×10^5	7.6×10^4	4.1×10^5	7.3×10^4	4.9×10^5	1.3×10^5	4.7×10^5	1.8×10^5
(µg)	TENAX	1.9×10^4	7.1×10^2	1.9×10^4	3.8×10^3	3.5×10^4	1.9×10^4	2.8×10^4	1.2×10^4
	Susp. solids	21	19	61	29	27	24	221	188
	Macrophyte	394	157	582	616	n.p.	n.p.	n.p.	n.p.
	Periphyton	n.p.	n.p.	34	57	236	90	104	90
	FAB	2.3	0.33	3.0	0.64	1.8	0.36	3.7	3.3
	Zooplankton	1.8	1.5	1.8	0.14	1.2	0.69	1.2	1.1
	Oligochaetes	6.7	0.62	2.1	1.9	7.2	3.8	3.2	0.26
	Mix fauna	3.3	2.0	0.26	0.14	1.5	0.68	0.30	0.30
	Fish	n.p.	n.p.	0.33	0.15	n.p.	n.p.	0.46	0.06

[a] M = macrophytes, no fish; MF = macrophytes, fish; P=phytoplankton, no fish; PF=phytoplankton, fish

[b] n.p. = not present.

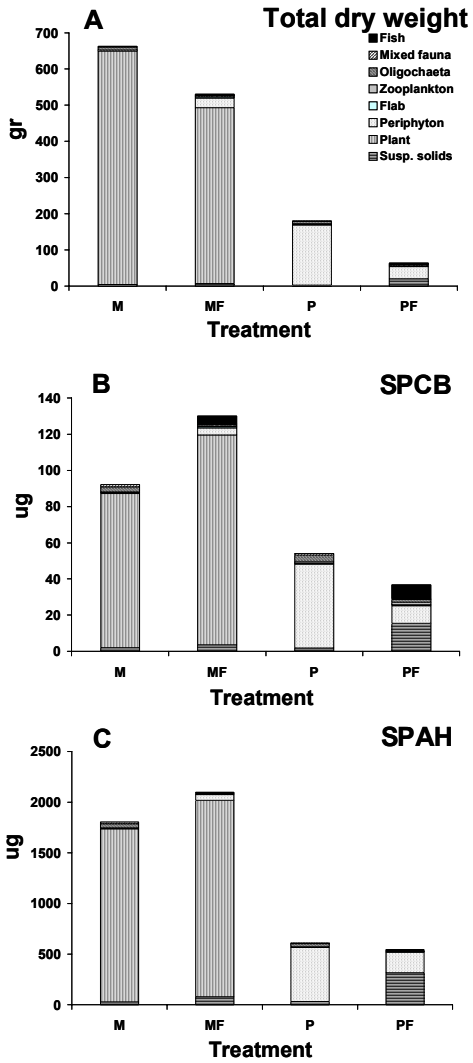

Figure 5.3. *Panel A shows the total amount of biomass (as gr dry weight) per compartment (present in each type of test system (n = 3). Panel B and C present the same picture for the total amount of* ***Σ****PCBs and* ***Σ****PAHs, respectively. Sediment mass (about 63.2 kg dry weight per model ecosystem) is excluded from the graph.*

When sediment is not taken into account, macrophytes (when present) dominate the mass distribution followed by periphyton and suspended solids (Figures 5.3B and C). In general, biological compartments that have a large total biomass also contain a large amount of ΣPAHs and ΣPCBs (Figures 5.3A-C). Nevertheless, although macrophyte biomass is larger without fish (M) than with fish (MF), the total amount of ΣPAHs and ΣPCBs contained in the systems without fish was smaller (Table 5.2), although not significant due to within-treatment variation (ANOVA, $p > 0.05$; results not shown).

This suggests that bioturbation of the sediment by fish results in a higher amount of ΣPAHs and ΣPCBs available for the macrophytes. It is unclear if these ΣPAHs and ΣPCBs are indeed bioaccumulated by or sorbed to the macrophytes. Although macrophytes were washed carefully before analyses, it cannot be excluded that in the presence of fish a higher amount of suspended solids is trapped in the macrophyte/periphyton complex, which was not washed out, thus resulting in a higher amount of ΣPAHs and ΣPCBs in this macrophyte compartment.

For periphyton, exposure via the water phase seems to be strongly influenced by the presence of macrophytes, which seem to act as a sink for the contaminants and consequently lower the amount of ΣPAHs and ΣPCBs available for uptake through the water phase. PCB and PAH uptake in the mix fauna is not governed by presence of such a possible sink but primarily by fish predation. Without fish more invertebrates are present (Figure 5.2), and consequently more ΣPAHs and ΣPCBs were found in this compartment. In fish (which was stocked in equal numbers) more PCBs were found when macrophytes were absent (PF). The latter was not observed for PAHs, most likely because fish are known to metabolize these compounds [*40,41*].

Mobilization by biomass

It appears that macrophytes mobilize substantial amounts of HOCs out of the sediment, and fish even further increase this mobilization. This is illustrated in Figure 5.4 where the relation between amounts of ΣPAHs and ΣPCBs mobilized from the sediment and total system biomass is shown. We assume that mobilization is primarily from the fast desorbing fraction, as quantified through the 6-h Tenax-extractable concentration [*42*].

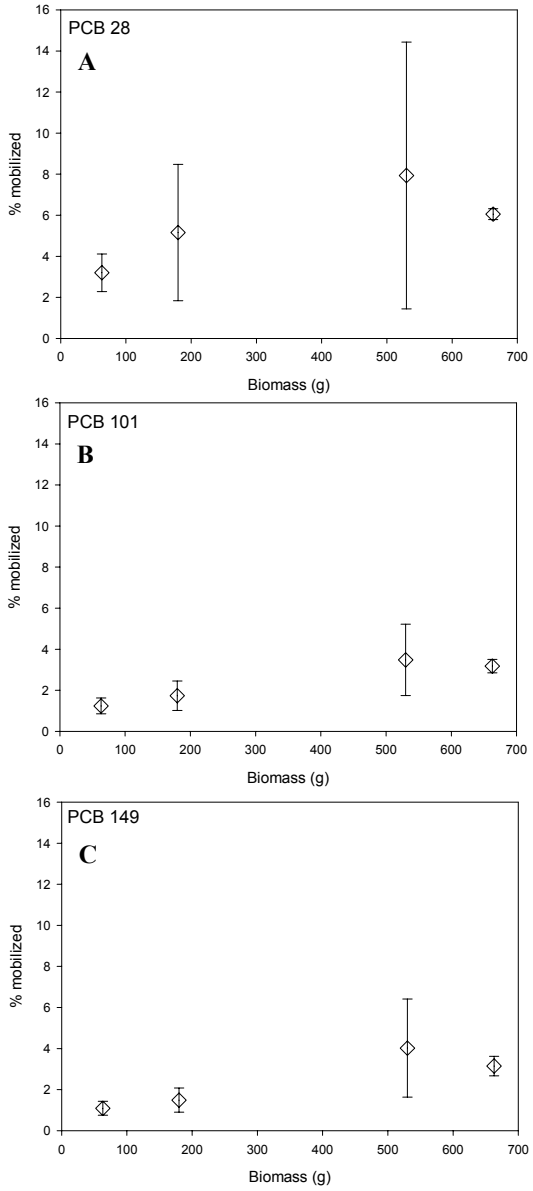

Figure 5.4. *Percentage of PCBs mobilized from the sediment (6-h Tenax-extractable) as function of total biomass in the test system. Systems are ranked in increasing biomass: P, PF, MF, M. Error bars show standard deviations.*

Mobilization is calculated as:

$$\%\text{mobilized} = \frac{\text{mass}_{\text{HOC,compartment,end}}}{\text{mass}_{\text{HOC,compartment,end}} + \text{mass}_{\text{HOC,tenax,end}}} \times 100\% \quad (1)$$

with $\text{mass}_{\text{HOC,compartment,end}}$ = the amount of HOC in a certain compartment at end of the experimental period; and $\text{mass}_{\text{HOC,tenax,end}}$ = the amount of HOC present in the 6-h Tenax-extractable fraction at end of the experimental period. In general, Figures 5.4A-C suggest that more PCBs are mobilized when total system biomass is higher. This trend can be observed for both lower (PCB 28), intermediate (PCB101), and higher (PCB149) chlorinated congeners. However, due to large variations between replicate treatments no significant differences between treatments were observed. Partitioning of individual PCBs and PAHs from 6-h Tenax-extractable fractions to other compartments is further illustrated in Figure 5.5 and Table 5.3, where concentrations in plants, oligochaetes, rest fauna, and fish (at t = 4 months) are plotted against the 6-h Tenax-extractable concentrations in the sediment at t = 4 months, according to:

$$\frac{\left(\frac{\text{mass}_{\text{HOC,compartment,end}}}{\text{mass}_{\text{lipids,compartment,end}}}\right)}{\left(\frac{\text{mass}_{\text{HOC,tenax,end}}}{\text{mass}_{\text{OC,end}}}\right)} = \frac{y}{x} = a \quad (2)$$

with a = slope of the regression; $\text{mass}_{\text{lipids,compartment,end}}$ = the amount of lipids in that specific compartment at end of the experimental period; and $\text{mass}_{\text{OC,end}}$ = the amount of organic carbon present in sediment at end of the experimental period.

Since the experiment was performed in a closed laboratory environment, external PAH or PCB influxes were assumed to be not significant. Consequently, when no PAHs or PCBs are present in the 6-h Tenax-extractable fraction, then also none will be found in macrophytes and the y-x intercept can be forced through zero ($y = ax$). The slopes of the y-x regressions (Table 5.3) can be considered as ecosystem based, semi-field derived lipid and organic carbon normalized biota to sediment accumulation factors (BSAF) for PCBs after 4 months of exposure. Figure 5.5 and Table 5.3 show that for macrophytes this slope of the regression lies between 1 and 2 which falls within the range of 1-2 suggested by the equilibrium partitioning theory (EPT) [*43-45*]. For oligochaetes, mix fauna, and fish the slope of the regression increases to 2.4 - 5.2, 3.5 - 9.8, and 8.4 - 9.2, respectively (Figure 5.5 and Table 5.3).

Table 5.3. *Regression results of the distribution of PCB and PAH congeners in the 6-h Tenax-extractable fraction versus macrophytes, oligochaetes, mix fauna, and fish at the end of the experimental period. Since the regression is assumed to start in the origin of the graph this results in y = ax.*

		PCB		PAH	
		a	R^2	a	R^2
Plants	M	1.51	0.86	0.88	0.72
	MF	1.73	0.83	2.02	0.64
Oligochaetes	M	5.20	0.82	0.016	0.76
	MF	2.40	0.84	0.004	0.53
	P	3.90	0.84	0.63	0.48
	PF	5.24	0.70	0.96	0.49
Rest fauna	M	7.42	0.96	0.007	0.74
	MF	9.79	0.60	0.001	-0.04
	P	5.50	0.92	0.79	0.45
	PF	3.45	0.69	0.39	0.41
Fish	MF	9.21	0.71	0.0003	0.41
	PF	8.44	0.77	0.046	0.44

These values exceed the ones being predicted by EPT and increase with trophic level, which suggests that biomagnification is relevant for these compartments. Note that data points in Figure 5.5 relate to different PCB congeners and are randomly distributed around the regression line. This suggests that BSAFs in this case are not significantly different for different congeners. Comparison of 95% confidence intervals of each regression revealed that for macrophytes all intervals overlapped and consequently M and MF did not differ statistically. For oligochaetes the MF treatment differed from the other treatments (M, P, and PF). This difference may relate to the lower numbers of worms in treatments containing fish plus the presence of macrophytes (acting as competing 'sink' for PCB). For mix fauna the PF treatment differed from the others, fish predation and lack of refugia (e.g., macrophytes) resulted in a different mix fauna community in this treatment (Figure 5.2), with probably different uptake and depuration mechanisms and consequently different partitioning of PCBs. No difference was observed for fish. PAH data were not used for these analyses, because of possible PAH degradation and larger uncertainties between PAH fast desorbing fractions and 6-h Tenax extractable concentrations [*40,46*].

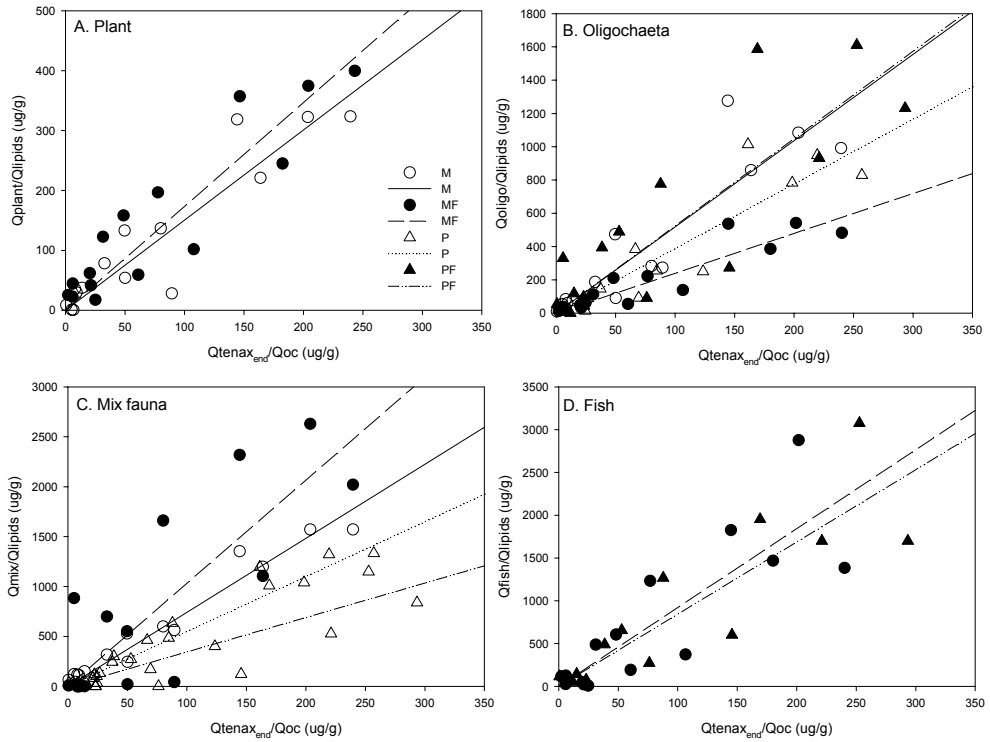

Figure 5.5. *Distribution of PCB congeners in the 6-h Tenax-extractable fraction versus macrophytes (A), oligochaetes (B), mix fauna (C), and fish (D) at the end of the experimental period.*

Effects of macrophytes and fish on mass distribution of HOCs

The presence of fish reduced the amount of HOCs in oligochaetes and mix fauna by a factor 2.7 (PCBs) and 3.4 (PAHs). Due to fish predation they comprise less biomass in the MF and PF systems and consequently also contain a lesser total amount of PCBs and PAHs. The presence of fish also resulted in a significant increase of higher chlorinated, less mobile PCBs, with exception of spiked PCB155, in suspended solids. Probably, due to intense interaction with the water phase, less hydrophobic (low chlorinated) or less sequestered PCBs (like PCB 155) can partition to the water phase faster and be scavenged by other compartments resulting in this discrepancy.

Figure 5.6 shows the results of PRC analysis of the PCB and PAH data. In the PRC graph deviations from the control (in this case the MF treatment) are presented on the

C_{dt}-axis while on the x-axis the different system compartments are plotted. The weight on the B_k-axis on the right-side of the diagram can be interpreted as the affinity of each congener with the response in the diagram [*47*]. In this type of analyses, deviations less than 0.5 are not very informative, and as a consequence for PCBs (Figure 5.6A) only the deviations of the compartments periphyton and mix fauna are relevant. Since all B_k-scores are positive no congeners decrease in the samples. PCB 031 (with the highest positive weight on the B_k-axis) is indicated to have increased the most in samples with the highest C_{dt} score; whereas the weight of PCB 170 indicates that its increase is smallest of all congeners. Thus, especially lower chlorinated and more mobile congeners are found in treatments deviating from the control (MF) (Figure 5.6A). The corresponding eigen-values of the PRC analysis are 0.068 and 0.009 for the first and second canonical axis, respectively. The fact that the first eigen-value is more than 7 times bigger than the second value indicates that congener response is dominated by one factor. Since the distribution of PCBs on the B_k-axis shows that lower chlorinated congeners have higher scores than higher chlorinated congeners this factor is therefore most likely $\log K_{OW}$. Deviations in PAHs between systems types are found in compartments periphyton, mix fauna, and also in suspended solids (Figure 5.6B). Since in fish-free systems the suspended solids compartment contained lower amounts of Flu-d_{10} and benzo(e)pyrene (BeP) it appears that the concentrations of PAHs and PCBs in suspended solids in these systems is altered by fish-mediated resuspension of sediment. Unlike in the PCB response, in the PAH response no overall governing factor could be observed.

While the presence of fish does not alter FAB biomass it significantly lowers total amounts of all PAHs except Flu-d_{10} measured in the FAB compartment (data not shown). Because of the increase in Flu-d_{10}, the decrease in all other PAHs is not reflected in ΣPAH (results not shown; available on request). Since FAB floats on the water surface its only exposure route is via the water phase meaning that it competes for PAHs and PCBs with e.g., suspended solids, which are more abundant in fish containing systems. We hypothesize that this lowers the amount of PAHs and PCBs in FAB. Flu-d_{10} is less sequestered in the sediment and thus more available and abundant in the aqueous phase.

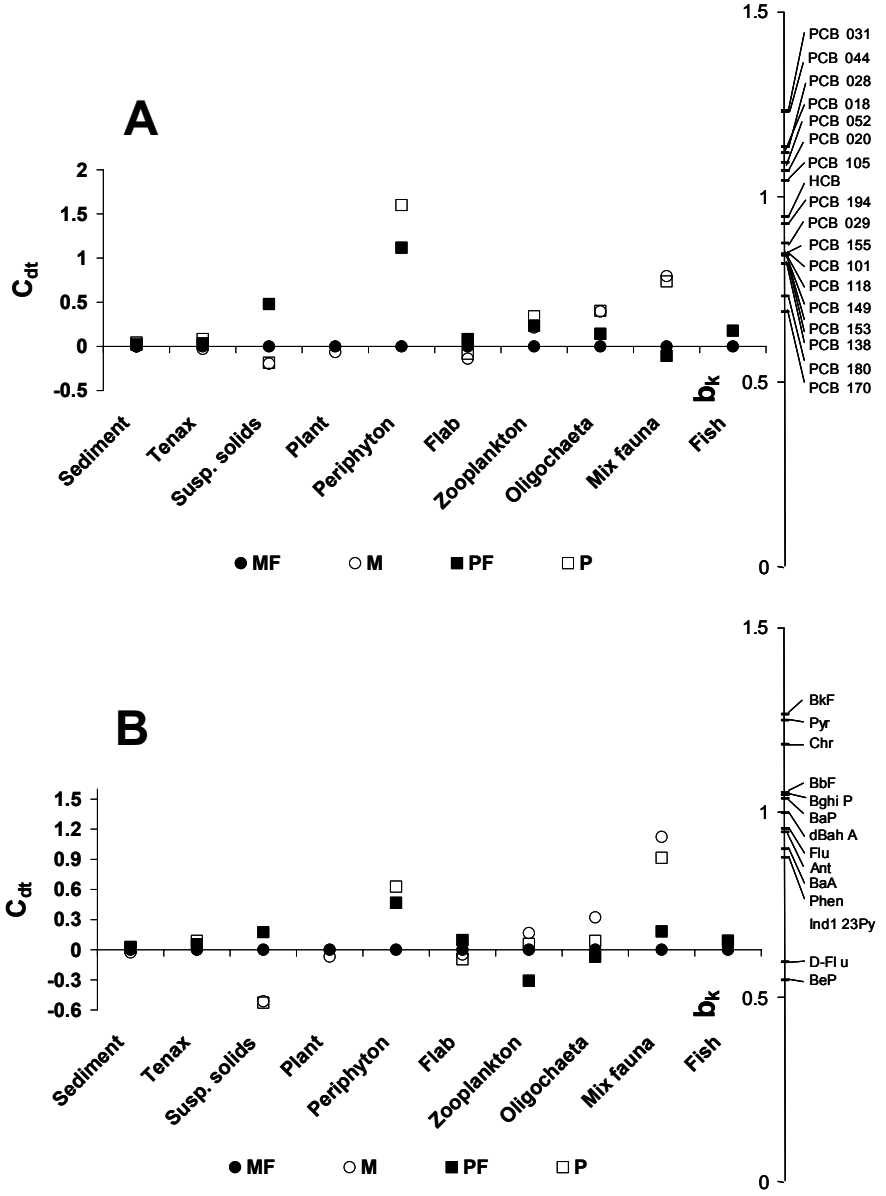

Figure 5.6. *Results of the Principal Response Curve (PRC) analysis of PCB (A) and PAH (B) data based on the mass distribution. On the x-axis the different system compartments are plotted and on the y-axis (Cdt) the deviation of the M, P, and PF systems from the MF systems (which are considered controls) is presented. On the Bk-axis on the right side of the diagram the congeners are plotted. MF= macrophyte-dominated with fish, M= macrophyte-dominated, PF= phytoplankton-dominated with fish, P= phytoplankton-dominated.*

As discussed before, presence of macrophytes results in significant differences in masses of PCBs and PAHs in the sediment, TENAX, periphyton, and fish compartments. The effect is most significant (ANOVA; $p < 0.05$) for added compounds PCB 29, 155, and Flu-d_{10} but was also observed for PCBs 18, 20, 28, and 31 (total concentrations in sediment) and PCB 44, 52, 101, and 105 (6-h Tenax-extractable concentrations). Macrophyte presence decreases amounts of periphyton and consequently has a significant influence on the total periphyton HOC content (ANOVA; $p < 0.05$). However, macrophyte presence also significantly influences other compartments like the sediment, which does not differ in size among treatments. This indicates that macrophytes, when present, provide a sink and can consequently 'drain' the sediment.

There is a very consistent difference between amounts of spiked and native HOCs observed in different system compartments (results available on request, see also Moermond et al. [*46*]). Especially spiked compounds are bioaccumulated in the biotic compartments, with a larger difference for the less hydrophobic PCB29 than for the more hydrophobic PCB155. For PCB 29 and its native counterpart PCB 28, the difference was statistically significant in the Sediment, TENAX, zooplankton, oligochaetes, and mix fauna compartments, while for PCB 155 and its native counterpart PCB 149 this was only the case for the TENAX compartment. A statistical significant difference between amounts of Flu and Flu-d_{10} could be observed in sediment, TENAX, FAB, oligochaetes, and mix fauna. In all cases differences were more pronounced when fish or macrophytes were present.

Lipid normalized HOC concentrations

Toxicological effects are related to actual concentrations in biota [*48*], rather than total mass distributions. Therefore, we also evaluated effects of ecological structure on concentrations of PAHs and PCBs in biota. Note that because all model ecosystems used the same sediments, statistical tests among treatments by using biota concentrations yield the same results as would have been obtained if biota sediment accumulation factors (BSAFs) were used.

In Tables 5.4 and 5.5 the influence of fish and macrophytes on ΣPCB and ΣPAH concentrations in different compartments of the test systems is presented. Data on individual PCBs and PAHs is available on request Table 5.4 shows that the presence of fish seems to have the largest influence on PCB and PAH concentrations in macrophyte and mix fauna compartments. When fish is present, macrophytes contain a significantly higher concentration of spiked PCBs. Although less significant (p =

0.08), this also seems to be the case for some of the higher chlorinated native congeners (PCB 105, 118, 149, 153, and 155). It is plausible that bioturbation by fish mobilized these PCBs, resulting in higher water concentrations and consequently a higher exposure to PCBs for the macrophytes. However, it is unlikely that only higher chlorinated PCBs are mobilized. Probably, lower PCBs are also mobilized from the sediment but may be accumulated less in the macrophyte compartment due to increased desorption from the plant material and scavenging by other compartments. Besides, in the absence of fish macrophytes have a significantly higher percentage of organic carbon and a higher lipid fraction (both $p = 0.04$), consequently diluting their lipid-normalized PCB concentrations. Probably, both processes amplify possible differences between treatments. The same response, although not statistically significant, can also be observed for PAH concentrations.

For the mix fauna compartment, the presence of fish did not only result in a lower PCB 28 concentration (Table 5.4) but also in significantly lower HCB, PCB 18, 31, 44, and 52 concentration (for all, $p < 0.04$) compared with the no-fish situation. On average ΣPCBlow (HCB, PCB 18, 20, 28, 31, 44, and 52) was a factor 3.2 lower when fish was present than when fish was not present. Since the percentage lipids of the compartment was a factor of 1.4 higher and significantly different ($p = 0.01$) when fish were not present, this difference is due to a concentration effect rather than a dilution effect. Thus, the difference is most probably caused by the difference in species composition of the mix fauna compartment between non-fish and fish containing systems (Figure 5.2).

Table 5.5 shows that in the presence of macrophytes both sediment and TENAX compartments contain lower concentrations of ΣPCBs and ΣPAHs although the treatment effect is not always statistically significant. Regarding individual compounds, differences are most clear with spiked (relatively mobile) compounds (results not shown) but are also observed in native PAHs. In systems with macrophytes less periphyton is present, and consequently a lower total amount of HOCs is found in this compartment (Figure 5.3). Additionally, Table 5.5 shows that not only total amounts, but also concentrations of PCBs and PAHs decrease when macrophytes are present, although this is only significant for PCBs. Concentrations of PCBs in oligochaetes are considerably lower (factor 1.3 to 1.6) when macrophytes are present, but this is not statistically significant. This lack of statistical significance is due to a high variation in numbers of oligochaetes, biomass, and lipid content within MF and P treatments.

Table 5.4. *Mean concentrations of* ***Σ****PCBs and* ***Σ****PAHs (mg/kg; ± standard deviation) in biota and results of the ANOVA analysis for the presence of fish as a determining factor. p-values are based on two-way ANOVA results of log-transformed data.* ***Σ****PCB$_{low}$ contains HCB, PCBs 18, 20, 28, 31, 44, and 52.* ***Σ****PCB$_{high}$ contains PCBs 101, 105, 118, 138, 149, 153, 155, 170, 180, and 194.*

		ΣPCB		ΣPCB$_{low}$		ΣPCB$_{high}$		ΣPAH	
Compartment	F[a]	mean	*p*	mean	*p*	mean	*p*	mean	*p*
Sediment	N	11.2 ± 1.5	0.64	4.4 ± 1.2	0.44	6.6 ± 1.3	0.83	319 ± 63	0.31
	Y	11.7 ± 4.4		5..0 ± 2.2		6.7 ± 2.3		379 ± 205	
Tenax	N	1.8 ± 0.4	0.46	0.82 ± 0.31	0.61	0.99 ± 0.01	0.45	19 ± 10	0.24
	Y	2.1 ± 1.0		0.91 ± 0.93		1.0 ± 0.3		20 ± 14	
Susp. solids	N	3.4 ± 4.1	0.94	0.35 ± 1.7	0.45	2.8 ± 2.9	0.97	7.6 ± 107	0.39
	Y	3.5 ± 4.5		0.75 ± 1.8		2.6 ± 2.8		52 ± 78	
Macrophytes[b]	N	1.9 ± 0.5	0.08	0.27 ± 0.12	0.20	1.6 ± 0.4	0.06	14 ± 4.5	0.51
	Y	3.6 ± 1.7		0.68 ± 0.42		2.9 ± 1.3		27 ± 21	
Periphyton	N	4.0 ± 0.8	0.77	1.3 ± 0.33	0.70	2.7 ± 0.5	0.74	30 ± 11	0.43
	Y	0.19 ± 2.9		$6.1 \times 10^{-2} \pm 0.98$		0.12 ± 1.9		44 ± 37	
FAB	N	3.4 ± 0.7	0.46	0.53 ± 0.21	0.57	2.9 ± 0.6	0.44	19 ± 7.7	0.56
	Y	4.4 ± 3.2		0.83 ± 1.0		3.6 ± 2.2		27 ± 31	
Zooplankton	N	4.1×10^{-2} ± 7.2[c]	0.52	1.0×10^{-2} ± 1.1[c]	0.52	$2.8 \times 10^{-2} \pm 6.1$[c]	0.52	46 ± 41	0.54
	Y	3.9×10^{-3} ± 12.5[c]		$1.1 \times 10^{-3} \pm 1.3$[c]		$2.6 \times 10^{-3} \pm 11.1$[c]		8.4 ± 54	
Oligochaeta	N	5.9 ± 3.2	0.34	0.76 ± 0.15	0.33	5.1 ± 3.3	0.34	18 ± 2.8	0.29
	Y	1.2 ± 4.2		0.18 ± 0.83		0.97 ± 3.7		20 ± 12	
Mix fauna	N	8.2 ± 3.2	0.42	1.2 ± 0.95	0.08	6.8 ± 2.3	0.65	28 ± 14	0.38
	Y	7.0 ± (5.8)		$9.6 \times 10^{-2} \pm 0.62$		6.6 ± 5.2		8.3 ± 8.1	

[a] N = fish not present; Y = fish present.

[b] No two-way but one-way ANOVA has been used because only two system types could be compared.

[c] Low numbers for the mean are an artefact due to the fact that many compounds in this sample were below detection limits.

Table 5.5. *Mean concentrations of* **Σ***PCBs and* **Σ***PAHs (mg/kg; ± standard deviation) in biota and results of the ANOVA analysis for the presence of macrophytes as a determining factor. p-values are based on two-way ANOVA results of log-transformed data.* **Σ***PCB_{low} contains HCB, PCBs 18, 20, 28, 31, 44, and 52.* **Σ***PCB_{high} contains PCBs 101, 105, 118, 138, 149, 153, 155, 170, 180, and 194.*

		ΣPCB		ΣPCB_{low}		ΣPCB_{high}		ΣPAH	
Compartment	M[a]	mean	*p*	mean	*p*	mean	*p*	mean	*p*
Sediment	N	12.3 ± 4.3	0.26	5.3 ± 2.1	0.17	6.9 ± 2.3	0.42	394 ± 201	0.13
	Y	10.7 ± 1.2		4.2 ± 9.8		6.4 ± 1.4		307 ± 50	
Tenax	N	2.2 ± 0.7	0.14	1.1 ± 0.7	0.21	1.1 ± 0.3	0.09	24 ± 15	0.04
	Y	1.7 ± 0.7		0.70 ± 0.66		0.94 ± 0.08		16 ± 1.7	
Susp. solids	N	5.0 ± 4.9	0.15	0.82 ± 2.1	0.37	3.7 ± 3.2	0.16	13 ± 110	0.68
	Y	2.4 ± 1.3		0.32 ± 0.27		2.0 ± 1.1		30 ± 37	
Periphyton	N	4.0 ± 1.7	0.02	1.3 ± 0.63	0.03	2.7 ± 1.1	0.03	39 ± 34	0.08
	Y	$8.7 \times 10^{-3} \pm 2.5$[c]		$2.9 \times 10^{-3} \pm 0.6$		$5.7 \times 10^{-3} \pm 1.8$[c]		33 ± 8.0	
FAB	N	4.9 ± 2.9	0.56	1.0 ± 1.0	0.79	3.9 ± 2.0	0.53	28 ± 31	0.76
	Y	3.2 ± 0.8		0.46 ± 0.15		2.7 ± 0.7		18 ± 8.3	
Zooplankton	N	0.28 ± 10.8	0.12	$5.1 \times 10^{-2} \pm 1.2$[c]	0.12	0.22 ± 9.7	0.12	4.1 ± 12	0.20
	Y	$5.7 \times 10^{-4} \pm 5.7$		$2.1 \times 10^{-4} \pm 1.0$[c]		$3.4 \times 10^{-4} \pm 4.7$[c]		95 ± 31	
Oligochaeta	N	7.0 ± 3.3	0.24	0.90 ± 0.56	0.22	5.9 ± 3.4	0.25	20 ± 7.0	0.32
	Y	1.0 ± 3.6		0.16 ± 0.59		0.84 ± 3.1		18 ± 10.4	
Mix fauna	N	6.5 ± 3.4	0.40	0.13 ± 1.1	0.32	5.8 ± 2.3	0.43	13 ± 15	0.12
	Y	8.8 ± 5.2		0.92 ± 0.75		7.7 ± 4.8		18 ± 17	
Fish[b]	N	13.1 ± 2.7	0.32	1.4 ± 0.57	0.16	11.6 ± 2.2	0.45	1.1 ± 0.17	0.83
	Y	11.4 ± 3.4		0.80 ± 0.31		10.5 ± 3.3		1.1 ± 0.56	

[a] N = macrophytes not present; Y = macrophytes present.

[b] No two-way but one-way ANOVA has been used because only two system types could be compared.

[c] Low numbers for the mean are an artefact due to the fact that many compounds in this sample were below detection limits.

The presence of macrophytes did not result in a significant difference in individual and total PCB concentrations in fish (Table 5.5) while it did for total amount of higher PCBs (ΣPCB-high) in this compartment (data available on request). Fish in non-macrophyte systems have a slightly higher, moderately significant ($p = 0.06$), biomass (Figure 5.3, Table 5.2) and also a higher amount of lipids. Although this increased biomass is sufficient to contain a significantly higher total amount of PCB mass (ANOVA, $p < 0.5$), PCB concentrations in the fish did not differ between macrophyte and non-macrophyte treatments (Table 5.5).

While the presence of macrophytes generally resulted in lower concentrations of PCBs in suspended solids, periphyton, FAB, zooplankton, oligochaetes, mix fauna, and fish compartments, Table 5.5 shows that this is not the case for PAHs. When macrophytes are present, lower PAH concentrations in Soxhlet and TENAX compartment are measured but PAH concentrations seem to increase in suspended solids, zooplankton, and macroinvertebrates. Possibly, PAHs mobilized from the sediment by macrophytes are also available for compartments which are in close contact to the sediment, such as macroinvertebrates, which reside at or close to the sediment-water interface [*49*], and zooplankton, which is linked to the sediment due to its ability to scavenge organic particles from its top layer [*50*]. These interactions close to the sediment could enable invertebrates to incorporate plant-mobilized PAHs from the sediment and attain a higher concentration of PAHs. This process is also assumed to occur in the fish compartment but since PAHs can be metabolized by fish [*40*] this process is not reflected in final concentrations in this compartment. However, compartments like periphyton and FAB, which are solely exposed to PAHs via the water phase, do not show an increase but even so a decrease in PAH concentration (with exception of Flu-d_{10} and benzo(a)pyrene in the FAB compartment) suggesting that PAHs are less available in the water column.

The differences in ecological structure or trophic status of our test systems, representing meso- and eutrophic conditions, did alter concentrations of PCBs and PAHs in biota. However these effects were not as explicit as in reported field studies, which investigated effects of eutrophication on contaminant cycling in marine benthic systems [*12*] and the effect of lake trophic status on the uptake of persistent pollutants in northern pike (*Esox lucius*) [*13,17*]. A main difference with our study, is that in these studies, the atmosphere was the primary source of HOCs. In contrast, we investigated systems in which the main source of PCBs and PAHs was the sediment. n systems where the main source of HOCs is the inflow via water or atmosphere ([*13, 7*]), phytoplankton has an important role as scavenger of water- or atmosphere-originating HOCs. An increase in phytoplankton density results in a dilution of its HOC concentration [*17*]. However, this process may increase concentrations in other

compartments. An increase in phytoplankton density may result in a higher intake of organic material (phytoplankton or detritus) by invertebrates and thus increase their net HOC uptake [*13*]. In our test systems phytoplankton does not have this crucial role. Since all test systems originally contained the same sediment and concentrations in invertebrates did not differ between systems, it seems that exposure of (benthic) invertebrates to sediment-originating PCBs and PAHs did not differ among system types. Also PCB and PAH concentrations in free-swimming zooplankton were similar among types of test systems, which indicates that exposure via the water phase or phytoplankton food did not differ.

In summary, the presence of fish increases concentrations in macrophytes, suspended solids and mix fauna (only significant for PCB concentrations) through bioturbation of the sediment and active structuring through predation. The hypothesis that macrophytes act as a sink and lower amounts and concentrations of PCBs and PAHs in other compartments is also confirmed. Total amounts and concentrations in sediment and TENAX compartments are lowered when macrophytes are present, thus potentially reducing risks of PCBs and PAHs to benthic and pelagic biota.

Since structure and behavior of tests systems in this study (e.g., species interactions) were similar to what is reported in (semi-)field situations [*22,37*] it is assumed that processes in our systems regarding fate of PCBs and PAHs also resemble those occurring in the field. In our test systems, the presence of young carp greatly impacted the presence of invertebrates and resulted in different species compositions in mix fauna and zooplankton compartments. This structuring influence of benthivorous fish was very important for the invertebrate PCB and PAH content. Additionally, macrophytes were able to mobilize HOCs from the sediment, which has important implications for transport of these compounds. On average, macrophyte-dominated systems yielded 565,9 ± 162.9 (s.d.) gram (dry weight) of plants at a system surface of 1.21m2. This plant biomass contained on average 55.1 ± 34.8 (s.d.) µg ΣPCB and 0.488 ± 0.415 (s.d.) mg ΣPAH. Recalculating this to field proportions, results in an mobilization from the sediment pool to macrophytes of 0.46 gr ΣPCB and 4.0 gr ΣPAH per hectare during the growth season. Extrapolating from the model ecosystem experiment this means that the macrophytes mobilize approximately 50 and 24 percent of PCB and PAH from the top centimeter of the mobile 6-h Tenax-extractable fraction. In flood plain lake systems, macrophyte biomass degradation followed by inundation by the river thus can induce PCB and PAH fluxes into the floodplain or downstream. This means that a clear macrophyte-dominated status, which is an preferred state in water management (e.g., Water Framework Directive [*51-53*]) can result in increased HOC mobilization and transport.

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Chapter 6

Modeling decreased food chain accumulation of PAHs due to strong sorption to carbonaceous materials and metabolic transformation

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Abstract

The predictive power of bioaccumulation models may be limited when they do not account for strong sorption of organic contaminants to carbonaceous materials (CM) such as black carbon, and when they do not include metabolic transformation. We tested a food web accumulation model, including sorption to CM, on data from a model ecosystem experiment with historically contaminated sediment. In combination with measured CM contents of the sediment, the model gave good fits for the biota that are known not to metabolize PAHs (macrophytes, periphyton, floating algal biomass). The same model was applied to invertebrates and fish but now with optimization of their metabolic transformation rates (km). For fish, these rates correlated empirically with log K_{OW}: Log k_m = -0.8 log K_{OW} + 4.5 (r^2_{adj} = 0.73). For invertebrates, log k_m did not correlate with logK_{OW}. Sensitivity analysis revealed that the model output is highly sensitive to sediment CM content and sorption parameters, moderately sensitive to metabolic transformation rates, and slightly sensitive to lipid fraction of the organism and diet-related parameters. It is concluded that CM-inclusive models yield a better assessment of accumulation than models without sorption to CM. Furthermore, inclusion of CM in a model enables metabolic transformation rates to be calculated from the remaining overestimation in the model results when compared to measured data.

Introduction

Models for bioaccumulation of hydrophobic organic chemicals (HOCs) in aquatic food webs usually comprise a combination of two models: an exposure model based on partitioning, which produces the input for a second model in which uptake and loss of a chemical in biota is described. At least two issues may limit the predictive power of bioaccumulation models when they are not included: (i) limited availability due to strong sorption to carbonaceous materials (CM) such as black carbon, kerogen and coal in sediment (1); and (ii) metabolic transformation (2). Correct modeling of bioaccumulation is important, because erroneous estimates of concentrations of polycyclic aromatic hydrocarbons (PAHs) and related compounds in biota may lead to inaccurate risk assessment.

In bioaccumulation models, uptake processes are uptake from water and assimilation from food, including ingested sediments. Loss processes are depuration into water, egestion through feces, internal processes like growth dilution and metabolic transformation, and loss due to reproduction (3-7). Thus, accumulation of a chemical in time can be described as [*3-5*]:

$$\frac{dC_{biota}}{dt} = k_{abs}C_w + k_{ass}C_{food} - (k_{excr} + k_{eges} + k_{grdil} + k_m + k_{repr})C_{biota} \quad (1)$$

with t time; C_{biota} the concentration in biota (µg/kg lipids); k_{abs} the rate constant for absorption from water (day^{-1}); C_w the freely dissolved concentration in water (µg/L); k_{ass} the rate constant for assimilation from food (day^{-1}); C_{food} the concentration in food (µg/kg lipids); k_{excr} the rate constant for excretion to water (day^{-1}); k_{eges} the rate constant for egestion through the gut (day^{-1}); k_{grdil} the rate constant for growth dilution (day^{-1}); k_m the rate constant for metabolic transformation (day^{-1}); and k_{repr} the rate constant for loss due to reproduction (day^{-1}).

This generic model is used widely, although rate constants applied vary among studies. Uptake through food can be modeled using just one type of food for each biotic species, but can also be extended to multiple food sources per species, including sediment organic matter [*4,5,8-10*]. Thus, a food web model can either be linear (e.g. phytoplankton is consumed by zooplankton, which is consumed by fish, which is consumed by a top predator) [*4*], or consist of numerous interactions, which can be described in a matrix form [*5,11*]. Rate parameters can be estimated using measurements or using empirical relationships, which may be based on the octanol-water partitioning coefficient K_{OW} and species weight correlations (allometric relationships) [*4,6,7*].

A major problem in bioaccumulation modeling is that model studies often show an overestimation of organic contaminant concentrations in biota in the field [*2,7,12*]. This overestimation may be caused by an overestimation of the freely dissolved concentration of the compound that the organism is exposed to, by an underestimation of metabolic transformation of the compound, and/or by a lack of steady state [*2,10,13*].

Exposure of organisms to organic contaminants is generally assumed to be through the water phase and through food, of which the latter in turn has also been exposed through the water phase [*3-7*]. If freely dissolved water concentrations are not measured directly, water concentrations can be calculated from concentrations in sediment using the organic carbon partition coefficient K_{OC} [*14*], which generally correlates with the octanol-water partition coefficient (K_{OW}) of a compound. However, when a generic, often laboratory derived, value for K_{OC} is used, water concentrations in the field can be overestimated by up to a factor of 1000 [*15-19*], because in the field not all contaminants present are fully available for partitioning from sediment to the water phase. Therefore, it may be better to describe sorption to

OC by a term for linear sorption to amorphous OC and strong non-linear Freundlich sorption to CM [*1,2,20,21*]:

$$C_{sed} = (f_{OC} - f_{CM})K_{OC}C_w + f_{CM}K_F C_w^{n_F} \quad (2)$$

with C_{sed} the concentration in sediment (µg/kg); f_{OC} the fraction organic carbon in sediment; f_{CM} the fraction carbonaceous material; K_F the Freundlich coefficient for sorption to CM $(\mu g/kg_{bc})/(\mu g/l)^n$, and n_F the Freundlich exponent. When C_{sed}, f_{OC}, f_{CM}, K_F, n_F, and K_{OC} are known, C_w can be calculated. In earlier studies [*22,23*] this equation was applied in bioaccumulation models for field data, some of them even without actual measured CM concentrations, and results were very promising. In this study, the sorption model is applied to data from model ecosystem experiments where CM was measured. Thus, the first objective of the present work was to investigate whether including sorption to CM improves model predictions for PAHs.

However, even when a term for non-linear Freundlich sorption to CM is added, model results may still overestimate measured concentrations in biota for PAHs [*2*]. It is hypothesized that this may be caused by metabolic transformation of PAHs. Metabolic transformation of PAHs has been found to be considerable in fish [*24-26*]. In invertebrates, metabolic transformation has been shown to be species-specific, generally less than in fish, and sometimes negligible [*25,27,28*]. Although many papers report on metabolic transformation, data on actual in vivo metabolic transformation rates are scarce. Therefore, a second objective was to quantify apparent in vivo metabolic transformation rates in invertebrates and fish.

Systematic studies evaluating alternative modeling approaches using one dataset are scarce. Therefore, we evaluated both objectives using an extensive dataset from 6 model ecosystems. Another advantage of the current dataset was that not only concentrations in biota but also sediment characteristics like the fraction of CM were present, which enables us to model strong sorption to CM ánd metabolic transformation. Research aims were (1) to assess whether the CM-inclusive model is consistent with this dataset for PAHs in biota that do not metabolize PAHs; and (2) to assess whether metabolic transformation rates for PAHs in invertebrates and fish can be estimated using the same CM-inclusive model. Data for the model were taken from a model ecosystem experiment with historically contaminated sediment [*22*]. The model was used to assess bioaccumulation in macrophytes, periphyton, floating algal biomass (FAB), zooplankton, invertebrates, and fish. Fish were small to assure that non-equilibrium plays no role. The model was first validated for uptake of PAHs from water in pelagic compartments (macrophytes, periphyton, FAB) both with and

without accounting for sorption to carbonaceous materials. Subsequently, the model was fit to the measured bioaccumulation data for invertebrates and fish, by optimizing metabolic transformation rates. A sensitivity analysis was performed on the parameters related to our research questions.

Methods

Data collection

Model ecosystem setup. Experimental details were reported earlier [*22*], here only a rough description is given. Six model ecosystems representing floodplain lake ecosystems were constructed, with a 10 cm layer of sediment originating from a polluted floodplain lake along the lower river Rhine, the Netherlands. The model ecosystems were 110 x 110 x 70 cm (length x width x height) glass aquaria in a climate controlled room at 20ºC. The model ecosystems were designed to contain different ecological structures: three systems were stocked with fish and macrophytes, and three systems were stocked with fish and received extra nutrients to promote algal growth. These systems had different ecological and physicochemical characteristics during the experiment. Fish (*Cyprinus carpio*) were obtained from laboratory cultures from the department of Fish Culture and Fisheries at Wageningen University. All other biota were collected at non-polluted reference sites. At the start of the experiment, three of the six systems were seeded with shoots of the macrophyte *Elodea nuttallii*. One week later, all model ecosystems were stocked with an invertebrate and zooplankton community and four weeks after that, three 3 cm-sized fish per system were added to the model ecosystems. The experiment lasted for 15 weeks after planting the macrophytes, which enables the systems to mature to representative, fully functioning ecosystems and which is short enough to prevent system degradation due to decaying plant material [*29*]. Periphyton, macrophytes, FAB, macroinvertebrates (split into oligochaetes and the remaining other invertebrates), zooplankton, and fish were sampled at the end of the experiment. Further details on sampling and analysis of CM and OC in sediment, lipids in biota, and PAH concentrations in sediment and biota are included in ref [*22*].

Food web accumulation modeling

Food web accumulation was modeled using a matrix-type food web model [*7,11*] and compared to measured data. Measured concentrations in biota that were below detection limits (for instance, a number of PAHs in fish) were not included in the

analysis. First, the model existing of equations 1 and 2 (assuming steady state) was validated by comparing measured concentrations with model predictions based on default parameters. To this end, all PAH data from macrophytes, periphyton and FAB were used. For macrophytes, periphyton and FAB, only uptake and loss from water was taken into account. Following [*7*], zooplankton was assumed to prey on 80% periphyton and 20% suspended organic matter, oligochaetes 100% on sediment organic matter, macroinvertebrates on 10% sediment organic matter, 10% FAB, 10% periphyton, 10% plants, 30% oligochaetes and 30% zooplankton, and fish on 50% oligochaetes and 50% sediment organic matter. Only the fast desorbing fraction, calculated from total sediment concentrations using the first term in equation 2, was assumed to be available for uptake [*2,9*].

Equation 1 was parameterized according to Traas et al. [*7*] except for reproduction which was assumed to be zero. Log K_{OC} values (Equation 2) were assumed to depend on log K_{OW} according to Karickhoff et al. [*30*]: log K_{OC} = log K_{OW} – 0.21. This regression can be assumed to represent partitioning to 'amorphous' organic matter within the linear sorption domain [*1,19,20*]. The Freundlich exponent n_F was assumed to be 0.7 [*1,31,32*]. Log K_F values (K_F in (µg/kg)/(µg/L)$^{0.7}$) for sorption to CM were taken from a regression with log K_{OW} reported by Koelmans et al. [*1*]: log K_F = 0.70 log K_{OW} + 2.82. These regressions were derived from in situ sorption data, that is, in the presence of possibly competing HOCs and dissolved organic carbon (DOC). For PAHs in macrophytes, FAB and periphyton, metabolic transformation was assumed to be zero [*11,13*]. The model was run using MATLAB, version 7.1.0.246 (R14, SP3). After this initial validation of the model, metabolic transformation rates for individual PAHs, as well as for all PAHs together were estimated for invertebrates and fish. These estimates were obtained by minimizing the residual sum of squares of the model predictions to the measured values using Maximum Likelihood optimization. The data were assumed to be log-normally distributed, and were log transformed before optimizing the model.

Sensitivity analysis

The sensitivity of selected model outputs (concentrations in oligochaetes and fish) to selected model parameters was determined. Anthracene, benzo[a]pyrene, and dibenz[ah]anthracene were taken as model compounds, because they had the lowest (4.54), medium (6.04) and highest (6.75) log K_{OW}'s of the tested PAHs. Sensitivity analysis focused on the parameters introduced or focused on in this study. The importance of strong non-linear sorption to CM was investigated by varying K_F and n_F, while the importance of metabolic transformation was investigated by varying k_m.

We also performed a sensitivity analysis on those parameters that were shown to be important in earlier reports: K_{OW}, fraction lipids and diet-related parameters such as food preference and the food assimilation rate [*8,33,34*]. Sensitivity analysis was performed by Monte Carlo analysis. All parameters were drawn randomly from a uniform distribution (plus or minus 10% of nominal values). Parameter sensitivity was judged using the UNCSAM program implemented in MATLAB [*35*]. The standardized regression coefficient (SRC) was used, based on an acceptance of the linear regression with $r^2 > 0.7$.

Results and discussion

Model validation for PAHs in compartments without metabolic transformation

Figures 6.1A and 6.1B show observed versus modeled PAH concentrations in periphyton and macrophytes. Results for FAB were similar to those for periphyton and macrophytes and are not included. For these compartments, only uptake and elimination through the water column were taken into account in the model. These results show that the default model with CM sorption accounted for, gives a satisfactory fit to the measured data (79%, 82%, and 83% of modeled values within a factor of 3 of the measured data for macrophytes, periphyton, and FAB, respectively. For a full overview of these percentages, see Table 6.1). This implies that for compartments that do not metabolize PAHs, the generalization of sorption to CM with a log K_F - log K_{OW} regression as provided by Koelmans et al. [*1*] apparently is adequate. A comparison of model results with versus without sorption to CM will be discussed later. Furthermore, calculated total elimination half lives $t_{1/2}$ (not shown) were below 5 days for all modeled PAHs in all compartments, which shows that steady state is reached within the duration of the experiment (105 days), and thus the assumption of steady state appears to be valid. Besides this, Hauck et al. [*23*] show that for a similar model (with field data, without measured CM contents) the model uncertainty determined using a Monte Carlo analysis is a factor of 10, and when CM contents are measured the model uncertainty is a factor of three. This model uncertainty is typical for this kind of models (see also the discussion in ref [*23*]). We conclude that our deviation of a factor of three for 78% of the data matches the model's uncertainty range.

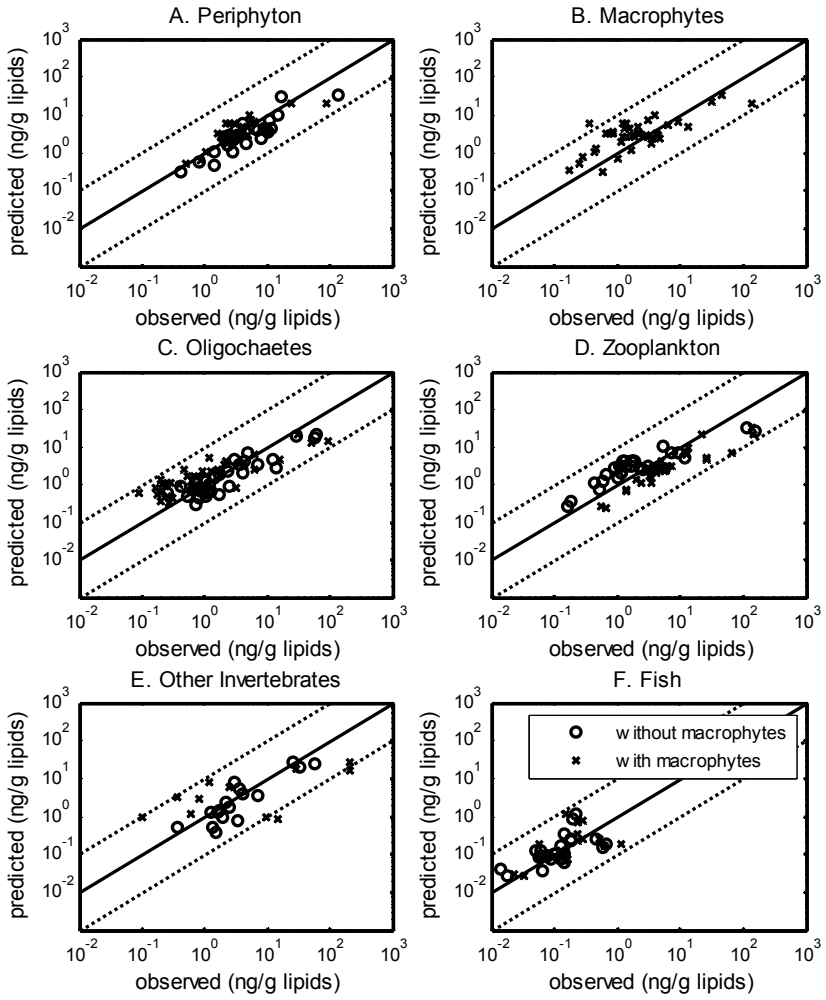

Figure 6.1. *Observed versus modeled polycyclic aromatic hydrocarbon (PAH) concentrations in Periphyton (panel A), Macrophytes (B), Oligochaetes (C), Zooplankton (D), Other invertebrates (E), and Fish (F). Results for floating algal biomass (FAB) were similar to those for macrophytes and periphyton and are not included. Bioaccumulation in macrophytes and periphyton was modeled with sorption to carbonaceous material (CM), bioaccumulation in all other biota was modeled with both sorption to CM and metabolic transformation. The middle line indicates the 1:1 line (measured = modeled); the upper and lower dotted lines indicate one order of magnitude difference from the 1:1 line.*

Table 6.1. *Deviation of modeled results from measured results (See Figure 1; main article) for PAHs in all compartments. Percentage of modeled data within a factor of 3 or 10 of measured data.*

Compartment	Within factor 3 (%)	Within factor 10 (%)
All	78	98
Fish	85	100
Oligochaetes	74	100
Invertebrates	64	95
Zooplankton	88	100
Macrophytes	79	97
Periphyton	81	88
Flab	74	100

Since the model output for all PAHs in both fish and oligochaetes is most sensitive to CM sorption parameters (see Table 6.2; discussion in last paragraph), the model was optimized by fitting the parameters a and b in the linear relationship log K_F = a log K_{OW} + b, using a maximum likelihood procedure, with and without also fitting n_F. The fraction of CM, for which the model output is also sensitive, is a measured variable, and although measurements can also be uncertain, optimizing the model for this variable is not appropriate. Optimizing the regression log K_F = a log K_{OW} + b for PAHs resulted in regression parameters (a = 0.72 and b = 2.78) that were practically identical to the regression parameters reported by Koelmans ([*1*]; a = 0.70 and b = 2.82). Figure 2 compares these regression lines. The good fit further implies that the rate parameters for uptake and elimination are valid.

For zooplankton, oligochaetes, macroinvertebrates and fish (Figure 6.1C-6.1F), the model was optimized by fitting the rate constants for metabolic transformation as will be discussed in the next paragraph.

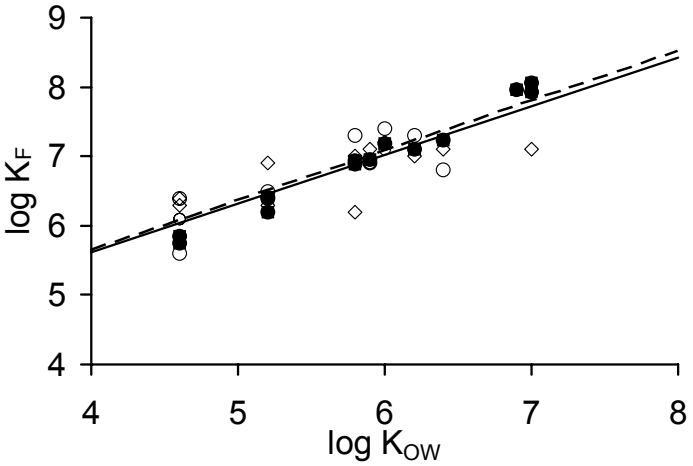

Figure 6.2. *Log K_F - log K_{OW} regression optimized on the current polycyclic aromatic hydrocarbons (PAHs) bioaccumulation data (dashed line: log K_F = 0.72 log K_{OW} + 2.78) compared with regression from the literature (solid line; Log K_F = 0.70 log K_{OW} + 2.82; from [1]) both with K_F in (μg/kg)/(μg/L)$^{0.7}$). Symbols relate to values obtained from field sorption data: ◊ from [31]; ○ from [32]; ● from [2].*

Table 6.2. *Sensitivity of the model outputs (concentration in oligochaetes and fish; $C_{oligochaetes}$ and C_{fish}, respectively) to the selected model parameters[a].*

	$C_{oligochaetes}$			C_{fish}		
Compound [b]	ANT	BAP	DBA	ANT	BAP	DBA
Log K_{OW} [c]	4.54	6.04	6.75	4.54	6.04	6.75
SRC	0.94	0.93	0.93	0.94	0.93	0.93
Parameter sensitivities	n_F (0.94)	n_F (0.90)	n_F (0.94)	n_F (0.93)	n_F (0.90)	n_F (0.94)
	f_{CM} (-0.20)	f_{CM} (-0.23)	f_{CM} (-0.15)	f_{CM} (-0.20)	f_{CM} (-0.23)	f_{CM} (-0.15)
	K_{OW} (0.12)	$f_{lipid, oligo}$ (-0.11)	$f_{lipid, oligo}$ (-0.09)	$k_{m, fish}$ (-0.12)	$k_{m, fish}$ (-0.17)	$k_{m, fish}$ (-0.11)
		$k_{m, oligo}$ (-0.09)	$\%OM_{sed}$ in $diet_{oligo}$ (0.08)	$f_{lipid, fish}$ (-0.11)	$f_{lipid, fish}$ (-0.16)	$f_{lipid, fish}$ (-0.11)
		K_{OW} (0.07)	$K_{m, oligo}$ (-0.08)		$k_{ass,in, fish}$ (0.07)	$k_{ass,in, fish}$ (0.09)
			$k_{ass,in, oligo}$ (0.07)			f_{OC} (0.06)
			f_{OC} (-0.06)			
			K_{OC} (0.06)			

[a] For each model output, the standardized regression coefficient (SRC) is reported and the most important parameters (with regression coefficients > 0.05; indicated between brackets) are reported in decreasing order of importance. The SRC is a measure of the total importance of all parameters included in the sensitivity analysis. The separate regression coefficients per parameter quantify the relative sensitivity of that parameter. See introduction for explanation of symbols.

[b] ANT = anthracene; BAP = benzo[a]pyrene; DBA = dibenz[ah]anthracene

[c] Values taken from Mackay et al. [*41*]

Model validation for PAHs in compartments with metabolic transformation

Metabolic transformation rates are reported to be species-specific [*24,28*], and it is also acknowledged that metabolic transformation rates in fish exceed those in invertebrates [*27,36*]. We therefore fitted the metabolic rates for fish separately from the metabolic rates for invertebrates (zooplankton, oligochaetes, macroinvertebrates), which were treated as one species group. Values for k_m for fish as well as for invertebrates were fitted per individual PAH and also using a single optimized k_m per species group. The latter optimization yields an average k_m for all PAHs grouped together. The results per PAH are given in Table 6.3 and ranged from 0.35 to 16 day^{-1} for fish, and 1.7×10^{-4} to 3.8 day^{-1} for invertebrates. Table 6.2 does not include all PAHs because part of them were below detection limits. The logarithm of these fitted individual metabolic rate constants (log km) was negatively correlated with log K_{OW} for fish: $\log k_m = -0.8 \log K_{OW} + 4.5$, with $r^2_{adj} = 0.73$ and $p = 0.01$. This calculated regression is valid in the log K_{OW} range of 4.5 - 6.2. For invertebrates, log k_m did not correlate with log K_{OW} ($r^2_{adj} = -0.15$ and $p = 0.67$), even when the relatively deviating value for pyrene was left out of the correlation. For fish, this is consistent with Bausssant et al. [*24*] and Jonsson et al. [*37*] who also reported that PAH metabolic transformation rates in fish decreased with an increasing log K_{OW}. For all PAHs grouped together, for invertebrates k_m was optimized to be 0.193 day^{-1} and for fish km was optimized to be 2.51 day^{-1}. Model results obtained using the log k_m – log K_{OW} regression for fish and the single fitted km for invertebrates are shown in figure 6.1 C, D, E and F. This figure shows satisfactory fits, with virtually all model results (99.4%) within one order of magnitude and 79.3% within a factor of three of the measured data and no systematic deviation. The model appears to be moderately sensitive to changes in this general k_m value (Table 6.2), which is further discussed in the next section.

Table 6.3. *Fitted metabolic transformation rates for polycyclic aromatic hydrocarbons (PAHs) in invertebrates and fish.*

PAH[a]	Log K_{OW}[b]	km (day^{-1})	
		Invertebrates	Fish
Anthracene	4.54	3.8	16
Phenanthrene	4.57	0.65	8.9
Pyrene	5.18	4.9×10^{-4}	0.96
Fluoranthene	5.22	0.96	4.2
Chrysene	5.80	1.4	1.3
B(a)Anthracene	5.91	0.54	1.7
B(e)Pyrene	6.21	4.2×10^{-2}	0.36

[a] All other measured PAHs were below detection limits in these biota

[b] Log K_{OW} values according to Mackay et al. [*41*]

Our k_m estimates can be compared with literature values. Most often, total elimination rates are reported, which include (and sometimes are dominated by) metabolic transformation. Our individually fitted metabolic transformation rates range from 0.35 to 16 day^{-1} for fish, and 1.7×10^{-4} to 3.8 day^{-1} for invertebrates. For fish, these rates were more than 95% of calculated total elimination rates, while for oligochaetes they were 9 - 77% of total elimination rates (depending on compound). Thus, for fish our calculated metabolic transformation rates can be compared to literature reports for both metabolic transformation and total elimination of PAHs. Van der Linde et al. [*25*] estimated biotransformation rates from a large set of organic compounds, and reported that total release rates varied between 0.1 and 1 day^{-1} for annelids and fish and between 1 and 10 for those insects that were able to metabolize PAHs. Leppänen and Kukkonen [*38*] reported total PAH elimination rates (including metabolic transformation) between 0.24 and 1.92 d^{-1} for feeding oligochaetes. Nuutinen et al. [*39*] reported metabolic transformation rates for fluoranthene in the amphipod *Hyalella azteca* to be 1.15 ± 0.1 day^{-1}. For various PAHs in fish, Baussant et al. [*24*] reported total elimination rates ranging from 0.6 to 1.2 day^{-1} and Jonsson et al. [*38*] reported total elimination rates between 0.09 and 1.45 day^{-1}. Watanabe [*26*] estimated total elimination rate constants from literature values for small fish, which were reported to be around 0.5, 0.47 and 0.46 day^{-1} for naphthalene, phenanthrene and benz(a)anthracene, respectively. De Maagd [*40*] reported transformation rates for *Pimephales promelas* of 0.7 and 11 day^{-1} for fluoranthene and benzo(a)anthrancene, respectively, and could not measure any biotransformation for naphthalene, phenanthrene, and anthracene. Hence, k_m values for invertebrates deduced from the current optimization are close to literature data, and for fish our k_m values seem somewhat higher than values from earlier studies. This may be due to the relatively low weight of our fishes (only a few grams). However, for all PAHs grouped together, this difference is only about a factor of 2. In summary, the current parameterization for PAHs appears to be consistent with independent literature values for uptake and elimination rates, constants for sorption to CM, as well as metabolic transformation rate parameters.

Sensitivity analysis

Results from the sensitivity analysis for the model output for fish and oligochaetes are reported in Table 6.2. These results show that the model output is most sensitive to n_F (regression coeffcients: 0.93 to 0.94) and f_{CM} (regression coefficients: 0.15 to 0.23). Especially nF influences the standardised regression coefficient to a large extent, for oligochaetes as well as fish, regardless of which PAH is used. Besides n_F and f_{CM}, also k_m, K_{OW}, fraction lipids, % OM in diet and assimilation rates are parameters that the

model is sensitive to. Small differences in the order of the parameters are visible among the three PAHs for oligochaetes, although absolute differences between the values of the regression coefficients are minimal among these PAHs. For fish, the first 5 parameters (n_F, f_{CM}, k_m, fraction lipids, k_{ass}) have the same order of sensitivity, irrespective of log K_{OW} of the compound.

Where n_F and f_{CM} are the two most important parameters for both oligochaetes and fish, the importance of km differs for these biota. For fish, k_m is the third parameter in the order of sensitivity, with regression coefficients of 0.11 - 0.17. For oligochaetes km is the fourth or the fifth (depending on compound) parameter in the order of sensitivity, with lower (partly insignificant) regression coefficients of 0.02 - 0.09. This means that modeling PAH metabolization is relevant for fish, but seems less crucial for oligochaetes.

The fact that the model is sensitive to changes in sorption parameters, lipid contents of the organisms and assimilation and diet parameters, is in accordance with Morrison et al. [*8,33*] and Burkhard [*34*].

Comparison of model approaches

To visualize the importance of including sorption to CM and metabolic transformation in the bioaccumulation model, Figure 6.3 shows the log K_{OW}-dependence of PAH model results (recalculated into Biota to Sediment Accumulation Factors; BSAFs) with measured data for oligochaetes (Figure 6.3A) and fish (Figure 6.3B). In these figures, three different model scenarios are compared: (1) excluding sorption to CM and excluding metabolic transformation (2) including sorption to CM, and (3) including both sorption to CM and metabolic transformation. The model without sorption to CM and without metabolic transformation (the upper, solid line in both panels) strongly overestimates the measured concentrations in biota. When sorption to CM is included (the middle, dashed line), modeled BSAFs are more than a factor of 10 lower, and the overestimation is reduced accordingly, regardless of log KOW of the compound. For biotic compartments that are not able to metabolize PAHs, like macrophytes and periphyton, this reduction is sufficient. This can also be observed in Figure 1A and 1B, where modeled and measured data are very close to the 1:1 line.

However, the CM-inclusive model still cannot explain the much lower measured BSAFs for fish, and the lower BSAFs for oligochaetes at log K_{OW} > 5.5. Only when sorption to CM ánd metabolic transformation are modeled, model estimates are in the same order of magnitude as measured values (the lower, dotted line in Figure 6.3). These results combined with the sensitivity analysis illustrate that including sorption to CM as well as metabolic transformation is important in bioaccumulation models.

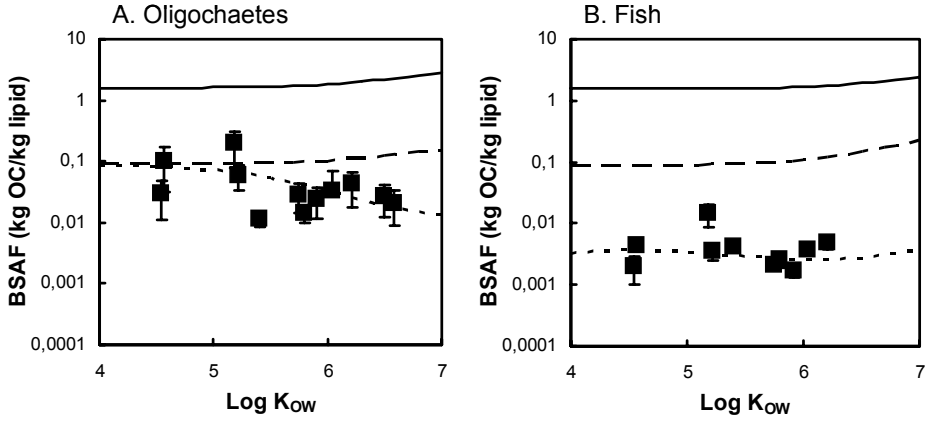

Figure 6.3. *Modeled polycyclic aromatic hydrocarbon (PAH) biota to sediment accumulation factors (BSAFs) in Oligochaetes (A) and Fish (B) as a function of* K_{OW}*. Upper solid lines: model without sorption to carbonaceous materials (CM) and without metabolic transformation. Middle, dashed lines: sorption to CM included. Lower, dotted line: sorption to CM and metabolic transformation included. Markers indicate average measured BSAFs (with standard deviations) in n = 6 model ecosystems.*

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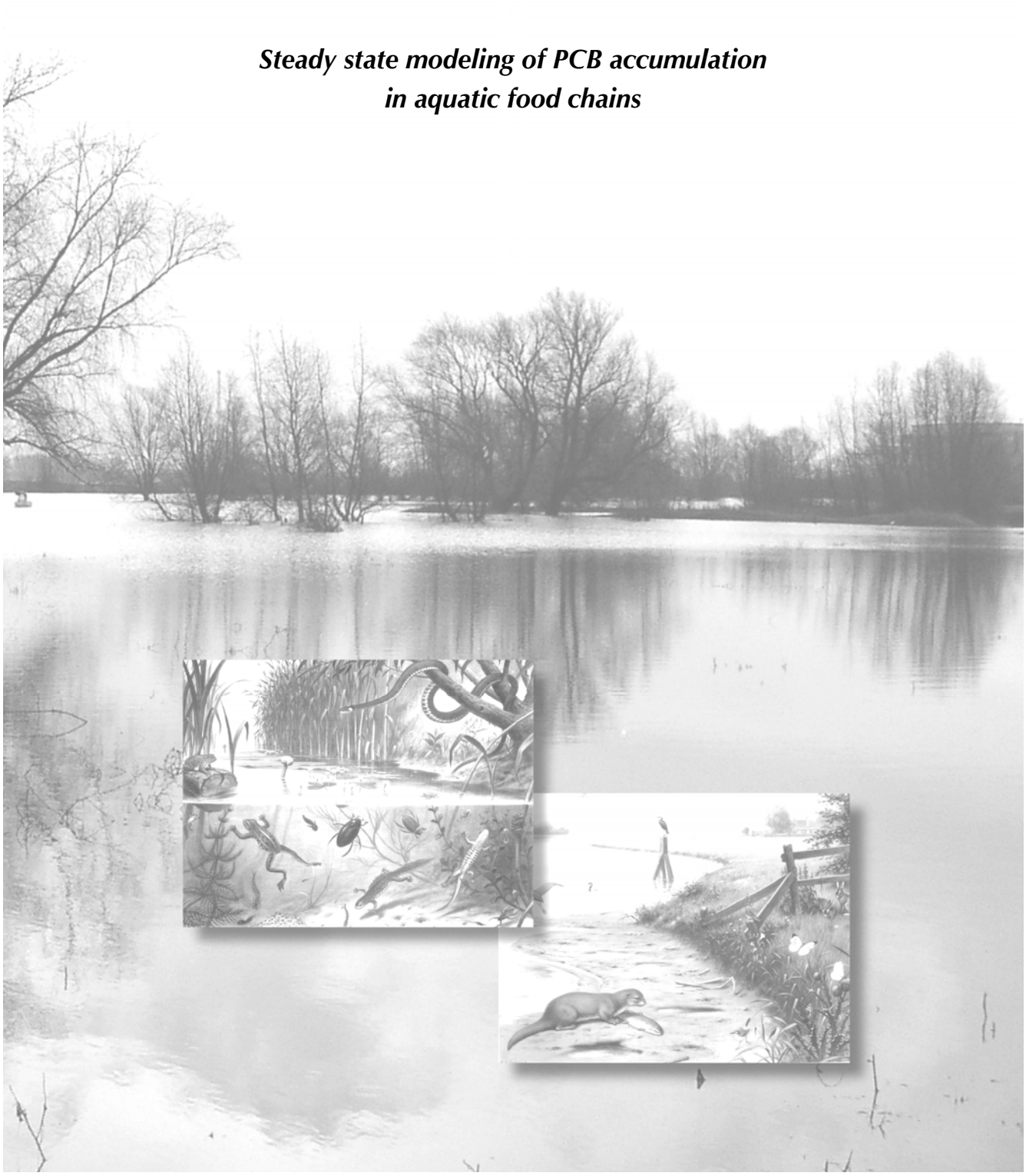
Chapter 6 - Addendum

Steady state modeling of PCB accumulation in aquatic food chains



Introduction and methods

The steady-state model which was applied to PAHs in Chapter 6 was also used to model food web bioaccumulation for Polychlorinated Biphenyls (PCBs). The results are discussed in this addendum to Chapter 6. Aims were to assess if the CM-inclusive model is consistent with the dataset for PCBs like it was for PAHs (Chapter 6) and to assess the influence of the possible absence of steady state on model results.

For information on experimental setup and general analytical methods, please refer to Chapter 6 of this thesis. PCBs analyzed were IUPAC numbers 18, 20, 28, 31, 44, 52, 101, 105, 118, 138, 143, 149, 153, 170, and 180. PCBs were analyzed on an upgraded Hewlett-Packard 5890 II Gas Chromatograph (Hewlett-Packard, Little Falls, Wilmington, DE, USA) equipped with a HP7673A auto sampler, two 63Ni Electron Capture Detectors, and two 50m capillary fused silica columns (CP Sil-8 CB and CP Sil-5/C18 CB, Varian, Bergen op Zoom, The Netherlands).

Food web accumulation modeling was performed as described in Chapter 6 of this thesis and [*1*], using a matrix-type food web model [*2*]. Metabolic transformation was assumed to be zero [*2,3*]. Sorption to CM was modeled using equation 3 from chapter 6, whith Log K_F = 1.02 log K_{OW} + 0.25 and n_F = 0.7 [*4*].

Results and discussion

The default food web model was used with the standard CM sorption model of Koelmans et al. ([*4*]; eq. 3 of Chapter 6). Figure 6A.1 shows observed versus modeled PCB concentrations in macrophytes, periphyton, floating algal biomass (FAB), macrophytes, oligochaetes, zooplankton, and macroinvertebrates. Results for fish were left out of this graph, since steady state for fish cannot be assumed for all PCBs. Total elimination rate constants for PCBs in fish, as estimated from model calibration, range from 5.7×10^{-3} to 1 day^{-1}. Elimination half-lives $t_{1/2}$ thus range from 0.65 to 122 days. These high elimination half-lives show that during the experiment, steady-state can not be assumed for PCBs with log K_{OW} > 6.2 (PCBs 101 and higher) in fish. For oligochaetes and macroinvertebrates, model estimates for total elimination rate constants for PCBs in these compartments range from 8×10^{-3} to 8 day^{-1} and elimination half-lives $t_{1/2}$ thus range from 0.09 to 85 days. This shows that for oligochaetes and macroinvertebrates, steady-state can not be assumed for PCBs with log K_{OW} > 7 (PCB 170 and 180). Lack of steady state for larger fish species and high log K_{OW} HOCs is previously suggested by Arnot and Gobas [*3*] and reported by Moermond et al. [*5*] for PCBs in carp (in experimental systems with short exposure

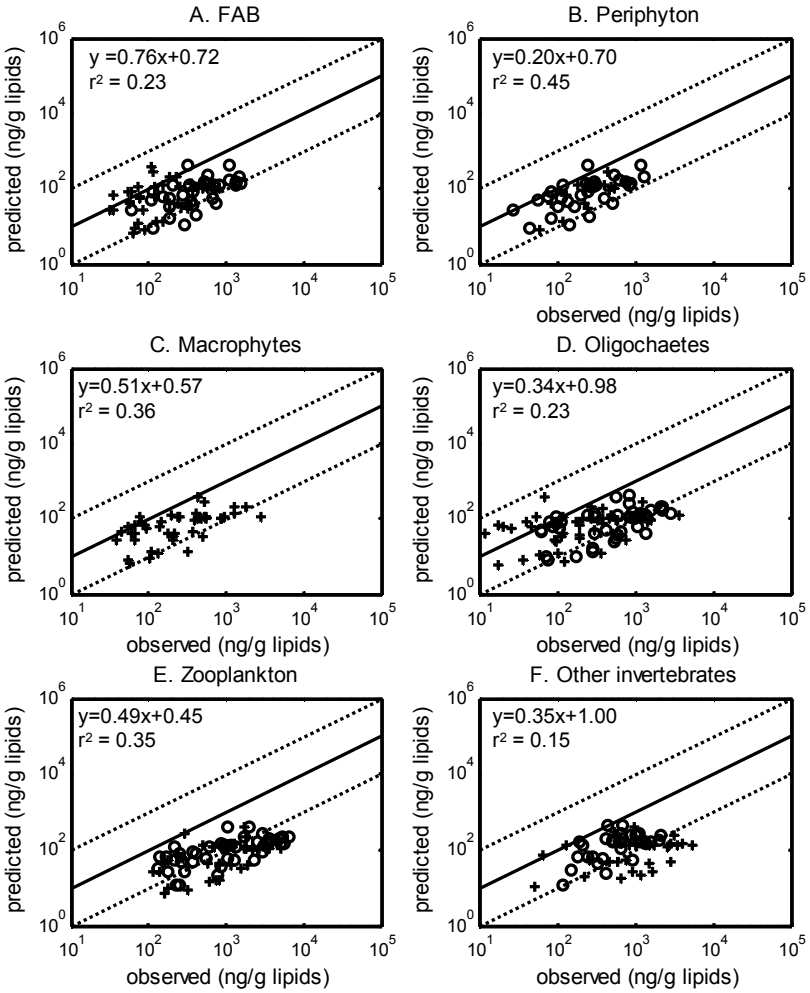


Figure 6A.1. *Observed versus modeled PCB concentrations in macrophytes, periphyton, FAB (Flab in the picture), zooplankton, oligochaetes, and rest invertebrates. + = sytstems with macrophytes, ○ = systems without macrophytes. The middle line indicates the 1:1 line (measured = modeled); the upper and lower lines indicate one order of magnitude deviation from the 1:1 line.*

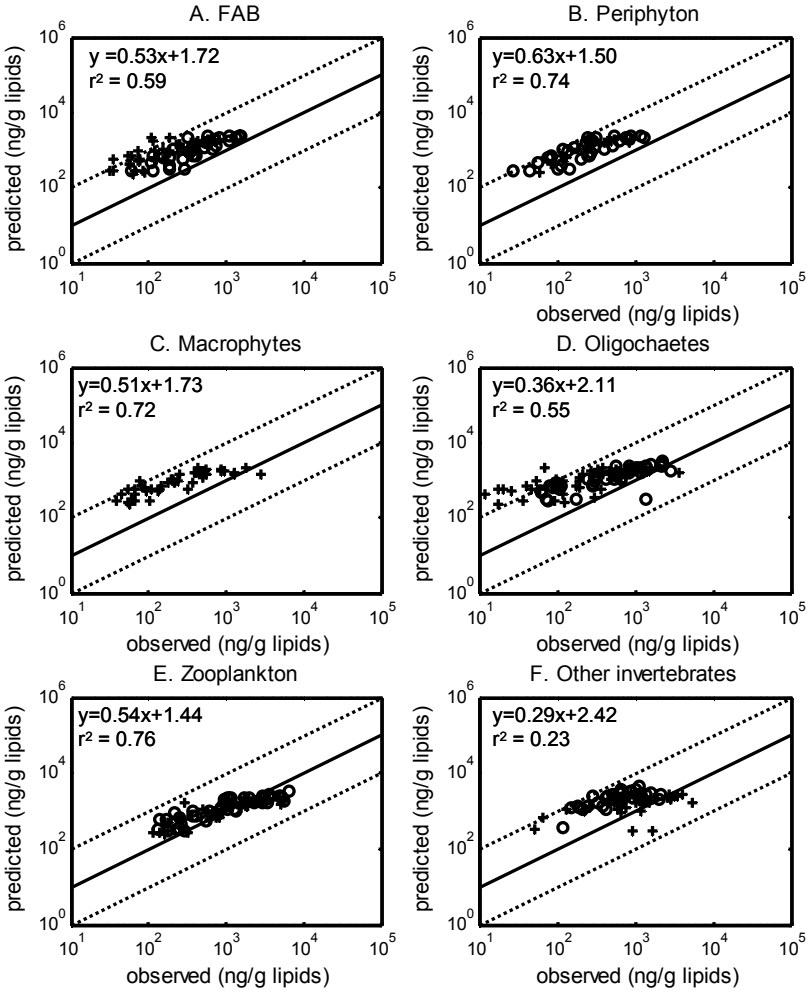


Figure 6A.2. *Observed versus modeled PCB concentrations in macrophytes, periphyton, FAB (Flab in the picture), zooplankton, oligochaetes, and rest invertebrates, calculating water exposure with the Karickhoff regression (log* K_{OC} *= log* K_{OW} *– 0.21; [7]). + = systems with macrophytes, ○ = systems without macrophytes. The middle line indicates the 1:1 line (measured = modeled); the upper and lower lines indicate one order of magnitude deviation from the 1:1 line.*

times) and Van Beusekom et al. [6] for polybrominated diphenylethers of similar hydrophobicity in barbel and bleak (in the field with accordingly long exposure times). This means that for fish and invertebrates, compounds that are not easily metabolize may require a dynamic instead of a steady-state model. For all other compartments, total elimination rates are lower and steady state can be assumed at the end of the experiment.

The results displayed in Figure 6A.1 show that measured concentrations are underestimated by the model, up to an order of magnitude for periphyton, macrophytes, FAB and oligochaetes and up to 1.5 - 2 orders of magnitude for zooplankton and macroinvertebrates. Around 70% of all modeled data is within a factor of 10 of measured data, but less than 30% within a factor of three (see also Table 6A.1). Modelled results are relatively scattered, which is reflected in the low values for r^2. In most compartments, the lack of fit is higher at higher biota concentrations, resulting in a slope deviating from the 1:1 line. For fish (results not shown) this is also the case; the fit is reasonably acceptable for compounds present in lower amounts (mostly compounds with a low log K_{OW} for which steady state can be assumed) and the measured results are underestimated by about a magnitude for the compounds with higher log K_{OW} where steady state cannot be assumed.

Table 6A.1. *Deviation of modeled results from measured results (See Figures 6A.1, 6A.2 and 6A.4) for PCBs. Percentage of modeled data within a factor of 3 or 10 of measured data for the model with sorption according to Koelmans et al. [1], Karickhoff [7], or with a fit for the log K_F - log K_{OW} regression*

Compartment	Within factor 10 (%)			Within factor 3 (%)		
	Koelmans	Karickhoff	Fit	Koelmans	Karickhoff	Fit
Oligochaetes	72	95	99	29	50	80
Invertebrates	70	96	99	27	53	77
Zooplankton	71	95	99	29	54	83
Macrophytes	67	95	99	27	59	80
Periphyton	64	99	100	24	69	80
Fab	47	100	100	8	94	76

In order to visualize the impact of sorption to Carbonaceous Materials (CM), model results with sorption to CM can be compared to model results without sorption to CM, thus only accounting for sorption to organic carbon as quantified by Karickhoff (log K_{OC} = log K_{OW} – 0.21; [7]) (Figure 6A.2). Whereas the model using the regression for sorption by Koelmans at al. [4] underestimated measured results, the mdel without sorption to CM overestimated measured results, but with a lesser order of magnitude. More than 50% of the modeled data are within a factor of three of the measured data (Table 6A.1), and the higher values for r^2 show that model results are less scattered than for the model with sorption to CM. But still, modeled results

deviate upto 1.5 orders of magnitude from the measured results. Three possible explanations for the systematic deviations for the CM-inclusive model are discussed below.

First, an explanation for the low estimations for the CM-inclusive model may be an underestimation of uptake rates or an overestimation of elimination rates. However, the defaults for these kinetic rate parameters rely on a robust body of earlier work [*2, 8-12*].

A second explanation is reduced sorption to the CM component in the sediment as compared to modeled sorption, due to dissolved organic carbon (DOC)-PCB sorption competition on the CM surface (OM-fouling). Lower sorption means higher availability and thus accumulation in the food chain. Recent reports show that this effect can be considerable (up to a factor 10-50; [*4,13-15*]) and that the attenuative affect is larger at higher HOC levels [*15*]. Indeed, the PCBs that are underestimated by the model are present in higher concentrations and are also the PCBs with the highest log K_{OW} values (log K_{OW} > 6). Accordingly, the lack of fit for higher PCBs may relate to the fact that they also have the higher concentrations and thus have a lower sorption due to increased competition. The order of magnitude of these attenuation factors and the lack of fit in modelled-measured values agree very well. It should be noted that the regression by Koelmans [*4*] is based on field measurements and thus already includes the effect of OM-fouling. However, variability of this effect has been found to be considerable [*13-15*]. Therefore, we hypothesize that this lack of fit is caused by an overestimation of modeled PCB sorption to CMs at higher concentrations or at higher log K_{OW}s due to sorption competition.

Besides sediment-dependent attenuation of sorption, sorption of PCBs to CMs also may be less for the non-planar (ortho-substituted) congeners than for planar PCBs [*17*]. A few studies have reported lower BSAFs for planar compounds than for non-planar compounds [*13,18*]. The Koelmans regression [*4*] does not account for these differences. Based on relative distribution coefficients between planar and non-planar PCBs (provided by Jonker and Koelmans; [*17*]), Traas et al. [*1*] modeled bioaccumulation of planar compounds with an increased sorption of 0.4 log units. This led to an improved fit for PCB accumulation for white bream and pike [*1*]. In the present study, the same planarity factor of 0.4 log units was applied and similar to what was shown by Traas et al. [*1*], this planarity factor reduced overestimation of planar PCBs by the model with CM and shows that planarity effects may also play a role (results not shown).

To determine if the lack of fit in the model might satisfactorily be reduced by a relative minor change in sorption parameters, within realistic ranges, the model was optimized using a maximum likelihood procedure. The parameters a and b in the linear relationship log K_F = a log K_{OW} + b were fitted, with and without also fitting n_F. As the model uses the steady state assumption, this was only done for the compartments and compounds where the steady state assumption was legitimate (not for fish and for PCBs 170 and 180 in invertebrates and oligochaetes). In Figure 6A.4, results are shown for bioaccumulation of PCBs using the optimized model with n = 0.7. It is clear that for this model, the highest percentage of modeled results is within a factor of three of the measured results (Table 6A.1), and scatter of model results is lowest of all three models (highest r^2 values).

The resulting optimized relationship is: log K_F = 0.55 log K_{OW} + 2.61 with n_F = 0.7, and is shown in Figure 6A.3 together with the original log K_F – log K_{OW} relationship for in situ K_F's reported by Koelmans et al. (log K_F = 1.02 log K_{OW} + 0.25; [*4*]). It appears that the fitted log K_F – log K_{OW} relationship yields identical K_F values at log K_{OW} = 5 and about a factor 10 lower K_F values at log K_{OW} = 7.5, as compared to the regression reported by Koelmans et al. [*4*]. Optimization of n_F together with a and b in the regression, yielded almost the same value for n_F (n_F = 0.708), and only a minor improvement in the goodness of fit, which does not bring the fitted K_F values closer to the regression reported by Koelmans et al. [*4*]. This implies that in the current range of aqueous PCB concentrations (i) the lack of fit is related to sorption affinity (K_F) rather than isotherm curvature, and (ii) that n_F = 0.7 seems a legitimate assumption.

In conclusion, using the steady-state model with sorption to CM, PCB concentrations can be estimated reasonably well for PCBs that are present in lower amounts, but for PCBs that are present in higher amounts the model underpredicts measured concentrations by upto 1.5 to 2 orders of magnitude. For those compounds and compartmens for which steady state cannot be assumed, a dynamical model would underestimate these results even further, so steady state probably is not an explanation for this lack of fit. A more plausible explanation may be reduced sorption of PCBs, mainly for those compounds that are present in higher amounts. Although Koelmans et al. (4) report a satisfactory agreement between regressions based on three different sediments for PCBs, differences may still exist between sediments. Possible mechanisms include differences in type of CM and sorption site blockage and/or competition by HOCs or organic (humic) materials [*4,13-15*].

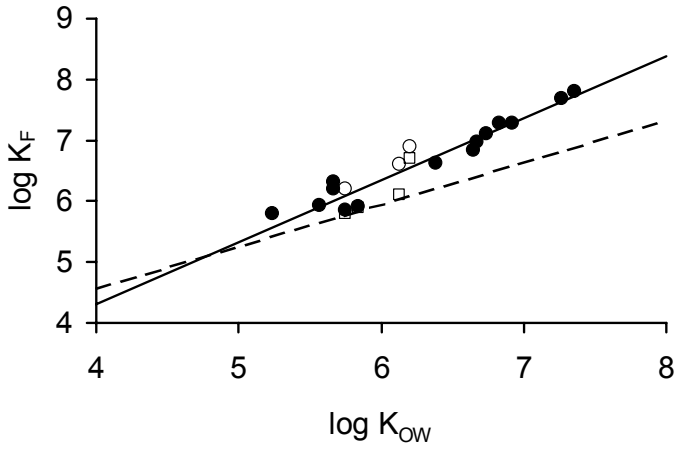


Figure 6A.3. *Log K_F-log K_{OW} regression (solid line; log K_F = 1.02 log K_{OW} + 0.25; [4]) compared with results from the model fit for PCBs (dashed line; log K_F = 0.55 log K_{OW} + 2.61). To facilitate comparison among regression models, n_F was fixed at 0.7, resulting in the optimized model for PCBs: ○ = values reported for Boston Harbour by Lohmann et al. [19]; □ = values reported for New York Harbour by Lohmann et al. [19]; ● = values reported for floodplain lakes by Moermond et al. [20].*

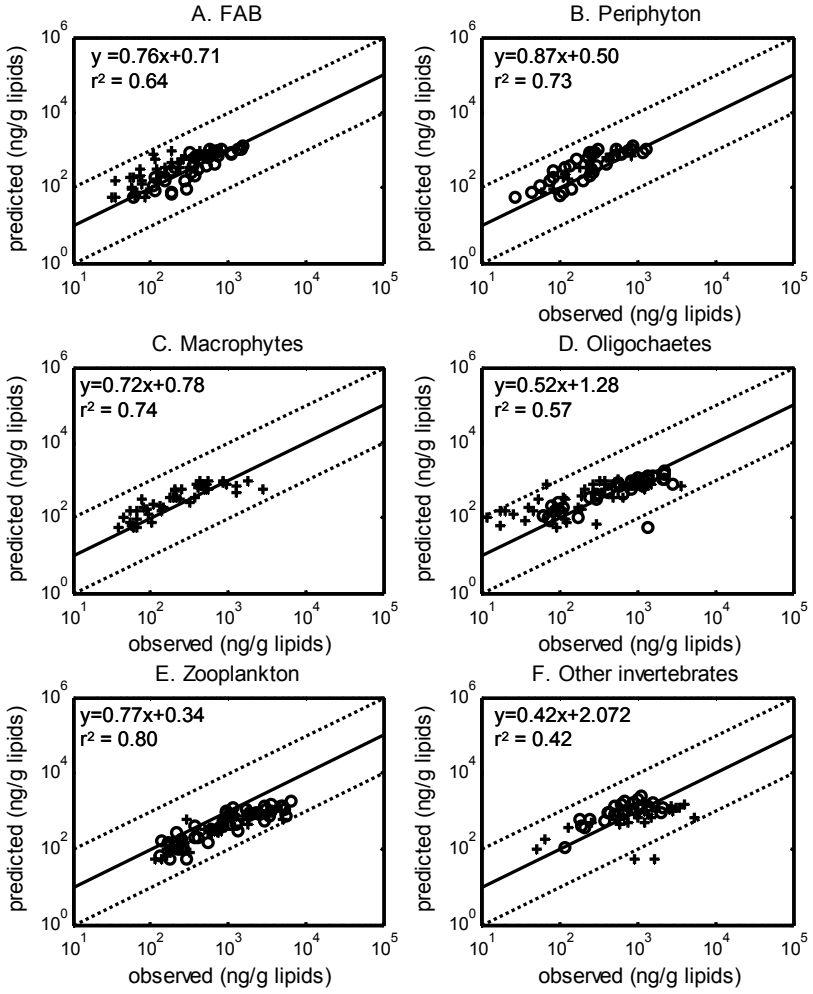


Figure 6A.4. *Observed versus modeled PCB concentrations in macrophytes, periphyton, FAB (Flab in the picture), zooplankton, oligochaetes, and rest invertebrates, calculating water exposure with a fit for the Freundlich sorption to CM: Log K_F = 0.55 log K_{OW} + 2.61 and n_F = 0.7. + = sytstems with macrophytes, ○ = systems without macrophytes. The middle line indicates the 1:1 line (measured = modeled); the upper and lower lines indicate one order of magnitude deviation from the 1:1 line.*

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Chapter 7

Summarizing discussion

Summarizing discussion

In this chapter, general conclusions are presented. First the research described in this thesis will be tied back to the original research questions. After that, some implications of the research for sediment quality guidelines, floodplain management, measuring/modeling bioavailability, and bioaccumulation modeling will be given.

Ecological factors may play an important role in the bioaccumulation of polychlorobiphenyls (PCBs) and polyaromatic hydrocarbons (PAHs). Bioaccumulation of these chemicals also appears to be related to the presence of black carbon (BC) in sediment. Particular fractions of sediment-bound toxicants seem to be unavailable to organisms, irrespective of the uptake route. Consequently, bioavailable concentrations in sediment may be much lower in the field than what is estimated using total sediment concentrations and laboratory-derived partitioning coefficients. To decide if sediment needs to be remediated, actual risks of these sediments need to be determined. It is not only necessary to develop practical concepts to accurately determine bioavailability, but there is also a great need for knowledge on the effects of food web structure on bioavailability and bioaccumulation, and models that can describe these processes.

Because of their unique combination of varying ecological conditions and pollution characteristics, floodplain lakes are a suitable area to study the interactions between contaminants and nutrient cycles on the ecosystem level, to assess the effect of these interactions on bioavailability of sediment-bound contaminants and to apply existing models to analyze these interactions.

The main research questions were:

- What is the extent and nature of bioavailability of sediment-bound PCBs and PAHs?
- What are the effects of lake ecosystem structure on fate and bioaccumulation of PCBs and PAHs?

An experiment in which bioaccumulation of PCBs by benthivorous carp (*Cyprinus carpio*) in enclosures in a floodplain lake is assessed, is described in Chapter 2. Fast-desorbing PCB fractions in the sediment were estimated by 6-h Tenax-extractable fractions with a correction factor. These fractions varied between 4 and 22% for PCBs and did not show a clear trend with log K_{OW}. However, bioaccumulation of PCBs in carp correlated much better with Tenax-extractable concentrations than with total

extractable concentrations. Nutrient additions in the enclosures had a positive effect on PCB accumulation.

In this chapter, results were described using a kinetic uptake model, including uptake of PCBs through sediment ingestion. Model results show that PCB uptake in carp can be explained from (1) uptake through invertebrate food, (2) uptake from fast-desorbing fractions in ingested sediments, and (3) uptake from water, where PCBs are in partitioning equilibrium with fast-desorbing fractions. It was also shown that for most PCBs, steady state was not reached after the 60 days of the experiment.

The effect of lake ecosystem structure on bioavailability and bioaccumulation was further assessed in Chapter 3. Here, bioavailability and bioaccumulation of PCBs and PAHs by benthic invertebrates are described in three ecologically different floodplain lakes (fish-dominated turbid, algae-dominated turbid, and macrophyte-dominated). In situ PCB and PAH biota to sediment accumulation factors (BSAF) for benthic invertebrates, as well as 6-h Tenax-extractable (fast-desorbing) concentrations and lake characteristics (including BC in sediment), were determined for different seasons from September 2000 until March 2002. Small but significant seasonal and lake effects on BSAFs were detected. The differences between oligochaetes and other invertebrates were small for PCBs and within a factor of 10 for PAHs. BSAFs for pyrogenic PAHs were much lower than for PCBs, which was explained by stronger sorption to BC.

Using these results, a model was developed to describe BSAFs for invertebrates, including a term to account for a lesser bioavailability due to very strong Freundlich sorption to carbonaceous materials such as black carbon, coal and kerogens, and a term to account for uptake of the bioavailable fraction of the contaminants through ingested sediment. Freundlich coefficients for in situ sorption to BC (K_F) were calculated from slow desorbing fractions and BC contents and agreed well with literature values for K_F.

Although the effect of sequestration or aging (and the subsequent reduction of bioavailability) on bioaccumulation of PCBs and PAHs by benthivorous biota seems obvious, it is not clear whether this also limits accumulation in higher levels of aquatic food chains. Thus, the effect of aging and ecosystem structure on bioaccumulation and fate of PCBs and PAHs in various biotic compartments in a model ecosystem are described in Chapters 4 and 5, while the results were modelled in Chapter 6. Polluted floodplain lake sediment was brought into indoor 1-m^3 model ecosystems that mimicked fish-dominated, macrophyte-dominated, algae-dominated, and fish- and macrophyte-dominated shallow lakes. To determine the effect of aging

on bioavailability and bioaccumulation in these systems, the sediment was spiked with two PCBs and a deuterated PAH, which subsequently could be compared with their 'native' counterparts.

In Chapter 4, it is shown that labile fractions for spiked compounds were higher than for their native analogues and decreased over time, suggesting sequestration in the sediment. In the majority of cases, 6-h Tenax-extractable concentrations correlated better with concentrations in biota than Soxhlet-extractable concentrations. Ecosystem structure affected food web accumulation in terms of concentrations in biota, but replicate variability was too high to detect clear treatment effects. Differences in accumulation between spiked compounds and their native analogues indicated an effect of aging for invertebrates, macrophytes and benthivorous fish. Thus, aging may translate directly into reduced uptake at higher trophic levels.

In Chapter 5, the effect of ecosystem structure on species composition and the amount of PCBs and PAHs in the biological compartments was analyzed thoroughly. An extensive statistical analysis was performed on lipid-normalized concentrations and total mass distribution of the contaminants in biota, suspended solids and sediments. Like for concentrations in biota (Chapter 4) also the mass balance shows that freshly spiked compounds were more mobile in the system than their more sequestered native counterparts. Macrophytes represented the largest amount of non-sediment (bio)mass in the systems and were capable of depleting up to 26 (PCB) and 31 (PAH) percent of the mobile (fast desorbing) fraction in the 7 cms of sediment in the systems. The major impact of fish on the test systems was their structuring of the invertebrate communities through predation. Benthivorous carp further caused resuspension of the sediment and consequently caused increased partitioning of PCBs and PAHs to other system compartments.

Model results from Chapters 2 and 3 are combined with existing models to obtain a bioaccumulation model for PAHs and PCBs in all biological compartments of the model ecosystems described in chapters 4 and 5. This new model, as described in Chapter 6, includes a term for strong sorption to measured black carbon concentrations. The model gave excellent fits for the biota that are known not to metabolize PAHs (macrophytes, periphyton, floating algal biomass). The same model was optimized for metabolic transformation rates and applied to invertebrates and fish. For fish, metabolic transformation rates correlated with log K_{OW}, but for invertebrates this was not the case. Finally, a sensitivity analysis was performed to assess model sensitivity of the newly introduced parameters compared to the most sensitive parameters in the original model. This analysis revealed that the model output is highly sensitive to sediment BC content and sorption parameters,

moderately sensitive to metabolic transformation rates, and slightly sensitive to lipid fraction of the organism and diet-related parameters. For PCBs, where steady state can not always be assumed, the model fits the data less well, as is described in the addendum to Chapter 6. For PCBs , total elimination rates are very small, resulting in half-lives of months to years. Dynamical modeling is therefore to be recommended for these compounds.

Using these results, conclusions can be drawn regarding the research questions which were defined:

What is the extent and nature of bioavailability of sediment-bound PCBs and PAHs in dynamical floodplain lakes?

Bioavailability of PAHs and PCBs in sediments is assumed to depend on the magnitude of the fast desorbing fraction of these compounds [*1-4*]. In this thesis, bioavailability of sediment-bound PCBs and PAHs has been characterized operationally using a 6-h Tenax extraction. This 6-h Tenax-extractable fraction of PCBs and PAHs is a measure for the fast desorbing fraction [*5*] although the ratio between the fast desorbing fraction and the 6-h Tenax-extractable fraction may differ among compounds. For example, for PAHs the fast desorbing fraction is 2-4 times the Tenax-extractable fraction and for PCBs they are almost equal [*5*]. The 6-h Tenax-extractable fractions in floodplain lakes for both compound groups were between 0.01 and 0.40 (Chapters 2 and 3), which means that contaminants in these sediments were available, but to a smaller extent than total concentrations would suggest. Despite of this reduced availability, benthivorous fish and invertebrates in floodplain lakes still rapidly accumulated substantial amounts of PCBs (Chapters 2, 3, 4, and 5). With respect to their concentrations in sediment, PAHs were accumulated less, because of the lesser PAH availability due to the presence of Carbonaceous Materials (CM), which comprises particles like coals, kerogen, char, and soot. The latter two are also referred to as Black Carbon [*6,7*]. For fish, lower PAH accumulation can also be caused by internal metabolic transformation of these compounds ([*8*],[*9*], Chapter 3, and Chapter 6).

Contact time between sediment and contaminants appeared to be of great influence on bioaccumulation in a model ecosystem experiment with sediments from these floodplain lakes (Chapter 4). Contaminants that have been present in the sediment for longer periods of time (years to decades), which is often the case in floodplain sediments, were less available (for Tenax extractions as well as for uptake by biota) than contaminants that were recently added. A higher bioaccumulation of freshly

added compounds was measured for all species in the food web, not only for those species that are in direct contact with the sediment. Thus, aging may translate directly into reduced uptake at higher trophic levels.

What is the effect of lake ecosystem structure on fate and bioaccumulation of PCBs and PAHs?

Bioaccumulation of PCBs in fish in enclosures in floodplain lakes increased with nutrient additions (Chapter 2). This shows that contaminant fate and trophic state of aquatic ecosystems are linked. However, more research is needed to identify the underlying mechanisms. In an ecosystem modeling study, calculations were performed for two large eutrophic lakes (Lake IJsselmeer and Lake Wolderwijd) and model ecosystems with different ecological structures [*10*] using the AQUATOX model [*11*]. These calculations showed that the distribution of organic contaminants over the biological compartments depended on compound, season, and system characteristics. The difference between macrophyte- and fish-dominated systems was mainly due to indirect processes, where invertebrates played a key role in the carbon cycle (as both predators of algae and prey of fish and as detritivores) and thus in the distribution of the contaminants. Seasonal changes in these calculations were mainly due to algal blooms; during algal growth a large proportion of the contaminants in the pelagic system were stored in the algae. An extra nutrient addition however did not change the calculated distribution over the biological compartments.

Measured bioaccumulated concentrations of PCBs and PAHs in invertebrates in flood plain lakes were not influenced greatly by seasonal effects or ecological structure (Chapter 2, Chapter 5). Although effects were statistically significant, their magnitude in terms of accumulation factors was small. The main difference with other reported studies [*12-20*] is that our systems were different in structure but did not differ much in trophy: they were all rich in nutrients and had relatively high biomasses. The absence of large differences in accumulation among our systems may also have been caused by the similar sediment composition and bioavailability of contaminants in our systems. The composition of the benthic invertebrate community was different among seasons and among lakes, but this seemed to have only a minor effect on the magnitude of accumulation of PCBs and PAHs. Differences between compounds (due to physical/chemical characteristics of the compounds such as hydrophobicity, planarity, ability to be metabolized) were much larger than differences due to ecosystem structure, seasons, or species composition.

As for total masses of PCBs and PAHs in certain compartments however, lake ecosystem structure appeared to have a large influence on the biomass of biota and therefore also on the mass distribution of PCBs and PAHs in biotic compartments. For instance, macrophytes are a large sink in macrophyte-dominated lakes and can take up more than 25 % of the bioavailable fraction (Chapter 5). Thus, changes in ecosystem structure strongly influence PCB and PAH dynamics and thus POPs in general, although concentrations within the biotic compartments are not significantly influenced by biotic biomass.

Implications for food chain bioaccumulation modeling

Three main factors can cause an overestimation of model results with regard to measured data: (1) an overestimation of exposure due to an overestimation of actual aquatic concentrations; (2) neglecting or underestimating metabolic transformation; and (3) erroneously assuming steady state. The empirical data obtained in Chapters 2 through 5 were used to improve and evaluate bioaccumulation models (food chain models in Chapters 2 and 3, and a food web model in Chapter 6). Existing models were adapted, and expanded with (1) bioavailability, through the incorporation of fast desorbing fractions and/or strong sorption to black carbon; (2) uptake of (available) sediment-bound toxicants in the gastro-intestinal tract; and (3) metabolic transformation of PAHs. When aquatic exposure concentrations are quantified accounting for sorption to BC, bioaccumulation model results improve substantially (Chapter 3, Chapter 6, [*21*]). Including metabolic transformation in the model can account for a further improvement of the model fit (Chapter 6). Finally, for non-metabolizable hydrophobic compounds like PCBs, steady state can not always be assumed (Chapter 2; Addendum Chapter 6). Total elimination rates are very small, resulting in half-lives of months to years. Dynamical modeling is therefore to be recommended for these compounds (Chapter 2; Addendum Chapter 6).

Furthermore, in the Netherlands, benthivorous fish like bream and carp are very abundant, and aquatic ecosystems are often dominated by the benthic food web. Including sediment as an exposure route in model calculations for benthivorous fish and invertebrates can be an important addition (Chapter 2). Measured results indicate only a small difference in accumulation between different invertebrate groups (Chapters 3 and 4). Thus, when modeling bioaccumulation in ecosystems, invertebrates can be treated as one group.

Implications for bioavailability assessment

In this thesis, the bioavailable fraction of PCBs and PAHs in sediments was assessed using a 6-h Tenax extraction method and through measurement of PCB and PAH levels in biota exposed to these compounds by these sediments. For benthivorous fish in field enclosures, 6-h Tenax extractable fractions appeared to correlate better with accumulation of PCBs than Soxhlet- (total) extractable fractions (Chapter 2). For PCBs and PAHs in macroinvertebrates in floodplain lakes this was also the case (Chapter 3). However, for biota in model ecosystems (Chapter 4) results were more complex, although for benthic organisms Tenax extractable concentrations generally correlated better with concentrations in biota than total concentrations.

When a first impression has to be obtained of the bioavailability of a compound in sediment, the 6-h Tenax extraction is a very practical method. The Tenax extraction provides a contaminant fraction, which is (more or less) related to the bioavailable fraction through a constant ratio; about 1 for PCBs and between 2 and 4 for PAHs, depending on individual compound [*5*]. Moreover, estimations of bioavailability based on Tenax or similar extraction techniques have been shown to correlate well with pore water measurements [*22,23*]. When exact information on the sediment is needed or the sediment has never been characterized before, applying Tenax extractions to measure a full desorption curve may be advised. However, measuring a full curve is relatively time-consuming, and thus may not always be worth the effort, depending on the specific questions researched.

As an alternative to measurement, when the fast desorbing fraction or the amount of carbonaceous materials in sediment is known, the concentration in water can also be estimated using partitioning models as refined in this thesis and similar recent research (Chapter 3, Chapter 6, [*6,7,21,24*]). With these models, potential risks can be assessed more precisely than when total concentrations are used.

Implications for sediment policy making

Until recently, sediment quality guidelines and risk assessment procedures were based on total amounts present in the sediment top layer. Accumulation and thus risk of organic pollutants however, depend not only on total amounts present, but also on the fraction of the total amount that is actually available for uptake (Chapters 2, 3, 4, 5 in this thesis, [*4,22,25,26*]). Recently, the Water Framework Directive has come into effect. Sediments should not pose an unacceptable risk to reach the environmental goals for the water column, either by spreading contaminants to

surface water or by negatively affecting ecosystems [*27*]. To reach this goal, in the Netherlands a circular on sediment remediation was published together with a guidance [*27,28*], in which it is issued that when total amounts of contaminants in sediments (first tier assessment) exceed intervention values, a more elaborate screening should be applied. In this second tier of assessment, the urgency of immediate remediation should be determined, by assessing risks for humans, risk for ecology, and risk for spreading of the contaminants. Assessment of bioavailability is explicitly mentioned here [*28*].

The 6-h Tenax extraction method has been shown to be a valid measure for bioavailability for invertebrates [*4,22,25,26*] under laboratory conditions. However, applicability and relevance of this method under field conditions, and for higher trophic levels was unknown. The research described in this thesis (Chapters 2, 3, and 4) focused on these latter issues and showed that it is also well applicable in field conditions and also revealed that for higher trophic levels in field situations, the 6-h Tenax extraction method often also correlates well with bioaccumulation.

Furthermore, when 6-h Tenax extractions or other desorption measurements are not available, modeling a partition coefficient in which black carbon (carbonaceous materials) as well as amorphous organic matter are accounted for, also gives a good measure for the actual availability of a compound (Chapters 3 and 6; [*7,21*]). Recently Oen et al., [*29*] applied the BSAF model presented in Chapter 3 to the gastropod *Hinia reticulata* and reported that this BC-inclusive model accounts for the low bioavailability of native PAHs to *H. reticulata*.

Implications for management of floodplain lakes

At present and in the near future, many floodplain lake sediments will be relocated and floodplains will be reconstructed. Thus, new floodplain lakes will be designed, varying in size, depth, distance to the river, etc. Consequently, these factors may affect the ecological structure of a lake. However, effects of species composition of benthic invertebrates, seasonal influences and ecological structure on actual risks seem lower than the differences in risk caused by the chemical characteristics of the individual compounds (Chapter 3 and 4). Contrastingly, the biomass of each biological compartment is different in systems with different ecosystem structures, and accordingly also the total amount of contaminants present in that compartment is different (Chapter 5). This means that structure has a large effect on contaminant cycles, even if concentrations in compartments are not affected.

Although water quality has improved and sediments in floodplain lakes are aged and thus are supposedly less toxic, the amount of contaminants in sediments that can be taken up by organisms in relatively short periods of time is still substantial (Chapter 2 and 5). This should be taken into consideration when floodplains are designed for further use like recreation, nature or farming. Floodplain lakes tend to be dominated either by fish or by macrophytes [*30*], which implies that the majority of PCBs and PAHs in the system that are not present in the sediment, are accumulated by these biotic compartments (Chapter 5). Besides this, the presence of fish increases concentrations in macrophytes, suspended solids and invertebrates (only significant for PCB concentrations) through bioturbation of the sediment and active structuring through predation (Chapter 5). Macrophytes act as a sink and decrease amounts and concentrations of POPs in other compartments; also total and bioavailable amounts and concentrations in sediment are decreased, which potentially reduces risks of HOCs to benthic and pelagic biota. However, the amount of HOCs that is taken up by these plants has important implications for transport. In flood plain lake systems, macrophyte biomass degradation followed by inundation by the river can induce HOC transport into the floodplain or downstream. For realistic flood plain lakes, the total amount of PCBs and PAHs in macrophytes can be compared with the amount in fish. In the scope of the research presented in this thesis, ΣPCBs and ΣPAHs were also measured in macrophytes and large fish (bream) in floodplain lakes [*31*] and amounted 0.02 mg ΣPCBs/kg dw and 0.11 ΣPAHs/kg dw for macrophytes and 1.3 mg ΣPCBs/kg dw and 0.05 mg ΣPAHs/kg ww for fish. This shows that at realistic maximum biomasses for macrophytes (1 kg dw/ha; [*32*]) and fish (440 g ww/ha; [*33*]), ΣPCB amounts in these compartments can be 200 and 590 mg/ha for both compartments. ΣPAH amounts can add up to 1100 and 20 mg/ha for macrophytes and fish, respectively. During winter floodings, both fish and macrophyte debris can be transported away from the systems, and thus organic contaminants associated with these compartments are also exported. The calculation shows that macrophytes are a more important carrier for HOCs than fish.

Nevertheless, it may be recommended to design floodplain lakes such that they are dominated by a pelagic food web including macrophytes, instead of a benthic, fish-dominated food web. Contaminated sediments in benthivorous fish-dominated lakes are much more resuspended and are therefore more a part of the pelagic system, resulting in higher concentrations in macrophytes, suspended solids and invertebrates (Chapter 5). Grazing cattle in floodplains may drink from these lakes and consequently may be exposed to contaminants. Calculations show that an average cow of 600 kg that drinks 100 liters of water per day [*34*] with 0.02 µg/L ΣPCBs in suspended solids (measured in the Afferdensche and Deestsche Waarden, results not shown), have an average daily intake of of 3.3 ng ΣPCBs / kg body weight from

drinking water alone. This does not exceed maximum daily intake levels of 10 ng/kg body weight (for humans; [*35*]), but in this maximum daily intake level also other routes of exposure are taken into account.

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Curriculum vitae

Caroline Tanja Antoinette Moermond is op 2 mei 1973 geboren te Middelburg. In 1991 behaalde zij haar VWO diploma aan de Christelijke Scholengemeenschap Walcheren in Middelburg. Na een jaar als uitwisselingsstudent op het St. Petersburg Junior College in Florida doorgebracht te hebben, is zij in 1992 begonnen met haar studie Milieuhygiëne de Landbouwuniversiteit in Wageningen. Wegens ziekte is deze studie in 1993 ruim een half jaar onderbroken, waarna zij begin 1994 een half jaar stage heeft gelopen bij het RIKZ in Middelburg. Hierna koos zij voor de specialisatie Ecologisch Waterbeheer, waarbinnen afstudeervakken zijn uitgevoerd in de richtingen Aquatische Ecologie, Waterkwaliteit en Toxicologie. De eerste twee afstudeervakken zijn uitgevoerd bij de toenmalige vakgroep Waterkwaliteitsbeheer en Aquatische Oecologie, het laatste afstudeervak is uitgevoerd bij de KEMA onder begeleiding van de vakgroep Toxicologie. Na haar afstuderen in 1998 heeft zij anderhalf jaar als toegevoegd onderzoeker gewerkt bij wat inmiddels de leerstoelgroep Aquatische Ecologie en Waterkwaliteitsbeheer was. Binnen deze aanstelling hield zij zich bezig met het uitvoeren van een modelstudie met AQUATOX naar de interacties tussen nutriënten, contaminanten en levensgemeenschappen in modelecosystemen en ondiepe meren. Tevens is zij in deze periode betrokken geweest bij de begeleiding van verschillende practica, werkcolleges, en de vernieuwing van een onderwijsdiktaat. In juli 2000 volgde tenslotte de aanstelling voor vier dagen per week als AIO bij dezelfde leeerstoelgroep, betaald door de NWO binnen het Stimuleringsprogramma Systeemgericht Ecotoxicologisch Onderzoek en mede gefinanceerd door het RIZA. Het onderzoek dat gedurende deze periode is uitgevoerd is in dit proefschrift beschreven. Gedurende deze periode heeft zij tevens de universitaire didactische kwalificaties gehaald en is zij betrokken geweest bij verschillende onderwijselementen binnen de leerstoelgroep Aquatische Ecologie en Waterkwaliteitsbeheer. Tijdens de aanstelling als AIO is in juni 2004 haar zoon Stefan geboren. Na afloop van de AIO aanstelling in 2006, is Caroline nog enige tijd bij de leerstoelgroep werkzaam geweest ter ondersteuning van de organisatie van het SETAC congres dat in 2006 in Den Haag gehouden is. Sinds 1 juli 2006 werkt Caroline bij het Stoffen Expertise Centrum van het RIVM in Bilthoven.

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Curriculum vitae

Caroline Tanja Antoinette Moermond is op 2 mei 1973 geboren te Middelburg. In 1991 behaalde zij haar VWO diploma aan de Christelijke Scholengemeenschap Walcheren in Middelburg. Na een jaar als uitwisselingsstudent op het St. Petersburg Junior College in Florida doorgebracht te hebben, is zij in 1992 begonnen met haar studie Milieuhygiëne de Landbouwuniversiteit in Wageningen. Wegens ziekte is deze studie in 1993 ruim een half jaar onderbroken, waarna zij begin 1994 een half jaar stage heeft gelopen bij het RIKZ in Middelburg. Hierna koos zij voor de specialisatie Ecologisch Waterbeheer, waarbinnen afstudeervakken zijn uitgevoerd in de richtingen Aquatische Ecologie, Waterkwaliteit en Toxicologie. De eerste twee afstudeervakken zijn uitgevoerd bij de toenmalige vakgroep Waterkwaliteitsbeheer en Aquatische Oecologie, het laatste afstudeervak is uitgevoerd bij de KEMA onder begeleiding van de vakgroep Toxicologie. Na haar afstuderen in 1998 heeft zij anderhalf jaar als toegevoegd onderzoeker gewerkt bij wat inmiddels de leerstoelgroep Aquatische Ecologie en Waterkwaliteitsbeheer was. Binnen deze aanstelling hield zij zich bezig met het uitvoeren van een modelstudie met AQUATOX naar de interacties tussen nutriënten, contaminanten en levensgemeenschappen in modelecosystemen en ondiepe meren. Tevens is zij in deze periode betrokken geweest bij de begeleiding van verschillende practica, werkcolleges, en de vernieuwing van een onderwijsdiktaat. In juli 2000 volgde tenslotte de aanstelling voor vier dagen per week als AIO bij dezelfde leeerstoelgroep, betaald door de NWO binnen het Stimuleringsprogramma Systeemgericht Ecotoxicologisch Onderzoek en mede gefinanceerd door het RIZA. Het onderzoek dat gedurende deze periode is uitgevoerd is in dit proefschrift beschreven. Gedurende deze periode heeft zij tevens de universitaire didactische kwalificaties gehaald en is zij betrokken geweest bij verschillende onderwijselementen binnen de leerstoelgroep Aquatische Ecologie en Waterkwaliteitsbeheer. Tijdens de aanstelling als AIO is in juni 2004 haar zoon Stefan geboren. Na afloop van de AIO aanstelling in 2006, is Caroline nog enige tijd bij de leerstoelgroep werkzaam geweest ter ondersteuning van de organisatie van het SETAC congres dat in 2006 in Den Haag gehouden is. Sinds 1 juli 2006 werkt Caroline bij het Stoffen Expertise Centrum van het RIVM in Bilthoven.

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