

**Ex situ treatment of sediments with
granular activated carbon.
A novel remediation technology**

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Ex situ treatment of sediments with granular activated carbon. A novel remediation technology

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To my parents

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CHAPTER 1

General Introduction

Hydrophobic organic compounds (HOCs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and various organochlorine pesticides are persistent and toxic compounds often identified in marine and river sediments (Figure 1). Therefore, sediments may serve as a secondary source of contaminants for bioaccumulation and biomagnification and may directly disrupt ecosystem functions through loss of valuable species [1]. In the past decades it has been shown that HOCs bind to sediment phases such as amorphous organic matter (AOM), mineral particles, oil, black carbon (BC) and wheathered oil residues [2-9]. Several studies have shown that especially the fraction of contaminants associated with low density organic material is relevant for risks to aquatic biota, as this fraction often equilibrates to the freely dissolved concentration in the pore water, whereas condensed particulate carbon phases such as soot and kerogen may significantly limit desorption of HOCs to the water column [8]. Thus, HOCs released into the environment through air pollution and deposition, wastewater discharges, industrial and agriculture activities have become important components of aquatic ecosystems including the sediment, which may pose long-term hazards to higher organisms in the food chain.

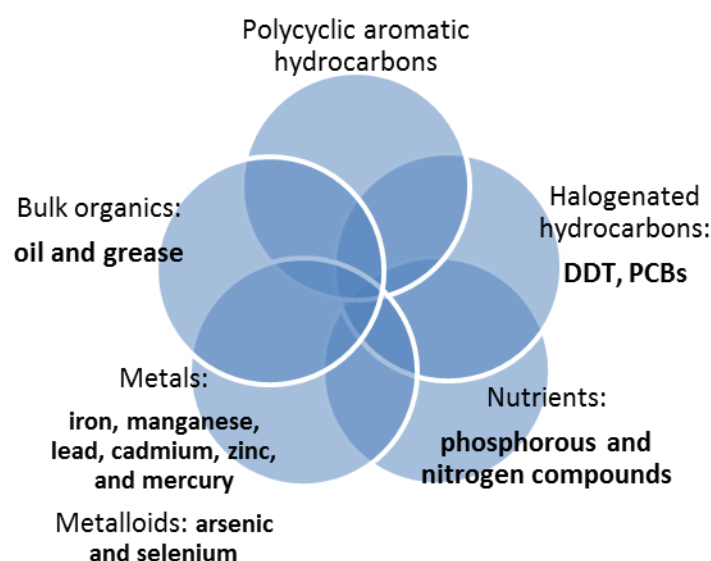


Figure 1. Major types of contaminants found in sediments [10].

To date, much work has been done on developing and implementing *in situ* restoration approaches for sediments, such as natural attenuation (NA), bioremediation, chemical treatments and capping with sand, silt or clay. Since sorption processes play a key role in reducing mobility and risks of sediment-bound contaminants in aquatic environments, activated carbon (AC) application to contaminated sediments has been proposed as an alternative approach to traditional remediation technologies such as dredging and

containment. Early laboratory and field studies demonstrated AC as an effective scavenger for HOCs [11-18]. Sediment remediation with few percent of AC has been shown to result in reduced freely dissolved HOC concentrations in sediment pore water [12, 15, 17-21], and in reduced bioaccumulation and toxicity of HOCs in benthic invertebrates [13, 14, 22, 23]. Thus, AC has been shown to significantly influence the fate and behavior of sediment-bound organic contaminants. Many studies exist on *in situ* sorbent amendments and the number of *in situ* applications is continuously increasing. Although AC binds organic contaminants very strongly, it might cause ecological side-effects i.e. might be harmful to some benthic species [24]. Therefore, AC *in situ* may have several limitations or may be not applicable in countries where sediment amendments with AC are not permitted. In addition, it is not certain whether sorption of HOCs to AC in natural environments can be sustained over a long period of time. Therefore, it is important to explore alternative sediment remediation approaches with AC that offer possibilities for site redevelopment and beneficial reuse of treated material. At the beginning of the present research project, datasets on AC application *ex situ* were not available and *in situ* amendments with granular activated carbon (GAC) were scarce [14, 18, 25].

The current research was meant to explore *ex situ* extraction of sediment by GAC as a novel approach in comparison to traditional AC sediment remediation technologies using amendments of PAC or GAC *in situ*. The aim of the present work was to (a) determine optimal size and dose of GAC for sequestering organic pollutants in sediment-GAC slurries, (b) determine kinetic limitations by quantifying sorption kinetic parameters in mixed sediment-GAC systems, (c) assess sorption competition among different HOCs or organic matter adsorbents ('OM fouling') and (d) evaluate the effects of mixing regimes. Moreover, it is important to investigate the effects of GAC addition on HOC sequestration in laboratory as well as pilot scale application studies. The obtained knowledge will help to study GAC suitability in *ex situ* remediation and feasibility for full scale application. The finding of the present work can be used in developing alternatives to existing remediation techniques, including addition of GAC to dredged sediment followed by storage in a disposal facility, isolation of dredged materials by GAC layers, and cleaning dredged sediments with subsequent deposition on land or beneficial reuse of treated material. Addressing these main research questions may help to increase public acceptance towards *ex situ* sediment treatment.

Recently, *in situ* sorbent amendments such as AC to contaminated sediments have been proposed as an alternative to traditional remediation technologies. A critical review of the state of the art for the use of PAC as *in situ* method for sediment remediation, covering technological as well as ecotoxicological angles is presented in **Chapter 2**. This Chapter reviews the main factors such as AC type, particle size, dosage, sediment and sorbate characteristics affecting the efficiency of AC amendment to sequester HOCs in aquatic sediments and to reduce bioaccumulation in benthic invertebrates. In addition, it discusses potential negative effects of AC on aquatic life. Finally, we discuss if the effects of AC addition can be predicted using fate and transport models. In this review, major knowledge gaps are revealed on sediment-AC-HOC interactions, controlling the effectiveness of HOC

binding and feasibility and efficiency of AC mediated risk mitigation measures. This formed the rationale for the research described in this thesis.

The effectiveness of GAC in binding sediment associated HOCs is strongly related to the amount and nature of sediment phases, e.g. amorphous organic carbon, oil fractions, black carbon, which might attenuate sorption to AC by pore blockage or sorption competition by co-adsorbing HOCs, natural organic matter molecules, and oil. For this reason the effectiveness of GAC application will strongly depend on dosage. Thus, in **Chapter 3**, GAC effectiveness in the presence of associated organic matter is evaluated. Further, the optimal dosage of GAC in terms of PAH pore water reduction in sediment for *ex situ* remediation is determined. Finally, distribution coefficients for short-term sorption processes i.e. days, which are key parameters controlling the effectiveness of sediment remediation with GAC, are estimated.

The efficiency of remediation methods using GAC largely depends on the rate by which contaminants are transferred from the sediment to the surface of GAC. To date, desorption kinetics of HOCs from sediments are usually described using multi-compartment first order models or diffusion models. Similar models have been applied to derive sorption rates of HOCs from aqueous solutions to activated carbons having a complex porous structure. Many studies usually address desorption from sediment against an infinite sink present in the water phase such as Tenax. However, in sediment-GAC mixtures with relatively low GAC dose, GAC may not always act as an infinite sink, implying that backward transport from GAC to sediment has to be taken into account. Kinetic parameters describing HOC transfer from sediment to GAC in intensively mixed systems are not known and HOC release from sediments amended with a low dose of AC hardly has been studied. Therefore, in **Chapter 4**, kinetic parameters for extraction of polycyclic aromatic hydrocarbons (PAHs) from sediment by GAC are estimated using a first-order multi-compartment kinetic model. The sediment-GAC exchange kinetic parameters for the relevant suite of PAHs are obtained following a tiered model calibration approach.

An essential requirement for a successful sediment treatment with GAC is effective transport of pollutants from the sediment to the GAC during the mixing stage. Previous studies have emphasized the importance of mixing conditions on the mass transfer of HOCs in AC-sediment systems. However, it is not clear to what extent turbulence in the GAC/sediment mixing step affects desorption kinetics of HOCs, for example by altering the sediment particle size distributions, and how this factor may influence the effectiveness of *ex situ* GAC extraction technology. In **Chapter 5**, the effect of mixing intensity on desorption of HOCs from contaminated sediment is determined. The kinetics of PAH desorption from sediment are estimated at a wide range of mixing regimes monitored by uptake in Tenax beads using a completely mixed batch reactor. Desorption data are interpreted using a radial diffusion model.

Sediment amendments with AC result in a significant reduction of HOCs pore water concentration on the short-term and these dynamics are studied in **Chapter 3 and 4**. To what extent these reduced pore water concentrations change over longer times and how they differ

among chemicals and for different AC remediation scenarios is also not known. However, it is well known that besides added AC, sediments contain considerable fractions of competing phases, e.g. AOM and BC, which exhibit strong nonlinear sorption for hydrophobic organic pollutants and may significantly limit desorption of HOCs to AC. Thus, it is highly relevant to investigate mass transfer of PAHs in GAC-treated sediment under field conditions and to identify the apparent affinity parameters for sorption of organic contaminants to GAC under natural conditions. In **Chapter 6**, the temporal variation and chemical dependence of treatment efficiency for three AC treatments, viz. mixing sediment with PAC, mixing with GAC, and sediment stripping with GAC are studied. Further, the kinetics of PAH mass transfer in the GAC stripping scenario are assessed. Finally, the *in situ* (pseudo-) equilibrium sorption constants of PAHs as well as PCBs to AC in all treatment scenarios are determined by using the concept of multiple domain sorption modeling.

To date, the efficiency of AC application has been shown for reduction of HOC pore water concentrations and concentrations in benthic invertebrates. However, AC effectiveness and safety have not been tested on the level of entire food chains including fish. In **Chapter 7**, the effects of the three treatments with AC (as studied in Chapter 6), viz. mixing sediment with powdered AC, mixing with granular AC, and sediment stripping, are evaluated with respect to concentrations of PAHs and PCBs in pore water, benthic invertebrates, zooplankton and fish. Moreover, biological side effects of AC amendments for the aforementioned scenarios are assessed in aquatic species of different levels of biological organization.

In the final chapter (**Chapter 8**), overarching answers to the main research questions (see above) will be formulated and an outlook regarding the actual use of *ex situ* GAC will be provided.

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CHAPTER 2

In situ remediation of contaminated sediments using carbonaceous materials: A critical review

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ABSTRACT

Carbonaceous materials (CM) such as activated carbons (AC) or biochars have been shown to significantly reduce pore water concentrations and risks by binding hydrophobic organic chemicals (HOCs) present in aquatic sediments. In the present study, we review the current state of the art for the use of CM as an extensive method for sediment remediation, covering both technical and ecological angles. The review addresses how factors such as CM type, particle size and dosage, sediment characteristics, and properties of contaminants affect the effectiveness of CM amendment to immobilize HOCs in aquatic sediments. We also review to what extent CM may reduce bioaccumulation and toxicity of HOCs and whether CM itself has negative effects on benthic species and communities. The review is based on literature and datasets from laboratory as well as field trials with CM amendments. The presence of phases such as natural black carbon (BC), oil or organic matter (OM) in the sediment reduces the effectiveness of CM amendments. CM additions appear to improve the habitat quality for benthic organisms by reducing bioavailable HOC concentrations and toxicity in sediment. Negative effects of CM itself on benthic species, if any, have been shown to be mild. The beneficial effects of reducing toxicity at low CM concentrations most probably outweigh the mild negative effects observed at higher CM concentrations.

INTRODUCTION

Economic activities associated with industry, growing population and agriculture have led to increasing emissions of pollutants to the environment, and aquatic sediments have been identified as a sink for many hazardous chemicals [1, 2]. Hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides, dioxins, methylmercury, and brominated flame retardants are of particular concern due to their high persistence and toxicity. Although these compounds adsorb strongly to particulate matter, sediment may become a source of pollution by chemical desorption or particle ingestion by biota, and thus may have considerable impact on the quality of aquatic ecosystems [3-7].

Management of such contaminated sediments includes reducing emissions, monitoring and classifying polluted sediments by risk for humans and ecosystems, and sediment quality assessments using water and sediment quality standards, as well as *in situ* and *ex situ* remediation measures for polluted sediments. Traditional technologies for maintaining concentrations of chemicals within sediment quality criteria mainly rely on removing the sediment by dredging or *in situ* capping with clean materials like sand, silt, or clay. Dredging is a highly site-specific technique, applied for the treatment of contaminated sediment deposits liable to erosion and variations in hydrologic conditions [8]. Treatment methods for dredged sediments are expensive [9], and economically-feasible methods like landfarming or ripening in depot are time-consuming [10, 11]. Dredging and capping techniques for long-term cleanup projects with large-scale treatment and complicated site topography require high

investments [8]. Intensive sediment treatment can also cause deterioration of benthic habitats and lead to resuspension of underlying sediment particles, temporarily increasing pore water concentrations of HOCs [12, 13]. Moreover, inefficient removal of contaminated sediment may result in residual HOC concentrations in sediment and pore water still exceeding target values [8]. In contrast, in situ capping aims to create a protective barrier for organisms and is a potentially effective remediation method. However, such barriers do not always sufficiently reduce contaminant transport. For instance, permeability of capping materials or wave pumping has been shown to cause contaminant transport in seabed sediments [14, 15]. Increasing the effectiveness of capping requires the use of “active barriers” such as modified zeolite materials, with higher retention time, instead of clean sediment or sand [16].

In the past few years it has been shown that carbonaceous materials (CM) like soot and charcoal, often referred to as “black carbon” (BC) or “hard carbon,” may bind sediment-bound HOCs very strongly, with sorption affinity constants up to one to two orders of magnitude higher than those for amorphous organic matter (OM) [17-20]. Recent societal demands for less disruptive, less expensive, and more efficient remediation processes have led to the exploration of the potential of adding CM, such as biochar [21] or commercial activated carbon (AC), to polluted sediment as a means of reducing pore water HOC concentrations. The proposed applications for in situ treatment of HOCs based on the addition of CM to sediments, or for *ex situ* methods such as mixing CM in sediment slurries during dredging, transportation, or processing, are very promising in view of their high effectiveness and low cost [13, 22-27]. The science underlying this field of CM application is rapidly evolving and appears to focus on a set of research questions that can be divided into three categories: (a) mechanistic and technical aspects of CM application, (b) ecological and ecotoxicological effects of CM application and (c) modeling the effects of CM amendments for various scenarios. The technical aspects include issues such as CM type, dosage and mixing procedure, i.e., all issues that optimize CM application as an efficient and cost-effective method. The ecotoxicological issues relate to the improvement of sediment quality due to the immobilization of HOCs, to possible negative effects of CM itself on aquatic organisms, or to the interplay between the latter two effects, which may balance each other out. Such studies concern the species, community, or ecosystem level and may yield safe limits for the use of CM in the aquatic environment.

The present review provides an overview of the state of the art as regards the environmentally safe use of CM as an extensive method for sediment remediation, covering both technical and ecological angles. The primary aim is not to summarize the environmental chemistry underlying the role of CM in aquatic sediments, as this has been covered by earlier reviews [18, 20, 28-30]. The key questions from a user’s point of view are what type of CM should be used; at what dosage; whether there is any influence of HOC type; how CM should be mixed with the sediment; whether CM amendment reduces bioaccumulation and risks; whether CM addition is ecologically safe; and whether the effects of CM use can be roughly predicted using simple models. These questions determine the order of the following sections,

starting with a brief history of CM amendment research. Our final aim was to identify knowledge gaps and prospects for CM amendment as a risk-reduction method for sediments.

CM AMENDMENT TECHNOLOGY

A brief history of CM amendment technology

In the late 1960s, it was discovered that organic matter in soils and sediments was the main binding phase for hydrophobic organic compounds [31], and the paradigm of normalizing the solid-water distribution coefficient to total organic carbon (TOC) was further developed in the 1970s [32, 33]. This concept was later challenged by several findings, including (i) elevated sediment-water partition coefficients, (ii) non-linear sorption isotherms, and (iii) multi-phasic desorption kinetics, as well as the presence of soot phases [18, 19, 28, 30]. These observations led to the suggestion that multiple-domain sorption takes place in sediments and that naturally present carbonaceous materials, like soot and chars, commonly referred to as BC, strongly bind HOCs [19, 20, 29, 34-37]. Further research focused on investigating the properties of BC [38, 39], developing methods for its quantification [19, 38-43], and obtaining a mechanistic understanding of sorption to BC [17, 44, 45]. Finally, in view of the similarities between BC and commercial AC, it was suggested to use AC for the immobilization of hydrophobic organic compounds in sediments and soils, just as is done in water treatment [46-50].

The first trials with CM addition involved laboratory tests focusing mainly on in situ applications for PCB- and PAH-contaminated sediments [12, 27, 51-54]. Subsequently, the first pilot-scale field experiments were conducted for in situ stabilization of HOCs using AC [23-25, 55, 56]. Additionally, cross-linked laboratory and in situ field studies have been performed to assess the impacts of environmental conditions on contaminant exposure [23, 57]. Both studies found that dietary patterns of clams (filter and deposit feeders) [23] and polychaetes (deposit feeders) [57] varied between exposure conditions and resulted in differences in bioaccumulation from untreated and AC-treated sediments. However, the literature on simultaneous in situ and *ex situ* AC amendment tests is limited to these two studies, which shows the need for further research. A summary of the reviewed literature and the main findings reported in it are provided in Table 1.

Carbonaceous materials-related research has become more focused on estimating AC sorption parameters for different compound classes associated with the sediment pore water. Activated carbon–water partitioning coefficients (K_{AC}) measured for systems involving AC and clean water appeared to correlate poorly with modeled data [58, 59]. This may be explained by attenuation of HOC sorption to AC. In situ sorption parameters for AC are better able to account for OM fouling and yield better agreement between measured and predicted aqueous HOC concentrations [60, 61].

Effects of CM type and particle size

This section discusses the effect of the type and particle size of AC on the reduction of contaminant availability and the design for sediment cleansing. An overview of the literature

on AC applications to reduce pore water HOC concentrations is provided in Table 1. Several studies showed a high effectiveness of virgin, coal-based AC, TOG, or TOG-NDS 50x200 mesh (75-300 μm), providing almost complete removal of aqueous HOCs ($>99\%$) [12, 13, 23, 24, 27, 52, 54, 57, 62-66]. Not only regular AC but also coconut charcoal proved to be an efficient sorbent for sequestering HOCs [67]. Regenerated AC was found to be equally effective as virgin carbons [13] and is commercially available at a much lower price and thus more suitable for field applications.

Several experiments clearly showed the importance of AC particle size for the reduction of aqueous concentrations of organic compounds [13, 64, 66, 67]. At equal dosages, smaller particle sizes decrease the aqueous phase contaminant concentrations more efficiently due to the larger external surface area of the sorbent and the short intra- and inter-particle diffusive path lengths [66, 68]. Based on particle size, there are two categories of AC. Granular activated carbon (GAC) is defined as having a minimum of 90% of the sample weight retained on a 180- μm standard sieve (80 mesh) [69]. Powdered activated carbon (PAC) is defined as a material with particle sizes primarily smaller than 180 μm [70]. Carbonaceous materials with particle diameters of 75 to 300 μm , which, according to the aforementioned classification of AC, can be regarded as fine particle GAC, have been found to be most efficient in immobilizing HOCs [12, 13, 23, 24, 27, 66, 71, 72] (see Table 1). Significant reduction of PAH pore water concentrations has been obtained after amendment of contaminated sediments using PAC with particle sizes of 15 to 149 μm [71, 73, 74]. Amendments with virgin coarse GAC were found not to be as effective in reducing aqueous HOC concentrations as fine GAC, due to the smaller number of particles per unit mass of treated sediment and soil [12, 67, 71]. No substantial decrease in aqueous PCB concentrations was observed in experiments with granular carbon (particle diameter 420–1700 μm) after 1 month [66, 71]. However, crushing the granules to 75 to 250 μm did result in effective reduction of aqueous PCB concentrations [13, 66].

The sorption of HOCs is affected not only by CM particle size, but also by pore geometry. For instance, the sorption capacity of macropores is believed to be lower than that of mesopores and micropores due to the smaller ratio of surface area to pore volume [68].

In conclusion, reduction of HOC pore water concentrations can be achieved using CMs of different types and origins. However, more effective reduction of freely dissolved concentrations, especially at short time scales, might be achieved by using sorbents with smaller particle size.

Effects of CM dosage in sediment remediation

Since HOCs repartition to CM, the degree of reduction of HOC in pore water is limited by mass transfer and depends on the CM dosage, i.e., the quantity of CM added to the sediment per unit of volume or weight [13, 22, 53, 66]. Many sediment factors affect the CM dose needed to achieve a particular reduction of pore water concentration, for instance, the presence of competing sorbing phases such as OM, BC, or oil [75].

Table 1. Summary of characteristics and results of studies into soil and sediment carbonaceous material (CM) amendment.

CM (Manufacturer)	Type	Origin	SSA ^a , m ² /g	Particle size, mm	Dose, wt %	Mixing regime, rpm	Treatment duration, d	Reduction in C _w , %	Reduction SPMD ^b uptake, %	in	Adsorbate	LogK _{AC} ^c	Reference
TOG®/TOG-NDS Calgon Carbon (Pittsburgh, PA, USA)	virgin granulated	coal	935	0.074-0.297 0.074-0.177	3.2	2-3	31	67	-		DDT	-	[13]
								83	80			-	
								28	74			-	
								180	84			-	
								28	87			7.5	
								180	92			7.6	
								-	-			7.5 ^d	
								0.34	70			-	
								1.7	81			-	
								3.4	84			-	
								0.34	87			-	
								28	44			7.4	[66, 77]
								1.7	74			7.7	
								3.4	87			7.4	
								0.025-0.075	97			-	
								0.7	82			-	
								938	94			-	[63]
								2.5	97			-	
								1032	-			-	[78]
								938	-			-	
								938	91			-	[65]
								938	80			-	
								938	87			-	[52]
								938	69			7.0	
								938	77			7.2	[12]
								938	77			7.3	
								938	97			7.1	[64]
								938	77			-	
								938	82			-	[54]
								938	96			-	
								938	98			-	[57]
								938	99			-	
								938	80,73 ^e			8.1	[23, 56]
								938	-			-	
								938	80 ^f			-	[57]
								938	37 ^g			-	
								938	99			-	[62]
AC (Sigma –Aldrich)	virgin powdered	-	-	0.037-0.149	0.2	6	78	37	-		PAHs	8.1	[73]
					0.5			71	-			8.6	
					2			93	-			8.1-9.1	
					4			94	-			8.5	

ACRS Aquacarb RS Westates Carbon (Santa Fe Springs, CA, USA)	re-activated granulated	coal	900	0.595-2.38	3.2	2-3	31	44	-	DDT	-	[13]
				0.074-0.177	3.2	2	31	83	91	DDT	-	[65]
				0.074-0.177	3.2		31	95	91	DDT	-	
					3.2			-	8		-	
				0.595-2.38	6.4		28	-	20		-	
					9.6			-	46		-	
							28	-	21		-	
					0.8		180	-	30		-	
						2-3	780	-	73	DDT	-	[13]
							28	-	50		-	
				0.074-0.177	1.6		180	-	80		-	
							780	-	95		-	
F400 Calgon Carbon (Pittsburgh, PA, USA)	virgin granulated	coal	1100	0.42-1.7	3.4	3	28	2	-	PCBs	-	[66]
				0.075-0.25				67			-	
				0.5-1	3.2	2-3	31	15	-	DDT	-	[13]
				0.074-0.177				66	67		-	
AC830 Aquacarb® Westates Carbon (Santa Fe Springs, CA, USA)	virgin granulated	coal	900	0.595-2.38	3.2	2-3	31	19	-	DDT	-	[13]
				0.074-0.177				43	45		-	
SAE Super (Norit, Amersfoort, The Netherlands)	virgin powdered	coal	1300		2	-	42	96 ^h ;55 ⁱ	-	PAH	-	[71]
					1			90	-		7.2	
				50%<0.015;3%>0	3			99	-		7.9	
				.150	6	-	2	>99	-	PAH	7.7	[74]
					15			>99	-		7.8	
Aquacarb 208 (Chemviron Carbons, Feluy, Begium)	virgin granulated	coal	1050 - 1200	0.43-1.7	2	-	42	60 ^j	-	PAH	-	[71]
Silcarbon TH90 Extra	powdered	-	-	0.02;80%<0.045	0.02-37 ^k	no mixing	365	50 ^l	-	PAH	-	[55]

^a SSA = Specific surface area, ^b SPMD = Semi-permeable membrane device, ^c LogK_{AC} values from [61], ^d Average LogK_{AC} value from [60]. ^e Reduction in the PCB uptake in polyethylene samplers for a 3.7% AC local dose after five years of AC amendment [56], ^f Relative reduction of uptake in POM samplers placed in subsurface sediment [57], ^g Relative reduction in POM uptake applied in surface layer [57], ^h Average % reduction of freely dissolved aqueous concentration in urban soil/water/PAC suspensions, ⁱ Average % reduction of freely dissolved aqueous concentration in creosote soil/water/PAC suspensions, ^j Average % reduction of freely dissolved aqueous concentration in urban soil/water/GAC suspensions, ^k Dependent on sediment depth [55], ^l Capping with PAC-clay mixture [55].

The dose is also influenced by sorption competition among HOC or OM adsorbates (OM “fouling”), and the physico-chemical properties of the adsorbates, such as hydrophobicity, sorbate planarity, and molecular volume.

In a number of empirical studies, a dosage of 3 to 4% AC proved sufficient to reduce HOC concentrations in the aqueous phase by 99% in 18 months [13, 23, 54] (see Table 1). Activated carbon dosage is often designed to double (i.e., outcompete) the existing TOC content of a sediment [13, 22, 53, 66]. Very recently, Kupryianchyk et al. [61] provided a mechanistic model to estimate the necessary AC dosage for a particular reduction of the initial pore water concentration. Their model calculates the required dosage as a function of HOC sorption affinity to AC, accounting for the sorption affinities to competing phases such as OC and BC. Single average *in situ* $\text{Log}K_{AC}$ values, with associated standard deviations (SD) were 7.2 (0.3) for PCBs ($\text{Log}K_{OW}$ 4.9–6.3) and 8.5 (0.5) for PAHs ($\text{Log}K_{OW}$ 5.2–6.9). The Freundlich exponents (n_F) were optimized per compound class and amounted to $n_{F,AC}=0.74$ (for PCBs) and $n_{F,AC}=0.82$ (for PAHs), suggesting non-linearity of the *in situ* PAH sorption to AC. An AC dose as low as 1% was found to be sufficient to reduce pore water concentrations of PAHs by up to 90% [61]. Despite the differences in sediments and PAC types employed, the variation of apparent $\text{Log}K_{AC}$ for PAHs and PCBs was found in a relatively narrow range. The $\text{Log}K_{AC}$ estimates were two to three orders of magnitude lower than the distribution coefficients for virgin PAC [76], which is most probably due to OM fouling. The *in situ* $\text{Log}K_{AC}$ value for PCBs can be compared to the mean value of 7.5 for tri-, tetra-, and penta-chlorinated PCBs, which was recently reported in the literature [60]. The higher $\text{Log}K_{AC}$ estimates for PAHs as compared to PCBs can be explained by the greater extent of π - π interactions and the higher planarity and molecular surface area of PAHs compared to PCBs [45].

The analysis by Kupryianchyk et al. [61] clearly illustrates how the *in situ* effectiveness of AC for HOCs can be limited by competing phases such as OM and BC. Furthermore, AC sorption strength, and more generally CM sorption strength, is affected by competition between co-adsorbing HOCs and by several HOC molecular properties, such as sorbate planarity. Several studies demonstrated that CM sorption is one order of magnitude weaker for nonplanar ortho-substituted PCBs than for planar PCBs with comparable K_{OW} values [18, 45, 79, 80]. This variation was assumed to be caused by different abilities to change to a planar conformation, and is also visible as the slight difference between *in situ* K_{AC} values for PAHs and PCBs inferred from data reported in the recent AC amendment literature [61].

Another factor that plays an important role in the affinity of HOCs for CM is molecular volume. Higher molecular weight compounds require larger solvent cavities for solvation, which requires more energy [81]. This is most probably the reason why these compounds have higher K_{BC} values.

The above description shows which factors eventually determine the redistribution of HOCs in AC-amended sediments following thermodynamic equilibrium, i.e., at long time scales. However, HOCs in AC-treated sediments are often not at equilibrium. For instance,

sediments treated with up to 3.4% AC demonstrated a progressive decrease in equilibrium aqueous HOC concentrations, by 77 to 97% after 1 month, by 92% after 6 months, and by 99% after 18 months [12, 13, 27, 54, 63, 64, 66] (for details see Table 1). Transfer of HOCs from sediment to AC is affected by various rate limitations. Desorption from sediment is often slow due to rate-limiting diffusive mass transfer along the porous structure within the solid [29, 30, 59, 68], which can have an overall impact on the remediation effectiveness. Subsequent adsorption of HOCs to AC may be kinetically limited by slow diffusion towards the sorbent particle center, which may take months or even years [10, 53]. Higher doses of AC imply a higher concentration of CM particles in the sediment, thus shortening diffusion path lengths and facilitating HOC transport.

Mixing CM with sediments

Mixing plays a crucial role in the effective reduction of aqueous concentrations of organic pollutants, because it stimulates the contact between HOC, CM, and sediment particles. The better the contact, the faster re-equilibration of HOCs between sediment and AC takes place. For initially mixed systems, the average sediment volume per CM particle may be assumed to be distributed spherically around the CM particle, and HOC mass transfer occurs via molecular diffusion, leading to much faster equilibrium conditions than in non-mixed systems [53]. The majority of experimental research has been dedicated to mixed sediment–AC systems that mimic anticipated equilibrium conditions in the field after long contact periods [13, 25, 27, 53, 54, 59, 66] (see Table 1). Brandli et al. [71, 73] performed laboratory experiments with intensively mixed (shaken end-over-end) systems, whereas Cornelissen et al. [55] evaluated AC amendment efficiency in non-mixed scenarios. We are aware of only one study that compared the effects of brief initial mixing of AC (2 min of mixing vigorously by hand and left undisturbed for up to one year) versus intensive mixing (up to one year at 100 rpm) [59]. After one month of contact time, the reduction of pore water PAH concentrations as measured by passive samplers was found to be equal in briefly and thoroughly mixed systems (97% vs 98%). However, the mixing regime was suggested to have a higher impact on sediments with higher PAH availability [59]. In conditions of large PAH availability, desorption from the sediment is a fast process with a large gradient towards the CM particle. Low availability implies slow desorption from the sediment particle and a low gradient.

So far, five pilot-scale studies have evaluated possible modes of AC addition and mixing into sediment under field conditions [23-25, 55]. These studies considered technical challenges and feasible solutions for site-specific applications of AC. Remediation of a tidal mudflat area was accomplished by covering the sediment surface with AC and mixing it into the biologically active layer (upper 30 cm) with a barge-mounted rotovator and a crawler-mounted slurry injector [23, 24]. Post-treatment evaluation revealed that the slurry injection system resulted in less homogenous mixing than the rotovator device, even though AC was unevenly distributed in the upper layer of sediment. Remixing or multidirectional mixing was

suggested to improve in situ AC amendment. The assessment five years after treatment showed that the sediment retained AC levels comparable to the target dose of 3.4% [56]. Mixing of AC with HOC-contaminated sediments has also been performed with a rototiller mixing unit, tine sled device and a trim pipe [25]. A novel form of pelletized AC (SediMite) has been applied in a wetland region with an air-blown dispersal device [25]. However, results regarding the mixing effectiveness of these units in terms of pore water concentrations or bioaccumulation are not yet available. Recently, marine underwater sediment treatment with PAC capping, relying on bioturbation-induced mixing (no initial mixing) has been reported [55]. This study compared different methods of sediment capping with the addition of PAC only, PAC mixed with clay, and PAC covered with sand. The results clearly showed that montmorillonite clay was an effective carrier material for AC, causing the anticipated positioning of sorbent layers on the seabed. Clay application resulted in reduced losses of fine particles and a more even distribution of PAC, as compared to other modes of sediment capping [55]. However, in contrast with earlier field trials [23, 24], Cornelissen et al. [55] observed only moderate effects of sorbent amendment, most probably due to ineffective mixing. Their best performing scenario used a PAC-clay mixture, and resulted in a reduction of only 50% of the pore water PAH concentration and a reduction of no more than a factor of 10 in the sediment-to-water flux. Recently, Cho et al. [56] confirmed that non-uniform distribution of AC in treated sediment retarded PCB mass transfer into AC particles. In summary, initial mixing of CM with sediment and subsequent remixing can be advantageous due to the more homogenous distribution of CM between sediment particles, which facilitates HOC mass transfer.

ECOTOXICOLOGICAL EFFECTS OF CM AMENDMENTS

As outlined in the previous section, many studies have demonstrated a high potential of CM for reducing aqueous and thus bioavailable concentrations of HOCs (see Table 1). We are aware of only a few studies that have shown reduced toxicity, i.e., reduced mortality in contaminated sediments after CM addition [57, 74, 82, 83]. Apart from this advantageous effect, however, CM itself has also been shown to cause negative effects on aquatic organisms in laboratory settings [51, 52, 74, 77, 84, 85]. Consequently, the application of AC as a useful and safe remediation technique requires information on possible ecological side effects, namely effects on biological parameters of various benthic species, potential impacts on exposed communities, and effects on the quality of the pelagic and benthic environment. Data at these higher levels of biological organization are still limited. This section reviews the existing evidence for the advantageous effects of CM on bioaccumulation and toxicity of contaminants, followed by a review of the information on possible negative effects of CM amendment.

Effects of CM amendment on HOC bioaccumulation

Since HOCs mainly partition between sediment organic matter and adipose tissue of aquatic organisms, the biota-to-sediment accumulation factor (ratio between HOC concentration in adipose tissue and in sediment) is often used as a measure of bioaccumulation from sediment. Several studies reported a 1–2 orders of magnitude decrease in biota-to-sediment accumulation factor after CM amendment [27, 51, 62, 65, 78, 86–90]. Early studies mainly investigated natural factors attenuating the bioaccumulation of HOCs from contaminated sediments namely, the type and amount of naturally present CM, (e.g., char, soot, coal) [51, 88, 89], structural and physico-chemical properties of the HOCs [51, 86], sediment characteristics [87, 91], and biological factors [87]. Several studies also focused on the effectiveness of CM amendment in terms of its potential to reduce bioavailable concentrations (see Table 1) and on the decrease in the bio-uptake of HOCs after different contact times between sediment and CM (see Table 2). It has been shown that bioaccumulation of PCBs decreases by 70 to 95% within 1 month [12, 51, 52, 63, 64, 77]. A recent study found a 90% reduction of PCB bioaccumulation in polychaetes (*Neanthes arenaceodentata*) exposed to sediment amended with 3.4% AC for 14 d under laboratory conditions [57]. Interestingly, only 40 to 48% reduction of PCB uptake was found in parallel in situ tests. This effect was explained by the deposition of fresh surface sediment with a new available fraction of PCBs [57]. Moreover, bioaccumulation of PCBs in polychaetes from in situ untreated sediment was significantly lower than that for *ex situ* sediment, indicating that environmental conditions might greatly modify toxicity effects on benthic organisms. Finally, it has been shown that CM actually decreases PAH and PCB toxicity of sediments to the amphipods *Ampelisca abdita* and *Gammarus pulex*, the mysid shrimp *Americamysis bahia*, the isopod *Asellus aquaticus*, and the aforementioned polychaetes, and increases the survival of these species [57, 74, 82, 83].

Occurrence of ecotoxicological effects

Toxicological effects of CM sediment amendment can be studied at species level, community level, or ecosystem level. An overview of the currently available literature is provided in Table 2. Studies at species level usually used endpoints such as survival, growth, egestion rate, lipid content, reproductivity, or behavior (avoidance, locomotion, ventilation). However, it has been shown that behavioral changes may occur at levels much lower than lethal or growth-inhibiting concentrations, either as a result of direct toxicity or as a protective defense mechanism [92].

Survival of benthic species is usually studied in laboratory tests with a standard duration of 28 d (see Table 2). Many organisms exposed to sediment amended with CM showed high survival rates [24, 52, 57, 65, 74, 82, 84]. Exposure to sediment enriched with 2 to 3% AC led to a 25% decline in the survival of the freshwater clam *Corbicula fluminea* and a 50% decline in the survival of the freshwater amphipod *Gammarus pulex* [74, 77].

Table 2. Summary of reported ecotoxicological effects of carbonaceous materials (CM) on single species and benthic communities.

Ecotoxicological endpoint	Species	CM: type, size and dose	Duration	Results	Reference
Mortality	<i>N. arenaceodentata</i>	AC: TOG (Calgon, Pittsburgh, PA, USA)	28 days	not significant	[52]
	<i>L. plumulosus</i>	75–300 µm, 3.4%;			
	<i>M. eduli</i>	ReAC: (Aquacarb RS, Westates Carbon, Santa Fe Springs, California, USA) 74-177 µm AC: TOG (Calgon, Pittsburgh, PA, USA) 74-177 µm, 3.4%	28 days	not significant	[65]
	<i>M. balthica</i>	AC: TOG (Calgon, Pittsburgh, PA, USA) 75-300 µm, 2.5, 1.3, and 0.7%	28 days	25, 15%, <5%, respectively	[63]
	<i>M. nasuta</i>	AC: TOG (Calgon, Pittsburgh, PA, USA) 74-177 µm, 3.2%	28 days	not significant	[24]
	<i>A. aquaticus</i> <i>C. volutator</i>	AC: Organosorb 200-1 (Desotec Activated Carbon, Belgium), 90% < 74 µm, <25%	28 days	not significant	[84]
	<i>G. pulex</i> <i>A. aquaticus</i>	AC: SAE Super (Norit, Amesfoort, The Netherlands), D ₅₀ =15 µm, < 30%	28 days	LC ₅₀ =3.1% not significant	[74]
	<i>N. arenaceodentata</i>	AC: TOG-NDS (Calgon , Pittsburgh, PA, USA) 75-300 µm, 3.4%	14 days <i>in situ</i> 14 days <i>ex situ</i>	not significant	[57]
Growth/condition index	<i>N. arenaceodentata</i>	AC: TOG (Calgon, Pittsburgh, PA, USA)	28 days	decrease by 50% w.w. non-significant decrease	[52]
	<i>L. plumulosus</i>	75–300 µm, 3.4%			
	<i>M. eduli</i>	AC: TOG (Calgon, Pittsburgh, PA, USA) 75–300 µm, 3.4%	28 days	minor decrease in average condition index	[65]
	<i>C. fluminea</i>	AC: TOG (Calgon, Pittsburgh, PA, USA) 74-177 µm, 3.2%	28 days	non-significant decrease	[63]
	<i>G. pulex</i> <i>A. aquaticus</i>	AC: SAE Super (Norit, Amesfoort, The Netherlands), D ₅₀ =15 µm, < 30%	28 days	not significant (AC < 3%) EC ₅₀ =5.3%	[74]
	<i>N. arenaceodentata</i>	AC: TOG-NDS (Calgon , Pittsburgh, PA, USA) 75-300 µm, 3.4%	14 days <i>in situ</i> 14 days <i>ex situ</i>	non-significant difference	[57]

Lipid content	<i>Limnodrilus sp</i>	Coal, 1.48% Charcoal, 1.48%	28 days	decrease by 28% decrease by 38%	[51]
	<i>L. variegatus</i>	AC: Organosorb 200-1 (Desotec Activated Carbon, Belgium), 90% < 74 µm, < 25%	16 weeks	decrease by 75%	[84]
	<i>H. reticulatus</i> <i>N. diversicolor</i>	AC: 100–400 mesh (Sigma-Aldrich, Oslo, Norway), 37–149 µm, 2%	28 days	non-significant decrease	[72]
	<i>N. arenaceodentata</i> <i>L. plumulosus</i>	AC: TOG (Calgon, Pittsburgh, PA, USA) 75–300 µm, 3.4%	28 days	non-significant decrease	[52]
	<i>N. arenaceodentata</i>	AC: TOG-NDS (Calgon, Pittsburgh, PA, USA) 75–300 µm, 3.4%	14 days <i>in situ</i> 14 days <i>ex situ</i>	non-significant difference significant decrease	[57]
Avoidance/preference	<i>A. aquaticus</i> <i>C. volutator</i>	AC: Organosorb 200-1 (Desotec Activated Carbon, Belgium), 90% < 74 µm, 4, 7, 15, and 25%	3 days	non-significant avoidance significant avoidance	[84]
	<i>G. pulex</i> <i>A. aquaticus</i>	AC: SAE Super (Norit, Amesfoort, The Netherlands), D ₅₀ =15 µm, < 30%	3 days	non-significant avoidance	[74]
	<i>G. pulex</i> <i>A. aquaticus</i>	AC: SAE Super (Norit, Amesfoort, The Netherlands), D ₅₀ =15 µm, < 30%	1 day 5 days	non-significant change	[74]
Locomotion/ventilation	<i>L. plumulosus</i>	AC: TOG (Calgon, Pittsburgh, PA, USA) 75–300 µm, 3.4%	28 days	non-significant decrease	[52]
Egestion rate	<i>L. variegatus</i>	AC: Organosorb 200-1 (Desotec Activated Carbon, Belgium), 90% < 74 µm, 1, 2, 4, 7, 10, 15, and 25%	10 days	1% AC disturbs normal feeding behaviour	[84]
Diversity, abundance	Benthic community	AC: TOG-NDS (Calgon, Pittsburgh, PA, USA) 50–200 µm, 3.2%	6 and 18 months	non-significant difference between AC and control sediment	[23]
		AC: Silcarbon TH90 Extra (Silcarbon Aktivkohle GmbH, Kirchhundem, Germany), 80% < 45 µm, AC-only, AC+sand, and AC+clay capping	5 and 11 months	significant decrease in abundance and richness	[55]
	Bacterial community	AC: Organosorb 200-1 (Desotec Activated Carbon, Belgium), 90% < 74 µm, 0, 2, 4, 10, and 20%	Several weeks	non-significant difference between AC and control sediment	[84]

As for growth rate, some studies demonstrated no effects of AC addition, or only mild effects (less than 7% reduction) for the clam *Corbicula fluminea*, the mussel *Mytilus edulis*, the polychaete *Neanthes arenaceodentata*, and the amphipod *Gammarus pulex* [57, 63, 65, 74]. Higher growth reductions have been reported for the isopoda, i.e., *Asellus aquaticus*, and worms, namely, $EC_{50} = 5.3$ and 3.4% AC, respectively [52, 57, 74]. Janssen et al. [57] did not observe any effects of sediment amended with AC on the lipid content of *Neanthes arenaceodentata* under laboratory and field conditions. However, other reports show decreasing lipid contents in worms. *Lumbriculus variegatus* showed lipid content reductions of 22, 28, and 38% after a 28-d exposure to sediments enriched with AC [84], coal [51], and charcoal [51], respectively. The reduced lipid content (74%) was caused by reduced feeding (92%) by these worms when exposed to sediment with 10% AC [84]. The results of chronic exposure of worms to sediment with 10% AC resulted in a gradual decrease in lipid content by 74% over four months [84] whereas egestion rates of worms exposed to 4% AC declined by 92% over 10 d [84]. Oil soot (0.34%) was reported to reduce sediment-to-water transfer of PAH, which was explained by a reduction of bioturbation activity by *Limnodrilus* sp. [85]. Preference/avoidance behavior responses were investigated for the species *Corophium volutator*, *Asellus aquaticus*, and *Gammarus pulex* using different sediments containing up to 30% AC [74, 84]. However, avoidance could not be proven from the data, due to inconsistent dose–response relationships. The absence of behavioral responses like locomotion and ventilation of *Asellus aquaticus* and *Gammarus pulex* has been demonstrated in whole-sediment behavioral toxicity tests [74].

Cho et al. [23] conducted *in situ* experiments to estimate AC amendment effects on the benthic community. Biodiversity and abundance were estimated after 6 and 18 months for sediment treated with up to 3.2% AC. No significant statistical difference was found before and after treatment with AC. A similar experiment to estimate effects of AC capping on the benthic community has been performed by [55]. They found that benthic macrofauna composition and biodiversity were affected by the AC amendments, with an AC–clay mixture having a lower impact on the community than AC only or AC covered with sand.

In summary, the available reports suggest that addition of CM to bed sediment has little or no effect on the survival of benthic organisms. The greatest effects seem to occur in worms, but they did not cause significant increases in mortality at the 3 to 4% CM levels used in this remediation scenario. It must be noted that community effects will be even less severe in field settings, where dilution, recolonization, and fresh input of organic matter will provide new habitat on top of treated sediments.

Mechanisms of ecotoxicological effects

Sediment-dwelling organisms like worms may be more susceptible to CM amendment, since they are exposed to CM not only via direct contact but also via ingestion of CM particles. As mentioned in the previous section, *L. variegatus* had a decreased lipid content and egestion

rate after long-term exposure to sediments enriched with CM [51, 84]. The literature suggests several mechanisms for such negative effects on benthic species.

First, *L. variegatus* may be affected by CM-enriched sediment due to the chemistry of CM (taste, smell, composition) [51, 84], since it has been shown that even 1% carbon amendment can affect the feeding activity of *L. variegatus* [93]. Another explanation may relate to the surface reactivity of CM, with its high affinity for lipids, carbohydrates, and proteins [94, 95]. It has been hypothesized that CM may sorb nutrients that serve as a food source for worms or impair digestion processes [52, 84], but no statistically or biologically relevant effect of AC has been found on enzyme activity or digestive fluid surfactancy in AC-amended sediment [52].

Toxicity of carbonaceous materials can also be explained by secondary effects on test conditions affecting habitat quality, e.g., an increase in the pH and decrease in the oxygen content of the test systems, which may be explained by the presence of metals [84]. Direct toxicity may originate from CM constituents, such as associated metals, which may constitute up to 3.5% of CM mass and can be released to pore water or overlying water or in the gut [84]. Consequently, whole sediment toxicity tests should rule out such artifacts if only effects of AC are to be detected [74].

It must be noted that reported effects of CM mostly originate from small-scale laboratory experiments and will probably be less relevant in ecologically realistic field settings. After all, under field conditions, the supply of nutrients will most likely outcompete the binding capacity of CM due to scale and prolonged supply, and will thus not be a limiting factor. Effects of pH or oxygen will be progressively attenuated by the large buffering capacity of (usually calcareous) sediments and natural re-aeration. Fluctuations of pH or oxygen will not be fundamentally different from the natural fluctuations of these variables due to community metabolism and aerobic respiration. Furthermore, apart from some deposit feeders, many sediment-dwelling organisms acquire their nutrients and oxygen from the overlying water and are thus relatively insensitive to conditions in the sediment bed.

The problem of toxicants associated with CM can be easily circumvented by using non-toxic AC, analogous to the use of AC in drinking water preparation and water purification. Finally, it must be noted that the highest impact of large-scale dispersal of AC will be the total physical disruption of benthic habitats and benthic communities. There is therefore a need for more ecological recovery studies to validate these expectations. So far, only one study demonstrated that the benthic community functionally altered by HOCs present in the sediment, recovered after addition of AC [96]. Studies on biodiversity development and recovery of functional endpoints in different field settings are thus highly relevant.

FATE AND TRANSPORT MODEL SIMULATION IN CM AMENDMENT SCENARIOS

To date, several CM amendment studies have used transport and fate models. These models aimed to improve mechanistic understanding and identify dominant processes governing

HOC transport in sediment [7, 22, 53, 59, 66, 68, 85, 97, 98]. Another rationale for modeling approaches has been the a priori estimation of AC dosage for effective remediation [61]. Other studies used biodynamic models based on a mass balance approach to understand and predict HOC bioaccumulation in organisms while accounting for the effect of AC [62, 63, 65, 77, 96]. Some studies combined HOC intraparticle diffusion models or desorption and adsorption by native or added particles with biodynamic modeling [53, 98, 99].

It is generally believed that slow sorption of HOCs to AC in sediment is controlled by diffusion from natural CM and subsequent diffusion to AC particles. Consequently, the exchange rate of contaminants among sediment particles, the surrounding water, and natural and applied sorbents (assuming perfectly mixed conditions) has been widely described using diffusion-based models. Typically, transport modeling in AC amendment studies involves modeling the release of HOCs from the sediment particles to water, followed by uptake in the AC particles [22, 53, 59, 68]. Mechanisms behind this mass transfer were explored by Ahn et al. [68]. They demonstrated that a branched kinetic model, comprising PAH macropore diffusion with kinetic exchange of PAHs between macropores and micropores, fitted the experimental observations better than an intraparticle diffusion model and a pore diffusion model. Defining macro- and micropores allows two types of sorption behavior to be modeled. Other dual domain diffusion approaches have used rapid porous diffusion in amorphous carbon as well as slow solid-phase diffusion in condensed-phase organic carbon [7, 97]. Werner et al. [53] used an intraparticle diffusion model to simulate the effects of AC dosage and particle size on the mass transfer of PCBs in sediment. Their simulations showed that increasing the AC dose, as well as reducing the AC radius, increased the observed reduction of the aqueous concentration of contaminants. This conceptually agrees with the earlier experimental observations related to effects of particle size, which have been discussed in the current review.

Several authors demonstrated a systematic overestimation of AC amendment efficiency [53, 73, 100]. For instance, Werner et al. [53] found that a K_{AC} value for virgin AC had to be reduced by a factor of 16 to obtain a good fit of their model to experimental data. They explained the difference by organic matter fouling, which was discussed in section 2.3. Model overestimation might also originate from the assumption of uniformly mixed, homogenous systems, ensuring short diffusion distances. In the case of non-mixed, spatially heterogeneous systems there is higher resistance to mass transfer, so a reduction of HOC pore water concentrations obtained in days for well mixed systems might take years to achieve [53].

Cho et al. [101] developed a heat transport model to indirectly estimate the importance of advective pore water movement and mechanical dispersion to PCB mass transfer in an intertidal mudflat. They concluded that for non-uniform distribution of AC particles in the sediment bed, the transport rate of HOC might be significantly improved by advective flow and mechanical dispersion. Overall, site-specific or external conditions like tidal pumping, bottom currents, and sediment resuspension would contribute to accelerating HOC binding in real non-mixed AC-amended sediments [101]. However, in contrast with their modeling

results, these effects were not evident at Hunters point, in their five-year post-treatment monitoring study [56]. Whereas these model studies emphasized the true diffusive transport mechanisms, Matilla & Verta [99] studied HOC fate using a CM-inclusive non-steady state mass balance model of chemical transport to obtain a more realistic estimate of the potential risks of organic chemicals. Inclusion of BC resulted in the best model fits and had a major effect on the mass balance.

Similarly, CM-inclusive models have been formulated for HOC bioaccumulation, which were applied either dynamically or in their steady-state solution. These models demonstrated the ability to predict concentrations of contaminants in organisms by species-specific combinations of all routes of uptake and elimination, while accounting for binding to CM [57, 62, 63, 77, 87, 96, 98, 102-105]. Biodynamic modeling parameterized for site-specific exposure conditions demonstrated different responses in terms of PCB tissue concentrations of three invertebrate species representing different dietary patterns [96]. The model was further used to test the effect of AC addition on the potential reduction of PCB availability and internal tissue concentrations. Model predictions clearly communicate the impact of AC amendment on bioavailability and total PCB concentrations to sediment management authorities [96], although they ignore local variability in AC and sediment distribution. Effects of ecological factors on HOC bioaccumulation have been studied by Moermond et al. [87, 104], who demonstrated that ecosystem structure, i.e., the dominant species, as well as chemical aging in sediment, affects HOC accumulation in aquatic organisms. The systematic overprediction of biota-to-sediment accumulation factors in steady-state models could be explained by (a) neglect of metabolic transformation of HOCs in the model and/or (b) neglect of binding to CM. McLeod et al. [63, 77, 106] explored geochemical and biological factors affecting HOC uptake and investigated the relative importance of dietary and aqueous uptake routes for HOC accumulation using a model approach. They argued that HOC reductions in the aqueous phase alone are not sufficient to effectively reduce HOC uptake by sediment-dwelling organisms, and emphasized the importance of addressing sediment ingestion as an exposure route from CM-amended sediments.

Recently, elaborate mass transfer and bio-uptake models have been developed that link sediment geochemistry with contaminant bio-uptake processes in order to simulate the long-term fate and bioaccumulation of HOCs [53, 98, 99, 106].

CONCLUSIONS AND PROSPECTS

The present review has provided an overview of factors that affect the effectiveness of CM amendment to immobilize HOCs in aquatic sediments, such as the type, size, and dosage of CM, sediment characteristics and properties of contaminants. An average in situ K_{AC} derived from literature data may be useful when designing an AC dosage for in situ sediment remediation. The effectiveness of a CM dosage may depend on the presence of other carbonaceous materials than AC, like BC, oil, and OM. For most applications, a 2 to 4% AC

dose appears to be sufficient. Other key factors for effective remediation are sufficiently small CM particle size and sufficient mixing.

Literature data suggest that the addition of CM to bed sediment in the 2 to 4% range has only mild direct effects, if any, on benthic organisms. Effects will probably be smaller in actual field settings. In contrast, the effect of CM amendment on the reduction of HOC exposure and toxicity is dramatic, with up to 100-fold pore water concentration reductions and significantly increased survival of benthic invertebrates in contaminated sediments. This implies that the net effect of CM addition will often be an improvement of habitat quality, especially for highly toxic sediments. Future work should combine CM and toxicant dose–response relationships for benthic species, so that the break-even point can be assessed more accurately and for different habitats.

Since sediment characteristics such as particle size, mineralogy, bulk density, biological activity, and contamination level are different for different locations, remediation strategies using AC should probably be site-specific. For instance, CM amendment can be a successful and cost-effective method for sites with depositional and cohesive characteristics, where the probability of sorbent translocation after incorporation into contaminated sediment is low and continuous sampling and monitoring could take place. Otherwise, natural processes like tidal pumping, wind shear stress, or bioturbation might affect aqueous HOC concentrations due to resuspension of particle-associated contaminants [101]. In the case of deeper waters, sloping areas or sites with lower sediment stability or more extreme erosion conditions, specific measures may have to be taken. For instance, CM layers may need to be stabilized with additional layers of sand, gravel, or clay [55]. Capping with such layers would decrease the risk of contaminated CM being dispersed within the aquatic environment and would limit the footprint of CM itself. In low energy environments, the use of powdered CM could be favorable, since HOC transfer from sediment to CM can be relatively fast. On the other hand, in situ application of powdered CM by spreading might be problematic due to the transportation of fine particles with the water to less contaminated sites.

The literature offers no descriptions of CM applications in intensive *ex situ* treatments of sediments. Further promising alternatives to existing in situ–techniques could include remediation techniques such as the addition of CM to dredged sediment followed by storage in a depot, isolation of dredged materials by CM layers, and cleaning dredged sediments with subsequent deposition or use on land.

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CHAPTER 3

Extraction of sediment associated polycyclic aromatic hydrocarbons with granular activated carbon

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ABSTRACT

Addition of activated carbon to sediments has been proposed as a method to reduce ecotoxicological risks of sediment-bound contaminants. In the present study, we explore the effectiveness of granular AC (GAC) in extracting polycyclic aromatic hydrocarbon (PAH) from highly contaminated sediments. Four candidate GAC materials were screened in terms of PAH extraction efficiency using single-step 24 h GAC extractions, with traditional 24 h Tenax extraction as a reference. Subsequently, sorption of native PAHs to the best performing GAC 1240W (0.45-1.70 mm) was studied for sediment only and for GAC-sediment mixtures at different GAC-sediment weight ratios, using 76 μm polyoxymethylene (POM) passive samplers. GAC sorption parameters for PAHs were determined by subtracting the contribution of PAH sorption to sediment from PAH sorption to the GAC-sediment mixture. It appears that the binding of PAHs and the effectiveness of GAC to reduce sediment pore water concentrations was highly dependent on the GAC-sediment mixing ratio and hydrophobicity of the PAH. Despite the considerable fouling of GAC by organic matter and oil, 50-90% of the most available PAH was extracted by the GAC during 28-d contact time, at a dose as low as 4%, which also is a feasible dose in field scale applications aiming at cleaning the sediment by GAC addition and removal.

INTRODUCTION

Anthropogenic activities such as combustion of fossil fuels, oil spills and increased industrialization have resulted in widespread pollution of aquatic sediments with a variety of hydrophobic organic compounds (HOCs). In the last decade, *in situ* addition of activated carbon (AC) to polluted sediments has been proposed as a effective remediation strategy to reduce risks of sediment-bound HOCs and to improve the ecological quality of surface waters [1, 2]. Sediment remediation with AC has been shown to result in reduced freely dissolved HOC concentrations in sediment pore water in laboratory and field settings [3-7], and in reduced bioaccumulation and toxicity of HOCs in benthic invertebrates [5, 6, 8].

Key to the effectiveness of AC in sediment remediation is its high sorption capacity, which is caused by a high specific surface area, well developed porosity and dedicated surface chemistry. Consequently, the majority of AC amendment studies use powdered AC (PAC) or fine granular AC (GAC) having particle diameters within the range of 75 to 300 μm . Small particles have large external surface area and, therefore, large accessible number of sorption sites per unit of weight [9]. Recently, risk reduction of sediment-bound HOCs in pilot field studies has been accomplished through addition of AC to the sediment biologically active layer (upper 30 cm) using commercial mixing units, by capping with a thin layer of AC, or by mixing AC in a layer of clay [3, 4, 10, 11].

The science underlying AC application to remediate polluted sediments is rapidly evolving and granular activated carbon (GAC) may be an effective alternative to PAC in *in situ* soil remediation [12]. In The Netherlands, intensive *ex situ* treatment of contaminated

sediments with GAC has been recognized as a promising and novel technique, which might be also relevant in other regions. The treatment includes the following steps: addition of GAC to a sediment slurry or stream, extraction of HOCs from sediment by GAC, separation of contaminated GAC from the cleaned sediment slurry, regeneration of GAC by thermal treatment, and re-use of cleaned sediment in the construction of for instance dikes, roads or highways. Separation of GAC from sediment at high volumes is feasible using industrial sieving units (Supplemental Information, Figure. S1 and S2).

Regeneration of GAC after sediment treatment reduces the treatment costs and contributes to the reduction of the AC in the environment. Furthermore, the reactivation step might modify carbon structural properties in a manner that enhances sorption of organic compounds [13]. The number of studies using GAC particles larger than 0.3 mm in the context of sediment remediation is limited. Previous studies have estimated the effectiveness of GAC to immobilize HOCs in bed sediments [6] and slowly mixed systems[7]. Under these conditions, GAC has been shown to be less effective as compared to PAC. However, in an intensive addition-removal scenario, where mixing conditions are more efficient and removal is by particle separation (sieving), GAC is the preferred candidate sorbent. In a recent field scale pilot study in The Netherlands, addition, 24 h mixing in a batch operational mode and subsequent removal of GAC (FigureS2), resulted in a reduction of the total polycyclic aromatic hydrocarbons (PAHs) concentration by a factor of 2 to 4.

The effectiveness of PAC or GAC in binding sediment associated HOCs is strongly related to the amount and nature of sediment phases that compete with AC for the binding of PAH. These include amorphous organic carbon, mineral particles, oil, black carbon (BC) and weathered oil residues [14, 15]. Recently, Kupryianchyk et al. [15] showed how limitations in AC performance can be quantified based on organic carbon and BC content. Refractory phases such as BC and weathered oil might significantly limit desorption of HOCs to AC [16, 17]. However, a substantial fraction of HOCs is known to be associated with light density organic carbon [18] composed of humic/fulvic substances, lignin and plant debris or mineral particles [19]. This fraction of HOCs can be expected to readily desorb and bind to AC particles in a sediment slurry. However, it is also known that natural organic matter (NOM) and oil might attenuate sorption to AC by pore blockage or sorption competition by co-adsorbing HOCs, NOM molecules and oil [20-23]. Since the added GAC would compete for the sorption of HOCs with natural sediment phases, its effectiveness would strongly depend on its dosage. Consequently, distribution coefficients for short-term sorption processes, and dosage level of GAC are likely to be important parameters controlling the effectiveness of intensive sediment remediations with GAC.

The aim of this work was to test this hypothesis and further explore the potential of GAC in the context of *ex situ* sediment remediation technology. To this end, the optimal dosage of GAC in terms of PAH pore water reduction in sediment for *ex situ* remediation was determined. Thus, the current work evaluated GAC effectiveness in the presence of associated organic matter. A ‘worst case’ sediment with very high PAH and oil pollution levels was selected, in order to explore the upper limits of the capacity of GAC. Initially, a suite of

candidate GAC materials was screened for maximum efficiency in extracting PAHs from sediment within 24 h. The effectiveness of GAC was compared to a single-step solid phase extraction (SPE) with Tenax beads, which currently is the most commonly applied material to remove HOCs from sediments under laboratory conditions [24]. Sorption of native PAHs to the best performing GAC was studied for mixtures at different GAC-sediment weight ratios and sediment only. For all these experiments, aqueous phase PAH concentrations were accurately determined using 76 μm polyoxymethylene (POM) passive samplers [8, 25, 26]. The sorption to GAC in the sediment-GAC mixtures was assessed by subtracting the contribution of PAH sorption to sediment from total PAH sorption in the mixture. Sorption data were interpreted in terms of aqueous phase concentration reduction ratios and distribution coefficients.

MATERIALS AND METHODS

Chemicals

Hexane and acetone (Promochem; picograde), methanol (Mallinckrodt Baker, HPLC gradient grade), ethanol (Merck, p.a.), acetonitrile (Lab-Scan, HPLC grade), calcium chloride CaCl_2 (Merck; p.a), sodium azide NaN_3 (Aldrich; 99%), sodium sulphate Na_2SO_4 (Merck, p.a.), sodium carbonate Na_2CO_3 (Merck, p.a.), sodium bicarbonate NaHCO_3 (Merck, p.a.), aluminum oxide-Super I (ICN Biomedicals) were used in the experiments. Prior to use, aluminum oxide was deactivated with 10% (w/w) Nanopure water (Barnstead). Other water preparations used Milli-Q water (Millipore Corporation). HPLC standard EPA 610 PAH Mix containing acenaphthene (ACE), acenaphthylene (ACY), anthracene (ANT), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[g,h,i]perylene (BghiP), benzo[k]fluoranthene (BkF), chrysene (CHR), dibenzo[a,h]anthracene (DBA), fluoranthene (FLU), fluorene (FL), indeno[1,2,3-cd]pyrene (InP), naphthalene (NA), phenanthrene (PHE), and pyrene (PYR) was obtained from Supelco Analytical, with purities of >98% except for PYR (purity > 96.6%).

Sediment

Sediment was dredged in 1997 from Amsterdam Petroleum Harbor (PH), The Netherlands, which was constructed for storage and transshipment of petroleum and coal, and stored at 4°C in the dark. The sediment was passed through a 2-mm sieve and well homogenized prior to sorption experiments. The sediment was characterized for dry weight, total organic carbon (TOC), black carbon (BC), total native content of PAHs and total native petroleum hydrocarbons (TPH). A summary of sediment characteristics is provided as Supplemental Information (Table S1).

Granular Activated Carbon

Granular ACs (1240W, 840W) and extruded carbons (RB 3W, RB 4W) were kindly provided by Norit. The Brunauer-Emmet-Teller (BET) and Barret-Joyner-Halenda (BJH) surfaces and pore widths were measured for all GAC types (Table S2) using Tristar micrometrics apparatus. The total pore volume (V_{tot}) was determined from the amount of nitrogen vapour adsorbed as a function of relative pressure ($p/p_0 = 0.9610$). The surface area was derived according to the BET model (S_{BET}). An average pore width w_{ads} ($4V_{\text{tot}}/S_{\text{BET}}$) was derived from the total pore volume and S_{BET} . Prior to the experiments, GACs were washed sequentially with warm (80°C) demineralized water to remove impurities [27]. Subsequently, all carbons were dried overnight at 105°C. Surface functional groups were determined with Boehm titrations, following previously published procedures [28, 29]. Experimental details and results of the Boehm titrations are provided as Supplemental Information (Table S2).

Polyoxymethylene

Polyoxymethylene (POM) sheets (76 μm thickness) were purchased from CS Hyde Company. POM passive samplers were prepared by cutting the sheets into 300 mg strips and cold-extracting them with hexane (30 min) and methanol (3x30 min). Sorbent pretreatment was based on earlier reported procedures for POM strips [25, 26]. After extraction, POM strips were air-dried and stored in a glass brown-colored bottle until use. POM samplers were cut into smaller pieces depending on the experiment.

Comparison of extraction efficiencies of four types of GAC

Four types of GAC (GAC 1240W, 840W, RB 3W, RB 4W) were evaluated for their efficiency in extracting PAHs from PH sediment in 24 h. For comparison, a single-step 24 h solid phase extraction (SPE) using Tenax beads was applied. Details of the extraction methodology are provided as Supplemental Information. Extraction efficiency was reported as residual fraction of original PAH concentration in the sediment after extraction.

Sorption experiments

Sorption experiments were performed in parallel for sediment only and for GAC-sediment mixtures at different GAC-sediment weight ratios.

Sorption to sediment. Sediment - water equilibration tests were performed to determine distribution coefficients K_{SED} for native PAHs. This setup also served as a control for the experiments in which sediment and GAC were mixed (see below). Brown-colored glass bottles, with volumes ranging from 0.05L to 2L were filled with Mili-Q water containing 100 mg/L NaN_3 and 0.01M CaCl_2 and increasing mass i.e., 0.75, 3.75, 7.50, 18.75, 37.50, 75.00 g (d.w.) of PH sediment. The bottles differed in total suspension volume but the solid-liquid

ratio was identical (i.e. 37 g/L) in the systems, except for the batch with the lowest mass of sediment, which had a solid-liquid ratio of 30 g/L. POM samplers (0.07- 6.7 g dependent on the batch) were added and the bottles were horizontally shaken at 160 strokes per minute for 28 days. This period is sufficient to reach equilibrium in 76 μm POM strips [25]. Subsequently, the POM strips were removed, rinsed and wiped with a tissue before extraction. Equilibrium aqueous phase PAH concentrations were calculated from the PAH concentrations in the POM samplers using previously published POM – water partitioning coefficients (K_{POM}) [25].

Sorption to mixtures of granular activated carbon (GAC) and sediment. Sorption of native PAHs to GAC-sediment mixtures (K_{MIX} , see Eq. 2, below) was determined using the same procedure as for sediment only (see above). In short, bottles with a volume between 0.05L and 2L received the previously described aqueous NaN_3 / CaCl_2 solution and the same series of 0.75 to 75.00 g (d.w.) of PH sediment as in the sediment-only sorption test. However, now a constant dose of 0.75 g GAC was added to each batch, prior to addition of sediment. This resulted in an almost identical liquid-solid ratio of the mixture (37.75 g/L), as compared to that in the sediment-only experiment (37 g/L), and in highly variable GAC-sediment weight ratios of 1.0, 0.2, 0.1, 0.04, 0.02 and 0.01 corresponding to GAC doses of 50, 17, 9, 4, 2 and 1%, respectively. Subsequently, POM samplers (0.07- 6.7 g) were added and the bottles were shaken and equilibrated as described above, again for 28 d. Previous studies used 28 d equilibration for a wide range of carbonaceous materials [26, 30]. It is well known that complete HOC uptake by GAC may take longer, especially in bed sediments [6]. However, for agitated suspensions, 28 d may be considered sufficient from the *ex situ* remediation perspective for which equilibration times of months would be less relevant. In the present study Freundlich and Langmuir sorption isotherms were used as conventional methods [31-34] to describe aqueous-to-sorbed concentration relations. Therefore, the associated constants obtained after 28 d of equilibration period were identified as (pseudo-)equilibrium constants (see below).

Chemical Analysis

Sediment samples were dried with Na_2SO_4 and homogenized. Total PAH concentrations were determined by Soxhlet extraction of dry sediment samples (~0.75 g) using 70 mL hexane/acetone (1:1) for 16h [35]. Extracts were concentrated to 1 mL, and cleaned up over aluminum oxide columns using 25 mL of hexane. Column eluates were reduced to 1 mL, switched to acetonitrile and rereduced to 6 mL. POM samplers were Soxhlet-extracted with 70 mL of methanol for 3 h [26]. Extracts were concentrated to 1 mL and switched to hexane. Further clean-up and analysis were identical to that of the sediment samples. Extracts from sediment or POM were analyzed with HPLC using a C18 reversed phase column with length 250 mm and diameter 4.6 mm (Grace). PAH were detected with a photodiode array detector

(UVD340U, Dionex) and fluorescence detector (HP 1046A). The mobile phase consisted of acetonitrile and water.

TPH extraction was performed according to NEN 5733 [36], see the Supplemental Information. Sediment total organic carbon (TOC) and black carbon (BC) were determined in triplicate, using the chemothermal oxidation method (CTO375) as described by Gustaffson et al. [16]. In this method amorphous organic carbon is removed by thermal oxidation at 375 °C followed by addition of HCl to remove possible carbonate residues. Subsequently, total remaining carbon was detected using an elemental analyzer (EA 1110 CHN, CE Instruments).

Quality assurance

Sorption experiments were performed in triplicate in brown-colored bottles to prevent PAH photolysis. Mass balances were validated in our previous work using the same procedures and equipment [26, 30]. Numerous blank and clean-up recovery samples were included in the sediment and POM extraction procedures, i.e. 1 blank sample per 6 samples and 1 clean-up recovery sample per 5 samples. The clean-up recovery samples were prepared by adding a standard PAH mixture prior to extraction. PAH recoveries ranged between 81.21±6.97 (InP) and 108.34±6.23 (BaP) % ($n = 7$), depending on the compound.

Data analysis

Sediment – water distribution coefficients (L/kg) for individual PAHs were calculated as

$$K_{SED} = C_S / C_W \quad (1)$$

where C_S (µg/kg) is the solid phase concentration (Soxhlet extraction) and C_W (µg/L) is the freely dissolved aqueous phase concentration (passive samplers). The partitioning of PAHs in the mixture of sediment and GAC can be described with the following equation

$$K_{MIX} = f_{SED} K_{SED} + f_{GAC} K_{GAC} \quad (2)$$

where K_{MIX} is a conditional GAC/sediment-to-water distribution coefficient, K_{SED} is the sediment-water distribution coefficient (Eq. 1), and K_{GAC} is the apparent GAC-water distribution coefficient in the presence of sediment. Note that the conditional K_{MIX} and K_{GAC} relate to the same system. Using, $f_{SED} + f_{GAC} = 1$ and rewriting yields

$$K_{GAC} = \frac{K_{MIX} - f_{SED} K_{SED}}{1 - f_{SED}} \quad (3)$$

Substitution of the relationships for the remaining distribution ratios (i.e., $K_{GAC} = C_{GAC} / C_W$, $K_{MIX} = C_{MIX} / C_W$) allows calculation of the concentration of PAHs in GAC:

$$C_{GAC} = C_W K_{GAC} \quad (4)$$

where C_{MIX} and C_{GAC} are the concentrations of PAHs in the sediment-GAC mixture and GAC only ($\mu\text{g/kg}$). Where applicable, a Freundlich isotherm model was used to describe the 28-d (pseudo-)equilibrium sorption data

$$C_{GAC} = K_{F,GAC} C_W^{n_{F,GAC}} \quad (5)$$

where, $K_{F,GAC}$ is a conditional Freundlich affinity (pseudo-)equilibrium constant ($\mu\text{g}^{(1-n)} \text{L}^n \text{kg}^{-1}$) and $n_{F,GAC}$ is the Freundlich (pseudo-)equilibrium exponent for sorption to GAC. Isotherms were also evaluated using the Langmuir sorption model

$$C_{GAC} = \frac{b C_{MAX} C_W}{1 + b C_W} \quad (6)$$

in which, C_{MAX} is the maximum loading of the carbon ($\mu\text{g/kg}_{GAC}$) and b is the Langmuir sorption (pseudo-)equilibrium constant ($\text{L}/\mu\text{g}$). Experimental data were analyzed with PASW Statistics 17.0 (SPSS, Chicago, IL).

RESULTS AND DISCUSSION

Sediment characteristics

Total PAH concentration measured in PH sediment (13 EPA PAH) was $1604 \pm 90.2 \text{ mg/kg}$, which illustrates the high level of pollution of the PH sediment. PAH concentration ratios ANT/178, FLU/(FLU+PYR), BaA/228 and InP/(InP+BghiP) were 0.66, 0.62, 0.47 and 0.53, which indicates the PAH contamination was from pyrogenic origin [37]. Individual PAH concentrations and total TPH content are summarized in the Supplemental Information (Table S1). FL (6.3%), PHE (19.1%), ANT (7.3%), FLU (20.3%), PYR (12.5%), BaA (6.7%) and CHR (6.1%) dominated the sum PAH concentration in PH sediment. Measurements with POM passive samplers showed that a subset of PAH made up 99.90% of the freely dissolved fraction with individual contributions: FL (21.3%), PHE (60.2%), ANT (5.7%), FLU (7.8%), PYR (4.5%), BaA (0.3%) and CHR (0.2%). Aqueous phase concentrations of the aforementioned compounds exceeded Dutch water quality criteria [38]. PH sediment had a high native black carbon (BC) content of 1.85%, which resulted in a BC/TOC ratio of 0.415 (Supplemental Information, Table S1).

Characterization and extraction efficiency of four types of GACs

The characteristics of GACs varied between the four tested types (GAC 1240W, GAC 830W, GAC RB 3W and GAC RB 4W) (Table S2). Single-step 24 h SPE with four types of GAC and Tenax were performed to determine the differences in residual fractions of PAHs in PH sediment. The Tenax extraction served as a control test for the selection of the best

performing GAC and allowed a direct comparison of all tested carbons. As shown in Figure 1, PAH extraction efficiency, in decreasing order, was Tenax, GAC 1240W, GAC 830W, GAC 3W and GAC 4W.

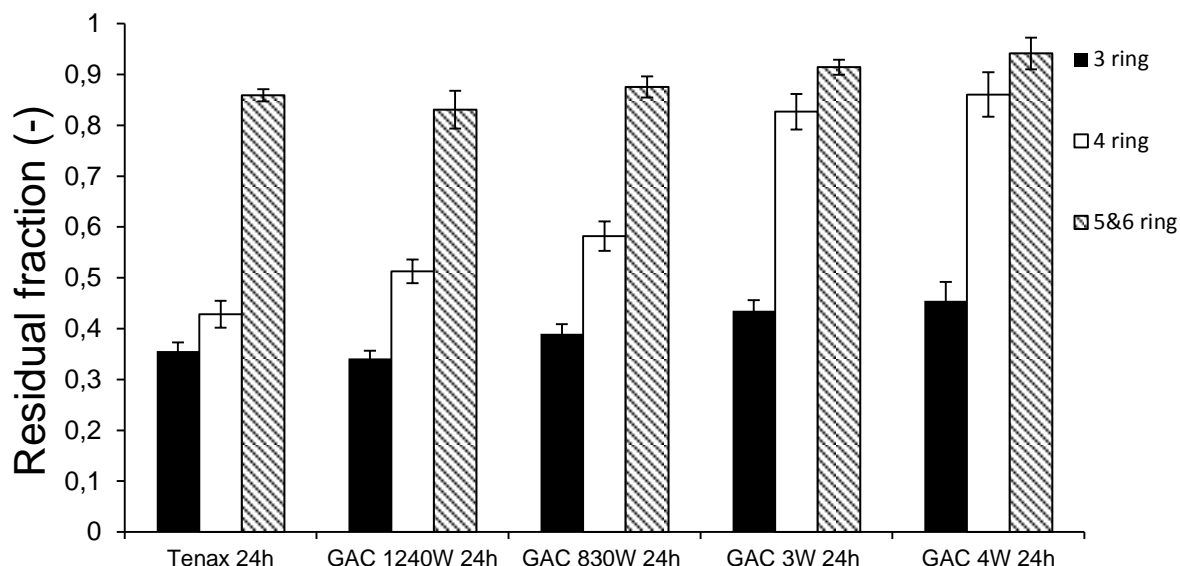


Figure 1. Residual fractions of low molecular weight compounds 3-ring PAHs (black bars), 4-ring PAHs (white bars) and high molecular weight PAHs (5&6 ring, grey bars) in PH sediment after 24 h extraction with Tenax and four types of GAC. Error bars represent standard deviation.

The differences in extraction efficiency were most pronounced for 4-ring PAHs, with almost a twofold higher residual concentration after GAC 4W as compared to Tenax. The significance of the differences between GAC and Tenax extraction results was tested using ANOVA, (multiple comparisons, Tukey HSD, $p < 0.05$; provided as Supplemental Information, Table S3). It appears that Tenax is only superior to the best performing GAC 1240W for 4-rings PAHs ($p = 0.001$), although the difference in residual mass is small (0.43 ± 0.03 versus 0.51 ± 0.02) (Figure 1). For 3-ring PAHs, no significant differences were observed after extraction with GAC 1240W, 830W and Tenax (Table S3).

Residual fractions of 5&6-ring PAHs were similar after treatment with Tenax and all tested GACs (Figure 1). PAH extraction efficiency decreased with increasing GAC particle size (Figure 1, Table S2). This is consistent with a pore sorption mechanism where smaller particles have larger external surface areas and shorter diffusion path lengths, leading to faster uptake. The GACs had comparable BET total surface areas, ranging from 997-1112 (m^2/g). However, the BJH adsorption cumulative surface area of pores between 1 and 25 nm radius were different for the GACs, except for GAC 1240W and 830W (Table S2). The higher extraction efficiency of GAC 1240W and 830W may be explained by the factor of 2 and 4

larger surface area of their pores as compared to that of GAC RB 3W and RB 4W, respectively. Furthermore, total volume of pores ($< 25\text{nm}$) and cumulative volume of pores between 1 and 25 nm for 1240W and 830W were 1.3 and 2.5-3.7 times larger than for the extruded GACs (RB 3W and RB 4W, Table S2). GACs 1240W and 830W provided the largest adsorption average pore width, whereas RB3W had the largest BJH adsorption average pore radius among all studied sorbents. Consequently, the poorest extraction efficiency was obtained for 3 and 4 mm extruded carbons (GAC RB 3W and RB 4W). These extruded carbon particles require longer diffusional timescales for PAH uptake and may also be more sensitive to NOM fouling and sorption competition by complex organic molecules than GAC 1240W and 830W.

Residual percentages of total (13 EPA PAH) ranged from 51 to 72%; GAC 1240W had the best overall efficiency (lowest residual concentration) (Figure S3), which is why GAC 1240W was selected as a superior candidate for further testing in the context of *ex situ* sediment remediation. Although particle size of GAC 1240W was much higher than that of Tenax beads, GAC 1240W extraction resulted in an almost identical residual fraction of PAH compared to that obtained by Tenax extraction (Figure 1 and S3). Noteworthy, the single-step 24 h solid-phase extraction with GAC 1240W may serve as a preliminary and rapid method for determination of PAH removal efficiency from any other sediments prior to *ex situ* remediation.

For all GACs tested, Boehm titrations indicated a high content of basic functional groups and low contribution of acidic groups, which is in agreement with the carbon surface reactivity towards non-polar organic compounds such as PAHs (Table S2). However, GAC 1240W had the lowest amount of basic functional groups among all tested carbons. Previous studies have emphasized the importance of carbon surface chemistry in the adsorption of organic compounds[39, 40]. In general, it is believed that high surface acidity reduces adsorption of non-polar compounds. However, specific types of oxygen containing functional groups might indicate variations in reactivity. For example, due to direct interactions with neighboring groups of the same/or different type, or due to interactions between the electron-rich regions located in the graphene layers with the π electrons of more distant functional groups. Apparently, the differences in chemical properties of GAC 1240W and GAC RB 4W (0.083 versus 0.133 mmol/g) (Table S2), are less important than the particle size effect.

Sorption Experiments

Sorption to sediment. PAH partitioning to sediment only was measured using the POM-SPE method [25, 26] (Table S4). Replication between systems of equal volume was excellent with ($n=3$) standard deviation (SD) in $\text{Log}K_{\text{SED}}$ of 0.01 - 0.1 for all PAHs. An exception was DBA, where SD ranged from 0.14 to 0.18 (Table S4). Small errors in replicated $\text{Log}K_{\text{SED}}$ and $\text{Log}K_{\text{MIX}}$ values are crucial for accurate estimation of $\text{Log}K_{\text{GAC}}$ values in the mixture (see below). As the $\text{Log}K_{\text{SED}}$ values were measured at almost identical solid to liquid ratio (30 - 37 g/L), a single mean $\text{Log}K_{\text{SED}}$ value per chemical ($n=18$) was calculated (Table S4). When

plotted against $\text{Log}K_{\text{OW}}$ (Supplemental Information, Figure S4), $\text{Log}K_{\text{SED}}$ shows a linear relationship ($R^2=0.965$) with a slope of 1.37 ± 0.079 and intercept -2.76 ± 0.461 . This shows that PAH sorption to PH correlates with hydrophobicity, sorbent surface area and/or molecular volume, which all are chemical properties that co-vary with $\text{Log}K_{\text{OW}}$. A slope larger than one is often observed for PAHs in sediments containing BC and may reflect the stronger sorption of high molecular PAHs due to stronger π - π interactions with the BC surface. However, at high PAH concentration organic matter may still constitute the main binding phase, due to sorption saturation of the BC surface. In addition, sorption to oil may contribute to the strong linear partitioning [14, 41].

Although the $\text{Log}K_{\text{SED}}$ values were measured at almost constant liquid-solid ratios, they are not true replicates because they were measured at system volumes varying over a factor of 40 (from 0.05 to 2 L). Interestingly, the $n=3$ replicated $\text{Log}K_{\text{SED}}$ values were about 0.05-0.1 log unit higher at the two lowest system volumes (Table S4; 0.75 and 3.75 g sediment added). $\text{Log}K_{\text{SED}}$ values for setups with 7.5 to 75 g of sediment added were very close and showed no trend (Table S4). $\text{Log}K_{\text{SED}}$ values obtained from the lowest system volumes, i.e. <3.75 g sediment added, were more often significantly higher than those measured in the larger volumes. For instance, the difference was significant for FL (Kruskal – Wallis, $\chi^2(5) = 13.838$, $p = 0.017$) but not for BbF (Kruskal – Wallis, $\chi^2(5) = 3.015$, $p = 0.698$) (for other compounds, see Table S4).

We have no conclusive explanation for the small deviations observed at low volumes. We hypothesize that either the small sediment mass may be less representative of the sediment and therefore prone to variation, or that mixing conditions are different at low system volumes. The hypothesis of lower accuracy at low system volume is consistent with the observation that for most PAHs, the errors in $n=3$ replicates are slightly higher at low system volume. Note that the observed trend in K_{SED} does not affect the validity of subtracting sediment sorption from GAC-sediment sorption in the mixtures. After all, this subtraction does not use the averaged K_{SED} , but uses the individual K_{SED} values measured at the same solid-liquid ratio as that of the GAC-sediment mixture (Table S4, Supplemental Information).

Sorption to mixed granular activated carbon and sediment. PAH distribution coefficients for mixtures ($\text{Log}K_{\text{MIX}}$) of different GAC to sediment ratios (0.01 – 1) were measured in triplicate. Errors were small (Table S5), similar to those for the sediment only systems (Table S4), which again supports the accuracy of the measurements (see also Figures S4-S10). $\text{Log}K_{\text{MIX}}$ clearly differs for different GAC/sediment ratios and PAH hydrophobicities (Figure 2, all data pooled). Plots for separate GAC/sediment ratios are provided as Figures S4-S10 in the Supplemental Information. The presence of GAC in the mixture clearly enhances the overall partition coefficient of the mixture, an effect most clear for PAHs with $\text{Log}K_{\text{OW}} < 5.2$ (Figure 2). For FL (lowest $\text{Log}K_{\text{OW}}$), the $\text{Log}K_{\text{SED}}$ for sediment only of approximately 3.16 increased three orders of magnitude to a value of 6.4 in a mixture ($\text{Log}K_{\text{MIX}}$) at a GAC/sediment ratio of 1. The effect gradually declines with lower GAC doses. This suggest that fouling processes are also likely to affect the binding of PAHs with $\text{Log}K_{\text{OW}}$ lower than

5.2. For PAHs with $\text{Log}K_{\text{OW}} > 5.2$, there is no considerable effect of adding GAC to sediment up to a mixing ratio as high as $\text{GAC/sediment} = 0.2$. Only if the ratio is increased to 1 (1:1 GAC:sediment) the distribution coefficients increase with one log unit (Figure 2).

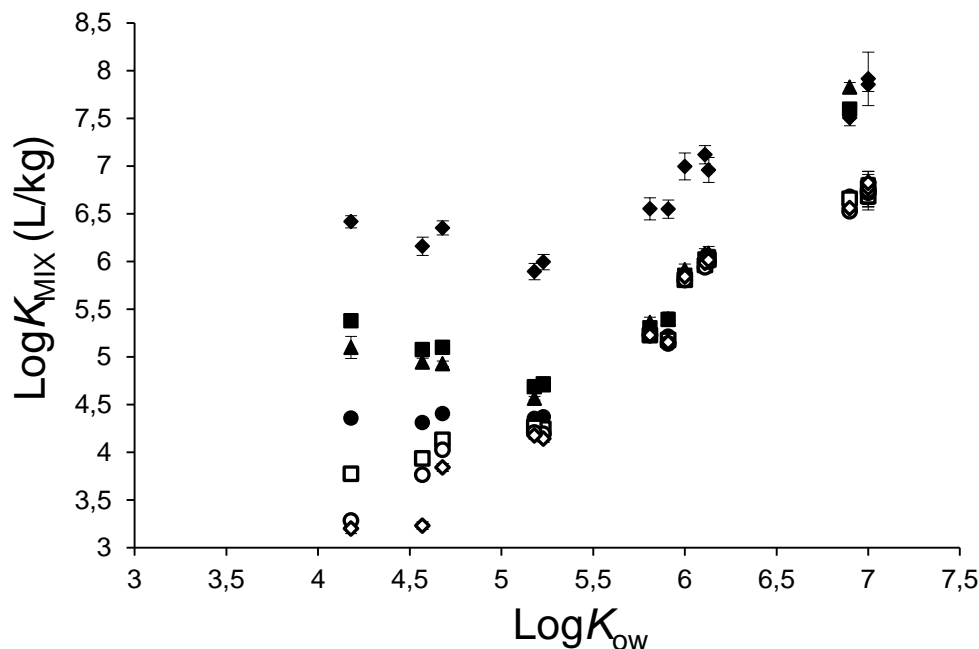


Figure 2. Distribution coefficients $\text{Log}K_{\text{MIX}}$ for mixtures of GAC and sediment at variable weight ratios $R = f_{\text{GAC}}/f_{\text{SED}}$, versus $\text{Log}K_{\text{OW}}$. $R=1$ (closed diamonds), $R=0.2$ (closed squares), $R=0.1$ (closed triangles), $R=0.04$ (closed circles), $R=0.02$ (open squares), $R=0.01$ (open circles), $R=0$ represents the $\text{Log}K_{\text{SED}}$ values for sediment without GAC addition (open diamonds). Error bars represent standard deviation.

The observed difference in behavior of low versus high molecular PAHs might be explained by the fact that pore water concentrations for low molecular PAHs were much higher (Supplemental Information, Table S1) and their kinetics are relatively fast. This may allow for a considerable redistribution of mobile PAHs from the sediment to the GAC present in the mixture. The limited effect of GAC addition on $\text{Log}K_{\text{MIX}}$ for the high molecular weight PAHs could also be explained by strong sorption of these hydrophobic compounds to BC particles. The fact that $\text{Log}K_{\text{MIX}}$ increases with increasing GAC/sediment ratios implies that the affinity of PAHs for GAC is higher than that for the sediment. We have no conclusive explanation for the fact that GAC does not increase $\text{Log}K_{\text{MIX}}$ at a ratio of 0.2, whereas it does at a ratio of 1. It can be speculated that the extra factor of five effectively eliminates any competitive effect of oil or organic matter fouling of the GAC, such that only under these conditions the GAC acts as an infinite sink towards the PAH present in the aqueous phase. Furthermore, it is possible that at high GAC loading, GAC starts to suppress the K_{SED} for the sediment phase as well, for instance by limiting rapid exchange of PAH to amorphous organic matter fractions at higher particle densities in suspension, thus further increasing the

competitive strength of the GAC. In other words, the distribution coefficients for $f_{GAC}/f_{SED} = 0.01 - 0.2$ obtained for PAHs with $\text{Log}K_{OW} > 5.2$ level off to reach the values reported for sediment without carbon amendment (Figure 2), probably due to the aforementioned sorption competition and/or fouling effects of sediment on GAC. Moreover, the $\text{Log}K_{MIX}$ may level off with increasing hydrophobicity of PAH due to intraparticle retarded diffusion in native BC, which would take much longer than the 28-d period used in the present study.

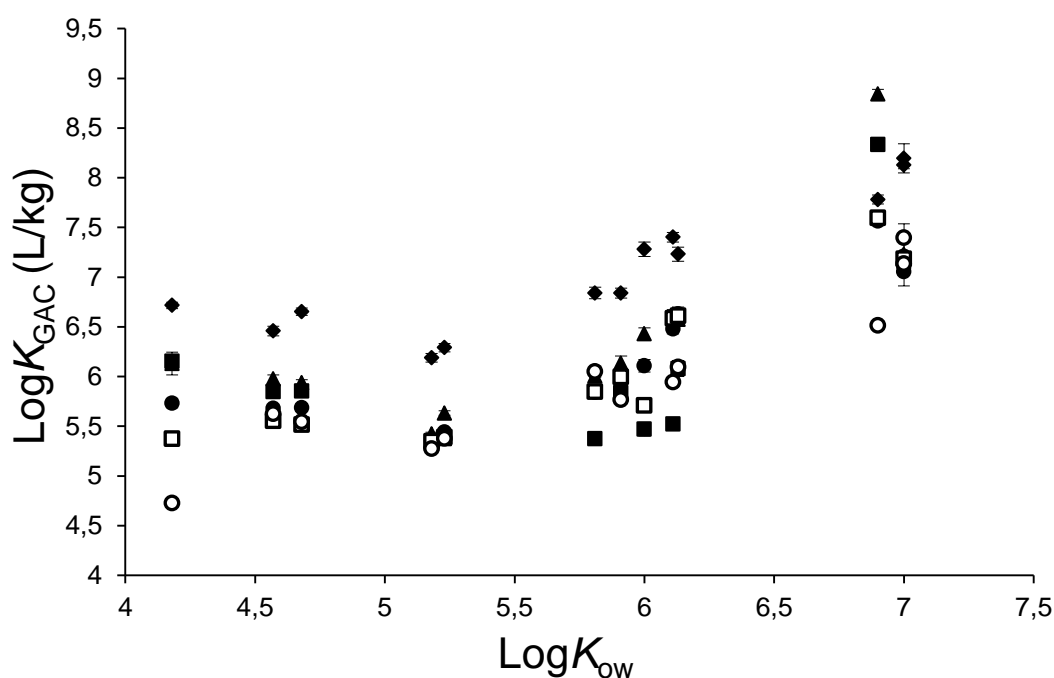


Figure 3. Apparent distribution coefficients of PAHs for granular activated carbon ($\text{Log}K_{GAC}$) in the presence of sediment plotted against $\text{Log}K_{OW}$ obtained at variable weight ratios $R=f_{GAC}/f_{SED}$. $R=1$ (closed diamonds), $R=0.2$ (closed squares), $R=0.1$ (closed triangles), $R=0.04$ (closed circles), $R=0.02$ (open squares), $R=0.01$ (open circles). Error bars represent standard deviation.

Apparent sorption to GAC in the presence of sediment was quantified by subtracting the amount of PAH sorbed to sediment without GAC treatment from the amount of PAH sorbed to the GAC-sediment mixtures (Eq. 2-4). This assumes that PAH partitioning to PH sediment can be quantified by concentration-independent linear partitioning, as was discussed previously, and is not affected by the presence of GAC. It is most plausible that the latter assumption holds as long as $GAC/sediment < 0.2$. However, at the highest GAC loading, K_{SED} might be suppressed, which, if neglected, would lead to an equal overestimation of K_{GAC} . The apparent distribution ratios ($\text{Log}K_{GAC}$) vary between 4.7 and 8.8 dependent on PAH hydrophobicity ($\text{Log}K_{OW}$) and the GAC/sediment ratio (Figure 3). The increase in GAC/sediment ratios from 0.01 to 1 leads to an increase in K_{GAC} of two orders of magnitude. Most importantly from a remediation perspective, even at the lowest ratio of 0.01 (1 % GAC added), the GAC sorption affinity for the low molecular PAH is still 1-2 orders of magnitude

higher than that of the sediment. Consequently, the effectiveness of GAC for PAH uptake is highest for FL, PHE, ANT and PHE that are present in the pore water at concentrations of 64, 180, 17 and 24 $\mu\text{g/L}$ (Supplemental Information, see Table S1, C_w), and therefore have priority in remediation.

The previous discussion was an interpretation of sorption data on the level of distribution ratios. This may be appropriate for the sediment only and GAC-sediment mixed systems. However, sorption to GAC only, either pristine or in the presence of sediment, is non-linear. Consequently, $\text{Log}C_{\text{GAC}}$ was plotted against $\text{Log}C_w$ to obtain isotherms for PAH sorption to GAC in the presence of sediment (Figure S11). Note that these isotherms are conditional in that they relate to different GAC/sediment mixing ratios as well as pseudo-equilibrium. The use of pseudo-equilibrium and pseudo-kinetic models is well-established in the recent literature on sorption of PAHs to GAC [31, 32, 42]. Following Lesage et al. [42] and Valderrama et al. [32], we argue that within short time intervals, sorption of PAHs mainly takes place in macro- and meso-pores. The micro-pore compartment is only relevant at much longer time scales [42], which however are not relevant for our intended GAC application. Consequently, the isotherms for sorption of seven PAHs to GAC were fitted to Freundlich and Langmuir sorption models, (Eqs. 5 and 6) (Table 1, Figure S12), in order to obtain model parameters for macro- and meso-pore sorption only. To our knowledge, these are the first reported Freundlich affinity (pseudo-)equilibrium constants for PAH levels as high as 1600 mg/kg in GAC-sediment mixtures, so we cannot evaluate these values against literature data.

The conditional Freundlich (pseudo-)equilibrium constants ($\text{Log}K_{\text{F,GAC}}$) ranged from 5.5 to 6.2 depending on the compound (Table 1, Figure S13). In addition, $\text{Log}K_{\text{F,GAC}}$ with respect to $\text{Log}K_{\text{OW}}$ were not significantly different (Kruskal – Wallis, $\chi^2(6) = 6.000$, $p = 0.423$). No correlation was found between Freundlich affinity (pseudo-)equilibrium constants and PAH molecular volume (data not shown). When fitted to the Langmuir equation, the sorption data resulted in a quality of fit more or less equal to that for the Freundlich equation (equal R^2 , Table 1). Interestingly, whereas b and C_{MAX} differ enormously among individual PAHs (Table 1), the term bC_{MAX} is more or less constant for all PAHs. This term is the initial slope of the Langmuir isotherm (Eq. 6), which agrees to the K_{GAC} at low C_w . This suggests that the first mentioned variations for b and C_{MAX} probably are artifacts from the fitting procedure, caused by insufficiently reaching sorption saturation levels. High values of sorption parameters (C_{MAX}), for PHE and FLU, have been reported elsewhere, although these values were obtained in clean PAH-AC systems [33, 34]. The inverse correlation between maximum sorption capacity and sorbent-sorbate contact area has been reported by Van Noort et al. [33]. The Langmuir sorption parameters for FL, PHE and FLU to fouled GAC show a similar tendency, which might imply that these compounds access the pore networks more easily [33].

Table 1. Freundlich and Langmuir isotherm (pseudo-)equilibrium constants for sorption of PAH to GAC 1240W in the presence of sediment.

Compound	Freundlich			Langmuir		
	Log $K_{F,GAC}$ ($\mu\text{g/kg}_{GAC}$)/($\mu\text{g/L}$) ⁿ	$n_{F,GAC}$	R ²	b (L/ μg)	Log C_{MAX} ($\mu\text{g/kg}_{GAC}$)	R ²
FL	6.04(0.04)	0.46(0.03)	0.993	0.27(0.07)	6.67(0.04)	0.988
PHE	5.76(0.21)	0.91(0.13)	0.979	0.03(0.02)	7.49(0.20)	0.930
ANT	5.91(0.07)	0.63(0.07)	0.981	0.13(0.06)	6.77(0.10)	0.971
FLU	5.75(0.15)	0.72(0.12)	0.960	0.05(0.03)	6.99(0.15)	0.958
PYR	5.55(0.12)	0.78(0.12)	0.969	0.04(0.03)	6.87(0.21)	0.972
BaA	5.83(0.09)	0.49(0.32)	0.679	1.89(3.38)	6.00(0.37)	0.669
CHR	6.23(0.39)	2.12(1.37)	0.587	0.07(2.77)	10.09(0.02)	0.512

Our current results suggest sorption attenuation of HOCs to GAC, similarly as observed in earlier studies [12, 22, 23, 43]. Two plausible competitive mechanisms, which might be responsible for the fouling of GAC, are direct site competition and/or pore blocking by dissolved organic carbon (DOC) [22, 23]. Especially at low GAC:sediment ratios (<0.1), excess of DOC and/or particulate matter might result in saturation of active sites located on the external surface of the sorbent, and blockage of pore pathways for target compounds to the internal structure. Consequently, DOC outcompetes PAHs in terms of mass [22]. The majority of adsorption sites available for low molecular weight compounds are located in the interior of sorbent pathways, where bulky DOC molecules have limited access [23]. Furthermore, deposits of complex organic molecules may primarily hinder sorption of heavy molecular PAHs, which are too large to diffuse into the sorbent pore networks during 1 month of contact time. Moreover, sorption to added GAC might be hindered by slow release of highly hydrophobic compounds from sediment particles. Therefore, it is more plausible that small molecules (FL, PHE and ANT) even at low GAC/sediment mixing ratios, will have priority in penetrating the coated sorbent compared to larger compounds (Figure 4). The results indicate that DOC molecules show little interference in the sorption of FL, PHE and ANT to GAC. This is also consistent with the pore filling mechanism, which favors small compounds [44, 45].

The reduction of sorption by sorption competition with DOC depends on the type and concentration of the sorbate, the nature of DOC and the effective porosity of the sorbent [21-23]. Furthermore, direct competition for sorption sites between co-sorbing target molecules may occur [46]. As shown in Table S2 (Supplemental Information) the average pore width of GAC 1240W might be sufficient for compounds with molecular diameters less than 1 nm to

access pores with average diameters >1.7 times of their molecular size [46]. The effect of fouling on the sorption of PAHs larger than BaA (Figure 4) might be explained by small pore widths being less accessible for bulky pollutants, which was also observed by Koelmans et al. [22]. However, at high GAC to sediment ratios i.e. (>0.2), the excess of GAC reduces the effect of competitive sediment domains and results in effective sequestration of targeted pollutants.

Using the pore water concentration data, the reduction of initial aqueous PAH concentrations in percent can be plotted as a function of GAC dose to the sediment (Figure 4). It appears that the lowest dose of 1% already reduces the pore water concentrations of the most relevant (available) PAHs such as FL, PHE, ANT by 30-80%. This range increases to 50-90% upon dosing 4% GAC. The obtained results imply that in the short term, as would be relevant for an *ex situ* remediation approach, the effectiveness of GAC decreases with increasing PAH molecular weight.

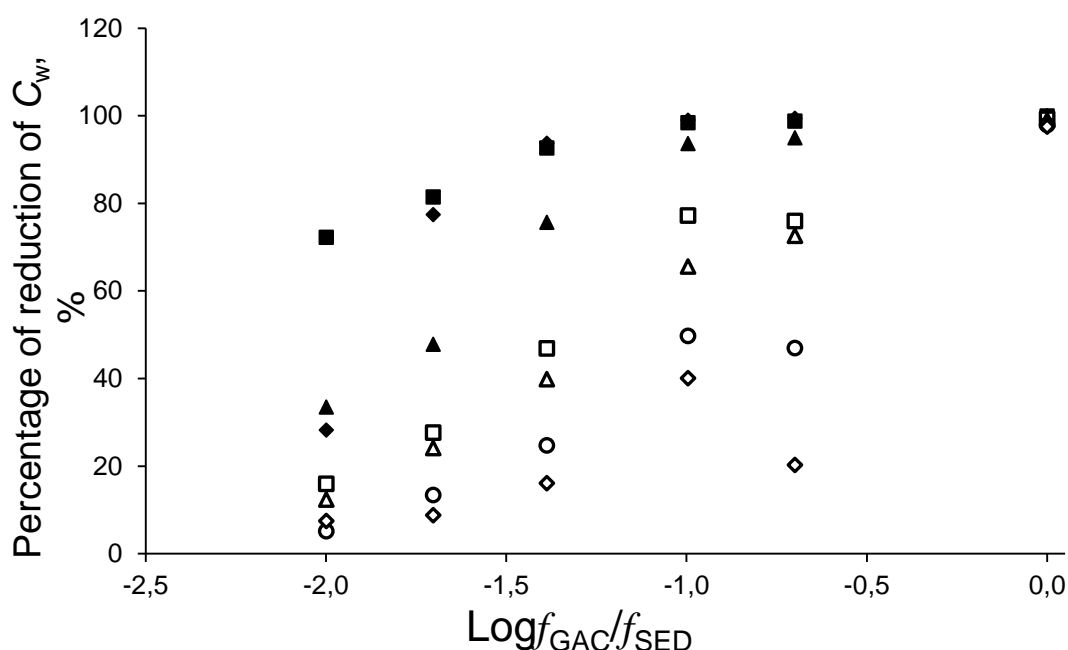


Figure 4. Effect of GAC dose on the reduction of freely dissolved PAHs in sediment amendments. $\text{Log } f_{\text{GAC}}/f_{\text{SED}} = -1.39$ agrees to 4% GAC. Reduction of FL in the aqueous phase (closed diamonds), PHE (closed squares), ANT (closed triangles), FLU (open squares), PYR (open triangles), BaA (open circles), CHR (open diamonds).

IMPLICATIONS

The present study provided data for binding of PAH to GAC in the presence of sediment, as it would occur in a completely mixed *ex situ* remediation scenario. Under the experimental conditions tested, any effects of organic matter fouling or sediment sorption competition on the binding of PAH is accounted for. Consequently, these are the relevant values for evaluating GAC efficiency in GAC sorbent applications, especially in non equilibrium sediment remediation scenarios. As expected, the binding of PAHs and the effectiveness of GAC to reduce sediment pore water concentrations depend on the GAC-sediment mixing ratio, i.e. the dose of GAC. At a dose of 4% GAC, 50-90% of the most available PAHs would be bound to GAC. These percentages relate to a 'worst case' sediment with total PAH concentration as high as 1600 ppm and native BC content of about 40% of TOC. Consequently, GAC efficiency can be expected to be higher for sediments with more common levels of pollution.

Supporting Information

The Supporting Information includes description of solid phase extractions with Tenax and four types of GAC, Boehm titration and determination of TPH in PH sediment.

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Supporting Information for Chapter 3

Determination of total petroleum hydrocarbons (TPH)

TPH extraction was performed according to NEN 5733 [1]. In short, 4 g (w.w.) sediment, 10 mL water and 50 mL acetone were cold extracted for 30 minutes at 175 strokes per minute, followed by a second extraction with 25 mL of hexane. To the resulting extracts, 50 mL of water was added. After phase separation a hexane subsample was analyzed for TPH, using a HP 5890 Gas Chromatograph (GC) equipped with a SIM DIST column and Flame Ionization Detector with nitrogen as the carrier gas. After 5 minutes at an initial temperature of 40 °C, GC temperature increased at 10 °C per minute to a final temperature of 300 °C. Carbon number fractions were determined using the retention times of a boiling point standard. TPH is determined as the area between C10 and C40.

Solid phase extractions with Tenax and four types of GAC

Tenax extractions. As a reference, single-step 24 h solid-phase extractions (SPE) with Tenax, were performed to determine the residual fractions of PAHs in Petroleum Harbor (PH) sediment. The results served as control tests for the selection of the best performing GAC, and allowed a direct comparison of GAC versus Tenax extraction efficiency. The single step SPE method was adapted from [2, 3]. In short, the extractions were carried out in 50 mL separatory funnels, which were filled with PH sediment (1.5 g dry matter), 40 mL of Mili-Q water containing 100 mg/L NaN_3 and 0.01M CaCl_2 , and 1.5 g of Tenax adsorbent. The separatory funnels were shaken end-to-end at 160 strokes per minute for 24 h. After 24 h the sediment suspension was separated from the sorbent, centrifuged and dried with Na_2SO_4 for determination of residual concentration of PAHs remaining in the sediment after Tenax extraction. The Tenax beads with preconcentrated PAHs and residual sediment samples were extracted in hexane/acetone (1:1) with microwave assisted extraction (MAE). All hexane/acetone extracts were primarily concentrated with a rotary evaporator, further reduced to 1 mL under gentle stream of nitrogen and switched to acetonitrile for PAH analysis. For details on the Microwave assisted procedure, the reader is referred to [4]. The Tenax extractions were carried out in triplicate.

GAC extractions. A series of 4 types of granulated carbons (GAC 1240W, 840W, RB 3W and RB 4W, kindly supplied by Norit, Amersfoort, The Netherlands) with varying particle size range (0.450-1.70), (0.60-2.36), 3 and 4 mm respectively, were evaluated for their efficiency in extracting PAHs from PH sediment. Single-step extractions of PAHs from sediment samples with all GACs were performed in the same way as Tenax extraction, also using a 1:1 (w/w) sediment to sorbent ratio. Briefly, 50 mL brown colored bottles were filled with 1.5 g (d.w.) sediment, 1.5 g GAC and aqueous NaN_3 / CaCl_2 solution, and shaken at 160 strokes per minute for 24h. The sediment was separated from GAC by sieving (500 μm), centrifuged and dried with Na_2SO_4 for determination of residual concentration of PAHs remaining in the sediment after GAC extraction. The extractions with GAC were carried out in triplicate. Further extraction steps and analysis were identical to that of the Tenax and sediment samples. The residual fractions of the total amount of 13 EPA PAHs remaining in the sediment after extraction were calculated by dividing the PAH quantity extracted, by the total quantity of PAHs determined in PH sediment by Soxhlet extraction (see main text). The lowest residual fraction of PAHs was found after extraction with GAC 1240W, which was selected for further tests (Fig. 1 and Fig. S1).

Boehm titration

The acidic surface groups (carboxyl, lactone and phenolic) and the total quantity of basic groups present on granular activated carbon (GAC 1240W) were determined with Boehm titrations as described elsewhere [5-7]. Since the method is based on the assumption that NaOH neutralizes carboxyl, lactone and phenolic groups, Na_2CO_3 neutralizes carboxyl and lactone groups and NaHCO_3 neutralizes carboxyl groups, the quantity of acid and basic groups can be calculated. In short, to four 100 mL Erlenmeyer flasks containing 20 mL of 0.05N NaHCO_3 , NaOH , HCl and Na_2CO_3 , ~0.2 g GAC was added. Additionally, two blank

bottles filled with 20 mL of 0.05N NaOH and 0.05N HCl were prepared. The bottles were shaken end-to-end for 24 h, after which the solutions were filtrated using 0.2 µm cellulose filters. The supernatants were titrated with the excess of base and acid with NaOH and HCl respectively. The titrations were carried out with Metrohm 702 SM Titrino (NaOH) and SCHOTT TitroLine easy (HCl).

Table S1. Characteristics of Petroleum Harbor sediment; concentrations of PAH in the sediment and aqueous phase concentrations determined with POM-SPE.

Compound	Log K_{ow}	C_{SED} , mg/kg	C_w , µg/L	Log K_{POM}^d
Fluorene (FL)	4.2 ^a	99.8 (6.5)	63.74 (7.42)	3.83
Phenanthrene (PHE)	4.6 ^b	304.8 (16.9)	179.99 (15.78)	4.20
Anthracene (ANT)	4.7 ^c	116.7 (5.3)	16.76 (1.71)	4.30
Fluoranthene (FLU)	5.2 ^b	323.5 (14.6)	23.98 (2.01)	4.56
Pyrene (PYR)	5.2 ^b	199.5 (5.9)	13.65 (1.16)	4.57
Benzo[a]anthracene (BaA)	5.9 ^b	106.9 (9.2)	0.75 (0.07)	5.46
Chrysene (CHR)	5.8 ^b	96.6 (11.4)	0.57 (0.07)	5.43
Benzo[b]fluoranthene (BbF)	6.0 ^a	92.0 (11.9)	0.14 (0.02)	5.80
Benzo[k]fluoranthene (BkF)	6.1 ^c	40.7 (4.1)	0.04 (0.01)	5.97
Benzo[a]pyrene (BaP)	6.1 ^c	105.9 (15.3)	0.10 (0.01)	5.96
Dibenzo[a,h]anthracene (DBA)	7.0 ^b	10.0 (3.2)	1.79*10 ⁻³ (3.65*10 ⁻⁴)	6.30
Benzo[g,h,i]perylene (BghiP)	6.9 ^b	45.9 (4.4)	1.34*10 ⁻² (1.43*10 ⁻³)	6.09
Indeno[1.2.3.c.d]pyrene (InP)	7.0 ^b	51.3 (4.2)	8.96*10 ⁻³ (1.55*10 ⁻³)	6.26
Σ13 EPA PAHs		1604.3 (90.2)		
TOC [%]		4.46		
OC [%]		2.61		
BC [%]		1.85		
BC/TOC		0.415		
TPH [%]		0.54 (0.041)		

^a Data taken from Maruya et al.[8]

^b Data reported by Jonker & Smedes [9]

^c Data from de Maagd et al. [10]

^d Data taken from Hawthorne et al. [11]

Table S2. Chemical and physical characteristics of coal based granular activated carbons. Data obtained from low temperature nitrogen adsorption isotherms and Boehm titrations performed for the quantification of functional groups present on GAC surface.

GAC Type	Particle size (mm)	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	$S_{\text{BJH}}^{\text{b}}$ (m^2/g)	$V_{\text{tot (BET)}}^{\text{c}}$ (cm^3/g)	$V_{\text{tot (BJH)}}^{\text{d}}$ (cm^3/g)	Average pore width $w_{\text{ads}}^{\text{e}}$ (nm)	BJH Average pore radius ^f (nm)	Carboxyl (mmol/g)	Lactone (mmol/g)	Phenolic (mmol/g)	Basic (mmol/g)
1240W	0.45-1.70	1112	113	0.607	0.129	2.182	2.283	0.019	0.016	0.020	0.083
830W	0.60-2.36	1112	113	0.607	0.129	2.182	2.283	0.030	0.014	0.026	0.099
RB3W	3	997	51	0.482	0.052	1.936	2.053	0.031	0.007	0.007	0.134
RB4W	4	1035	29	0.470	0.035	1.816	2.475	0.012	0.023	0.010	0.133

^aBET surface area

^bBJH adsorption cumulative surface area of pores between 1.0 and 25.0 nm radius

^cSingle point adsorption total pore volume of pores less than 25.0 nm radius at $p/p_0=0.96107$

^dBJH adsorption cumulative volume of pores between 1.0 and 25.0 nm radius

^eAdsorption average pore width (4V/A by BET)

^fBJH adsorption average pore radius (2V/A)

Table S3. Multiple comparisons, ANOVA (Tukey HSD, $p < 0.05$) between residual fractions obtained after GAC extractions versus residual fractions after Tenax-SPE. The p values are reported for 3, 4 and 5&6 ring PAHs.

24 h - SPE extraction		PAH		
		3 ring	4 ring	5&6 ring
Tenax vs.	GAC 1240W	0.774	0.001	0.602
	GAC 830W	0.110	0.000	0.910
	RB 3W	0.001	0.000	0.098
	RB 4W	0.000	0.000	0.011
GAC 1240W vs.	Tenax	0.774	0.001	0.602
	GAC 830W	0.018	0.002	0.218
	RB 3W	0.000	0.000	0.010
	RB 4W	0.000	0.000	0.001
GAC 830W vs.	Tenax	0.110	0.000	0.910
	GAC 1240W	0.018	0.002	0.218
	RB 3W	0.030	0.000	0.329
	RB 4W	0.003	0.000	0.042
RB 3W vs.	Tenax	0.001	0.000	0.098
	GAC 1240W	0.000	0.000	0.010
	GAC 830W	0.030	0.000	0.329
	RB 4W	0.550	0.142	0.641
RB 4W vs.	Tenax	0.000	0.000	0.011
	GAC 1240W	0.000	0.000	0.001
	GAC 830W	0.003	0.000	0.042
	RB 3W	0.550	0.142	0.641

Table S4. Partitioning coefficients ($\text{Log}K_{\text{SED}}$ (SD)) for PAHs, in individual sediment – water equilibration systems, and mean $\text{Log}K_{\text{SED}}$ values.

Sediment (d.w.) (g)	$\text{Log}K_{\text{SED}}$												
	FL	PHE	ANT	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DBA	BghiP	InP
0.75	3.28(0.03)	3.29(0.04)	3.86(0.05)	4.18(0.03)	4.22(0.04)	5.19(0.05)	5.26(0.07)	5.84(0.06)	6.00(0.10)	6.06(0.06)	6.81(0.16)	6.55(0.08)	6.90(0.08)
3.75	3.24(0.03)	3.25(0.03)	3.88(0.02)	4.18(0.03)	4.21(0.04)	5.20(0.05)	5.29(0.08)	5.90(0.15)	6.08(0.05)	6.04(0.07)	6.89(0.18)	6.59(0.07)	6.88(0.10)
7.50	3.17(0.03)	3.19(0.03)	3.77(0.02)	4.11(0.03)	4.14(0.02)	5.14(0.05)	5.18(0.05)	5.80(0.06)	5.96(0.06)	5.98(0.06)	6.70(0.15)	6.54(0.07)	6.77(0.04)
18.75	3.18(0.04)	3.20(0.03)	3.81(0.02)	4.12(0.02)	4.16(0.02)	5.11(0.04)	5.20(0.05)	5.81(0.06)	5.95(0.05)	6.00(0.07)	6.69(0.14)	6.54(0.04)	6.78(0.04)
37.50	3.14(0.03)	3.22(0.03)	3.86(0.02)	4.12(0.02)	4.16(0.03)	5.13(0.04)	5.20(0.05)	5.81(0.06)	5.93(0.04)	5.99(0.06)	6.70(0.14)	6.58(0.04)	6.75(0.04)
75.00	3.15(0.03)	3.22(0.02)	3.86(0.02)	4.13(0.02)	4.16(0.01)	5.13(0.04)	5.20(0.05)	5.81(0.06)	5.94(0.04)	6.00(0.06)	6.70(0.14)	6.52(0.04)	6.74(0.04)
$\chi^2(5)^a$	13.838	13.147	11.941	11.596	11.037	11.221	12.360	3.015	11.566	9.596	10.235	3.897	12.154
p	0.017	0.022	0.036	0.041	0.051	0.047	0.030	0.698	0.041	0.088	0.069	0.564	0.033
$\text{Log}K_{\text{SED}}^b$	3.20(0.05)	3.23(0.04)	3.84(0.04)	4.14(0.04)	4.18(0.04)	5.15(0.04)	5.23(0.04)	5.84(0.08)	5.99(0.07)	6.02(0.04)	6.77(0.11)	6.56(0.05)	6.82(0.09)

^a Kruskal – Wallis tests for significant differences between individual sediment-water equilibration systems.

^b Single mean values of sediment – water partitioning coefficients ($\text{Log}K_{\text{SED}}$) with associated errors (SD, $n=18$) obtained from sediment - water equilibration tests, without carbon amendment.

Table S5. Granular activated carbon – sediment partitioning coefficients ($\text{Log}K_{\text{MIX}}$ (SD)) for a series of PAHs.

Sed (d.w.) (g)	GAC (g)	LogK _{MIX}												
		FL	PHE	ANT	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DBA	BghiP	InP
0.75	0.75	6.42(0.06)	6.16(0.10)	6.35(0.07)	5.99(0.08)	5.89(0.09)	6.55(0.09)	6.55(0.11)	7.00(0.14)	7.12(0.09)	6.96(0.13)	7.91(0.28)	7.51(0.08)	7.85(0.07)
3.75	0.75	5.38(0.04)	5.08(0.04)	5.10(0.03)	4.72(0.02)	4.69(0.02)	5.39(0.06)	5.30(0.06)	5.85(0.07)	6.02(0.06)	6.04(0.08)	6.77(0.17)	7.59(0.05)	6.80(0.05)
7.50	0.75	5.10(0.12)	4.94(0.04)	4.93(0.03)	4.71(0.02)	4.57(0.02)	5.40(0.07)	5.36(0.06)	5.91(0.06)	6.08(0.05)	6.09(0.07)	6.79(0.16)	7.83(0.05)	6.83(0.04)
18.75	0.75	4.36(0.05)	4.31(0.03)	4.40(0.03)	4.37(0.03)	4.35(0.02)	5.22(0.05)	5.26(0.06)	5.83(0.06)	5.99(0.05)	6.06(0.07)	6.72(0.15)	6.68(0.05)	6.81(0.04)
37.50	0.75	3.78(0.04)	3.93(0.04)	4.13(0.03)	4.25(0.02)	4.26(0.01)	5.18(0.04)	5.23(0.05)	5.81(0.06)	5.96(0.05)	6.02(0.07)	6.68(0.14)	6.65(0.04)	6.77(0.05)
75.00	0.75	3.28(0.03)	3.76(0.02)	4.03(0.02)	4.19(0.02)	4.21(0.01)	5.14(0.04)	5.23(0.06)	5.80(0.06)	5.94(0.05)	6.00(0.07)	6.72(0.14)	6.52(0.04)	6.74(0.04)



Figure S1. Industrial sieving unit for separation of GAC from high volume sediment slurries.



Figure S2. Separation of granular activated carbon from treated sediment. Picture shows detail of sediment being sieved using the unit depicted in Figure S1.

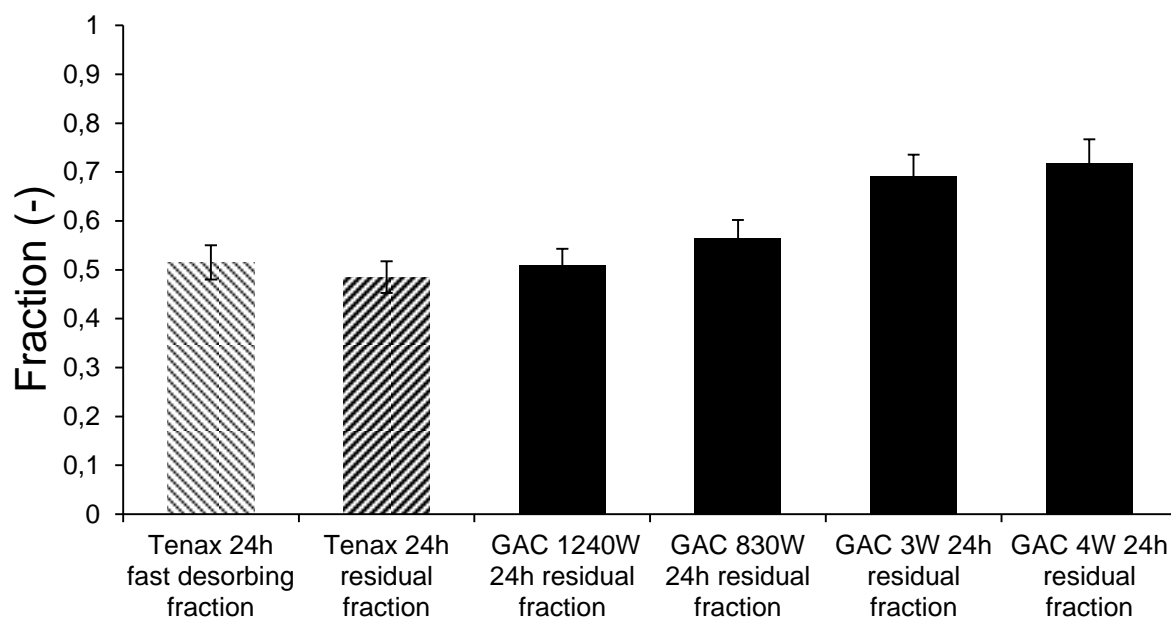


Figure S3. Fast desorbing (in 24 h) fraction of total PAHs (13EPA PAH) in PH sediment as determined with Tenax extraction and residual fraction of total PAHs in PH sediment as determined with Tenax extraction (grey bars). Residual fractions of PAHs after extractions with four types of GAC (black bars). Fast and residual Tenax-based fractions (grey bars) together make up 100% of PAH present in the sediment.

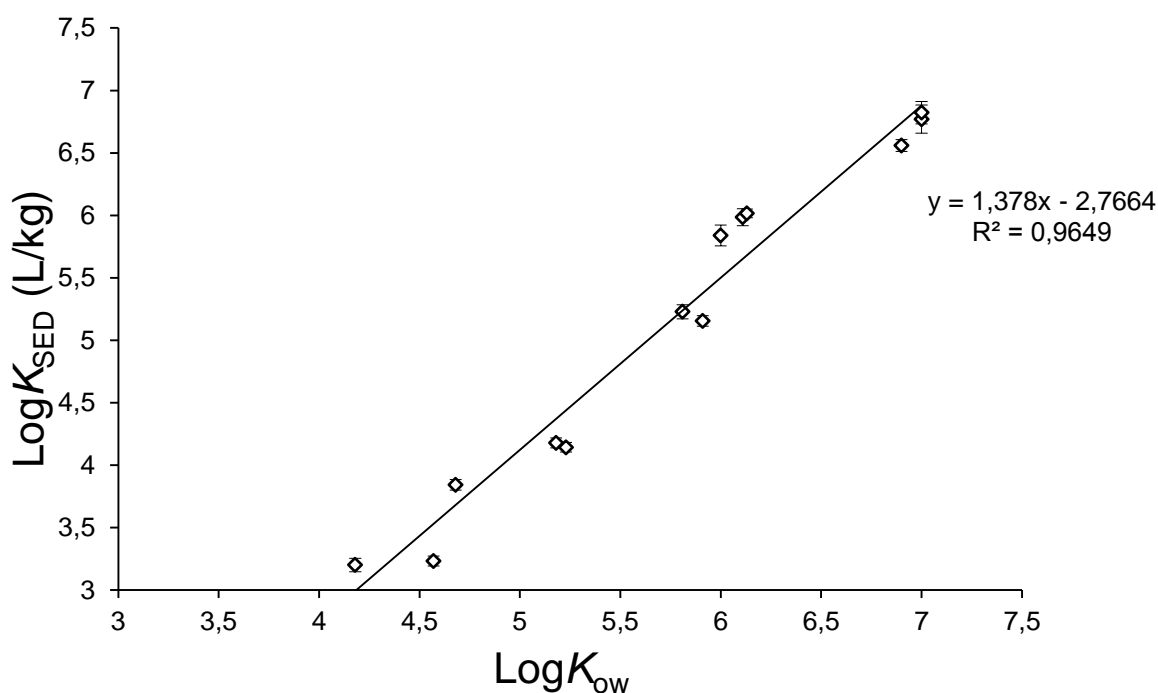


Figure S4. Single sediment – water partitioning coefficients ($\text{Log}K_{\text{SED}}$) obtained in this study as a function of PAH $\text{Log}K_{\text{OW}}$.

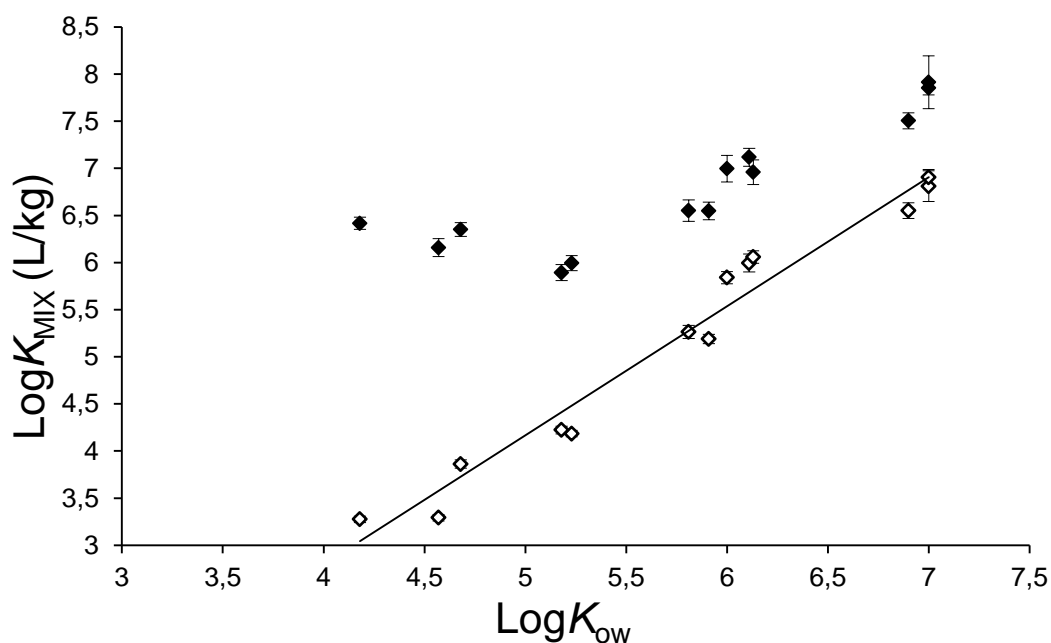


Figure S5. $\text{Log}K_{\text{MIX}}$ distribution coefficients at $f_{\text{GAC}}/f_{\text{SED}} = 1$ weight ratio as a function of $\text{Log}K_{\text{OW}}$ (closed symbols) and sediment – water partitioning coefficients obtained from the individual control system without carbon amendment (open symbols).

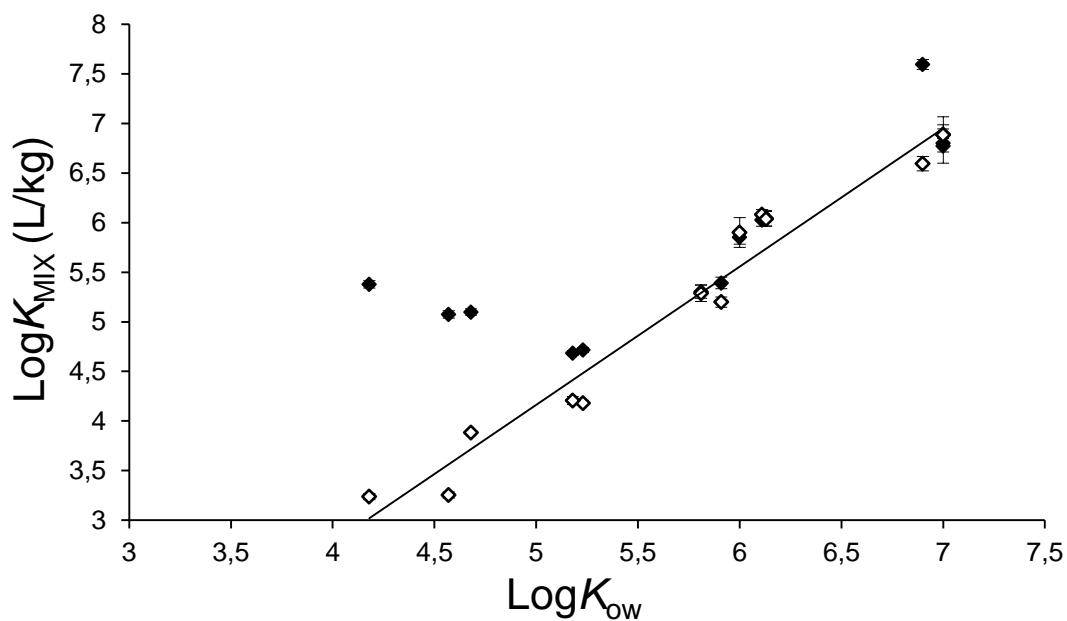


Figure S6. $\text{Log}K_{\text{MIX}}$ distribution coefficients at $f_{\text{GAC}}/f_{\text{SED}} = 0.2$ weight ratio as a function of $\text{Log}K_{\text{OW}}$ (closed symbols) and sediment – water partitioning coefficients obtained from individual control system without carbon amendment (open symbols).

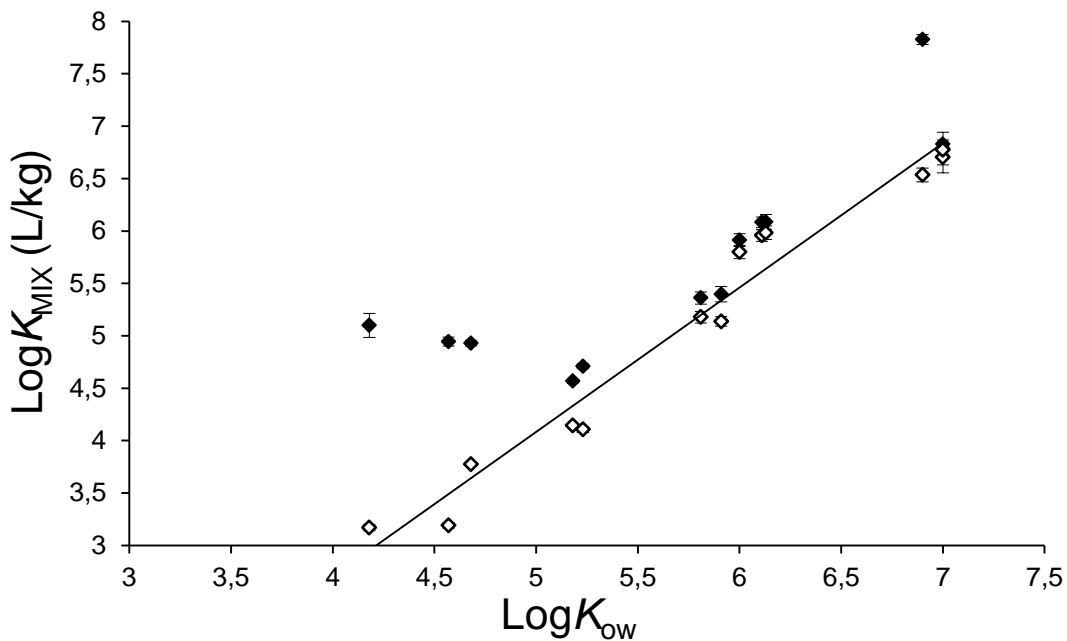


Figure S7. $\text{Log}K_{\text{MIX}}$ distribution coefficients at $f_{\text{GAC}}/f_{\text{SED}} = 0.1$ weight ratio as a function of $\text{Log}K_{\text{OW}}$ (closed symbols) and sediment – water partitioning coefficients obtained from individual control system without carbon amendment (open symbols).

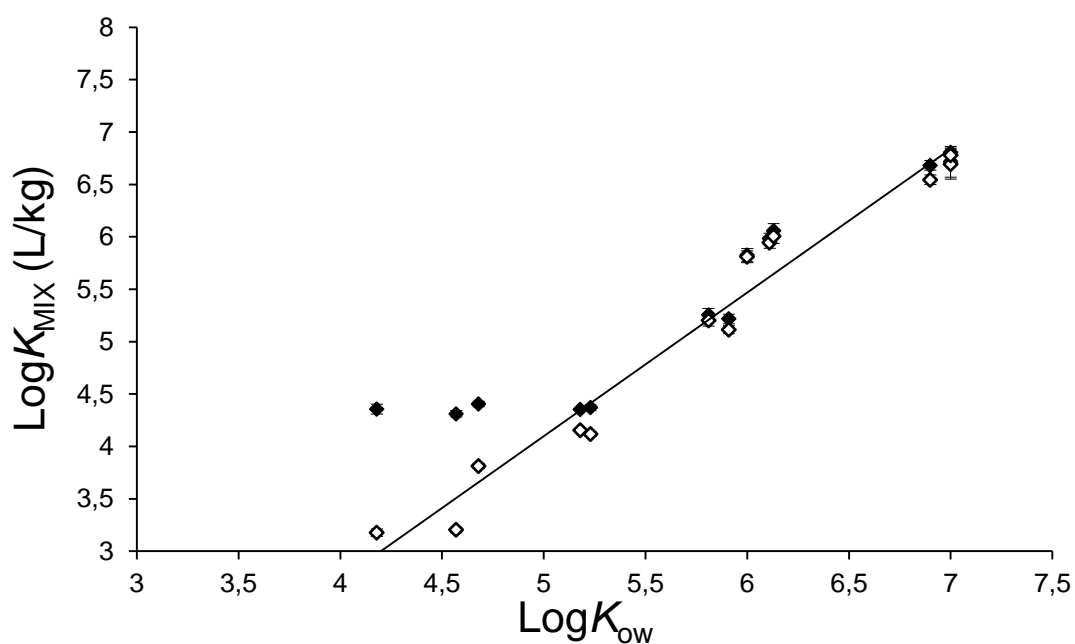


Figure S8. $\text{Log}K_{\text{MIX}}$ distribution coefficients at $f_{\text{GAC}}/f_{\text{SED}} = 0.04$ weight ratio as a function of $\text{Log}K_{\text{OW}}$ (closed symbols) and sediment – water partitioning coefficients obtained from individual control system without carbon amendment (open symbols).

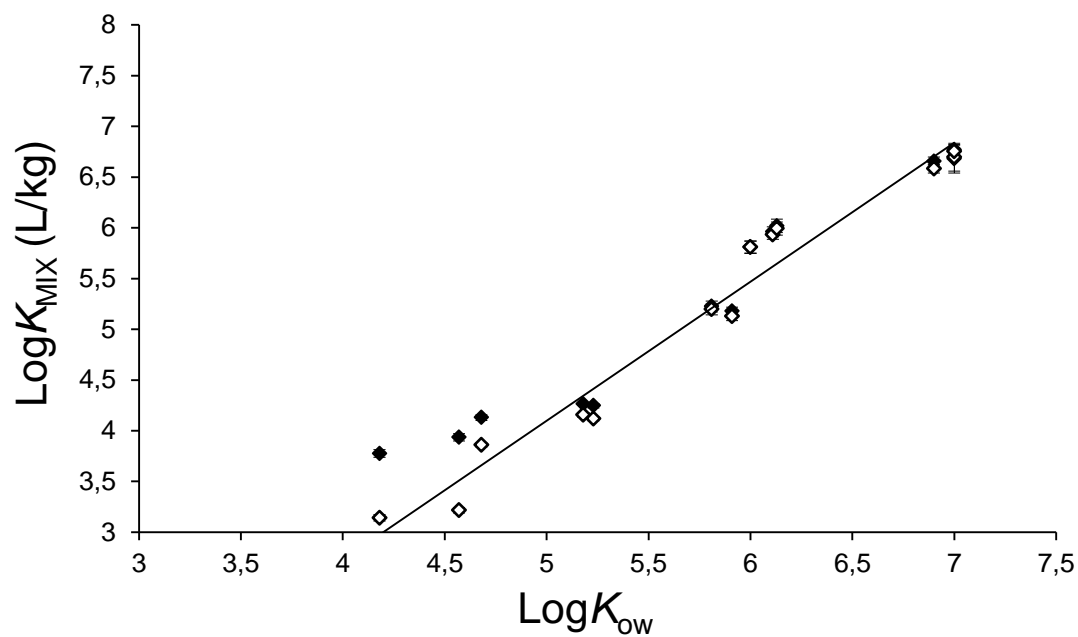


Figure S9. $\text{Log}K_{\text{MIX}}$ distribution coefficients at $f_{\text{GAC}}/f_{\text{SED}} = 0.02$ weight ratio as a function of $\text{Log}K_{\text{OW}}$ (closed symbols) and sediment – water partitioning coefficients obtained for individual control system without carbon amendment (open symbols).

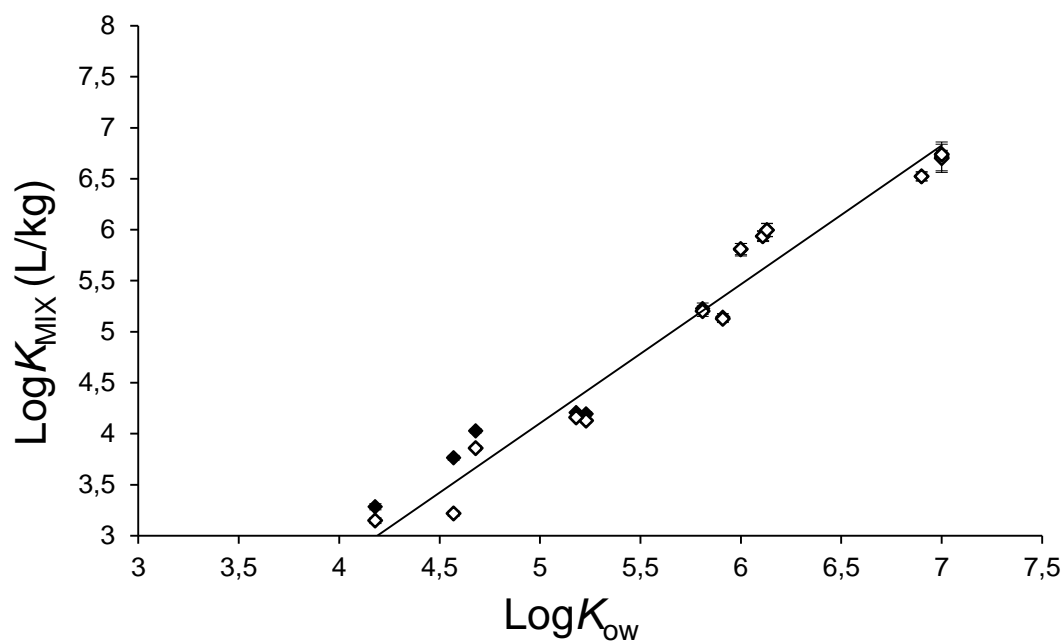


Figure S10. $\text{Log}K_{\text{MIX}}$ distribution coefficients at $f_{\text{GAC}}/f_{\text{SED}} = 0.01$ weight ratio as a function of $\text{Log}K_{\text{OW}}$ (closed symbols) and sediment – water partitioning coefficients obtained from individual control system without carbon amendment (open symbols).

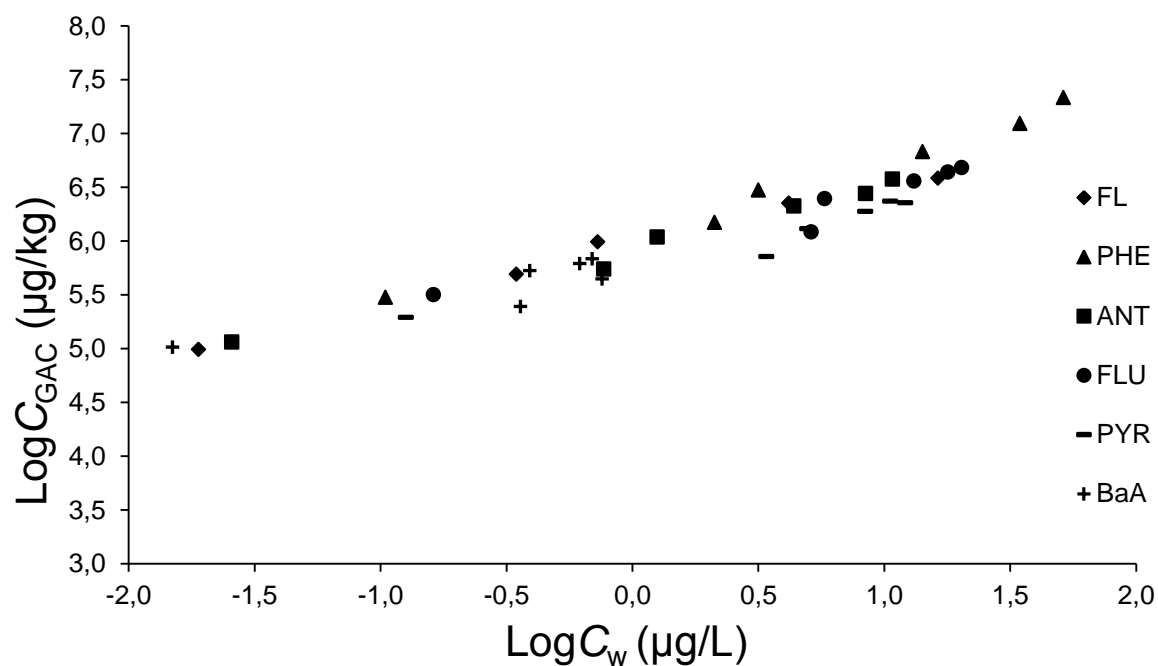


Figure S11. Isotherms for sorption of PAHs to GAC in the presence of sediment.

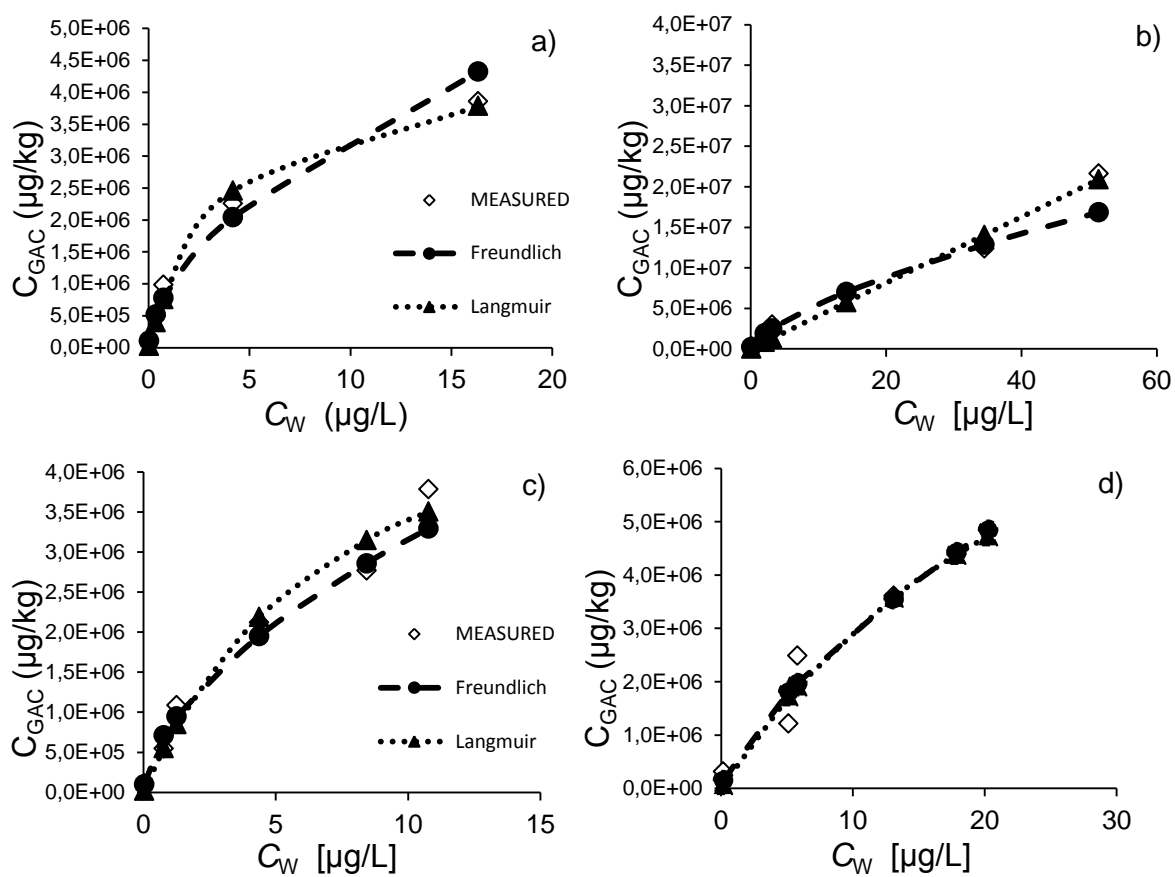


Figure S12. Apparent sorption isotherms for (a) FL, (b) PHE, (c) ANT and (d) FLU. Open symbols without lines represent experimentally determined values, closed symbols with dashed curves indicate data obtained from fitting to Freundlich isotherm equation, and closed symbols with dotted lines represent values obtained from fitting to Langmuir equation.

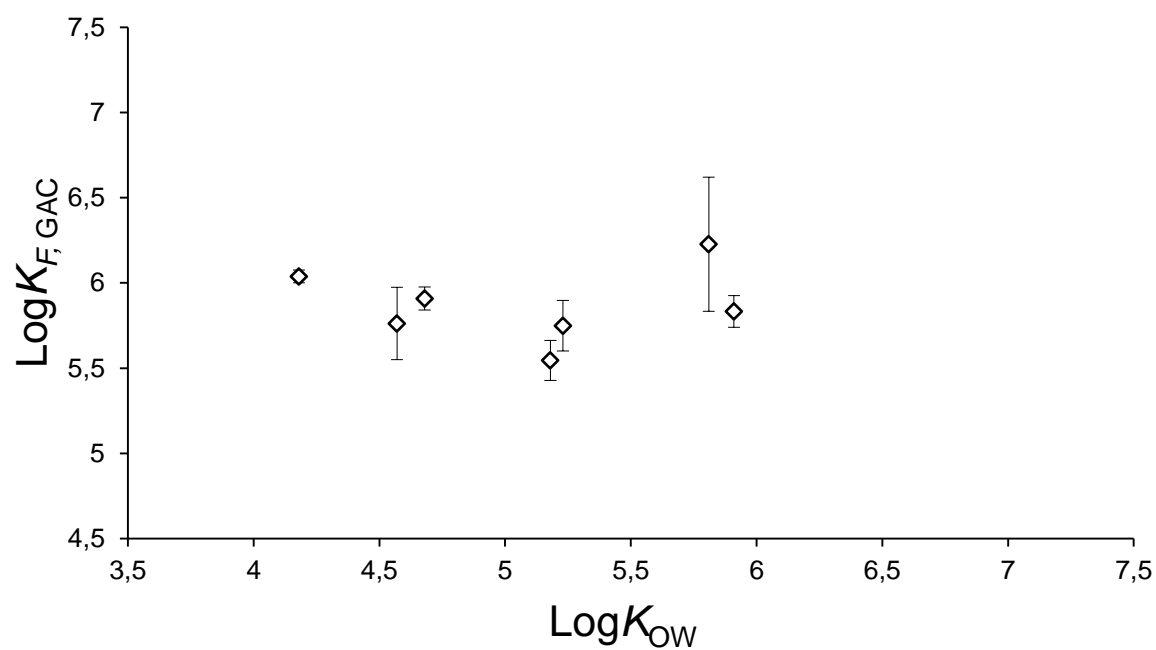


Figure S13. Freundlich affinity (pseudo-)equilibrium constants ($\text{Log}K_{\text{F,GAC}}$) ($\mu\text{g}/\text{kg}_{\text{GAC}}/(\mu\text{g}/\text{L})^{n_{\text{F,GAC}}}$) as a function of octanol-water partitioning coefficients for GAC in the presence of PH sediment.

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CHAPTER 4

Kinetics of hydrophobic organic contaminant extraction from sediment by granular activated carbon

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ABSTRACT

Ex situ solid phase extraction with granular activated carbon (GAC) is a promising technique to remediate contaminated sediments. The methods' efficiency depends on the rate by which contaminants are transferred from the sediment to the surface of GAC. Here, we derive kinetic parameters for extraction of polycyclic aromatic hydrocarbons (PAH) from sediment by GAC, using a first-order multi-compartment kinetic model. The parameters were obtained by modeling sediment-GAC exchange kinetic data following a tiered model calibration approach. First, parameters for PAH desorption from sediment were calibrated using data from systems with 50% (by weight) GAC acting as an infinite sink. Second, the estimated parameters were used as fixed input to obtain GAC uptake kinetic parameters in sediment slurries with 4% GAC, representing the *ex situ* remediation scenario. PAH uptake rate constants (k_{GAC}) by GAC ranged from 0.44 to 0.0005 d⁻¹, whereas GAC sorption coefficients (K_{GAC}) ranged from 10^{5.57} to 10^{8.57} L kg⁻¹. These values are the first provided for GAC in the presence of sediment and show that *ex situ* extraction with GAC is sufficiently fast and effective to reduce the risks of the most available PAHs among those studied, such as fluorene, phenanthrene and anthracene.

INTRODUCTION

In industrialized regions, aquatic sediments are often contaminated with toxic and persistent hydrophobic organic compounds (HOCs), such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine hydrocarbons, thus posing a threat to the chemical and ecological status of water systems [1]. Emissions and transport of HOCs have resulted in HOC concentrations exceeding sediment and water quality criteria, particularly in densely inhabited or highly industrialized areas, depositional zones and industrial harbors. Typically, HOCs bind to organic matter components in the sediment, like amorphous and condensed carbon phases, often referred to as black carbon (BC) [2].

In the past decade, *in situ* addition of activated carbon (AC) to polluted sediments has received considerable interest as a remediation approach aiming at reducing risks of sediment-bound contaminants, and improving the quality of marine and freshwater habitats [3, 4]. Several field studies have demonstrated the high potential of sediment and soil amendments with AC as a means to reduce aqueous concentrations and bioaccumulation of HOCs in aquatic organisms in various environmental settings [3, 5-9]. Since addition of carbonaceous sorbents leads to significant reduction of contaminant mobility and availability for biouptake [10, 11], the number of *in situ* applications is continuously increasing. However, *in situ* treatment may be incompatible with local regulations or ecological protection goals, or may be less desirable if reuse options for dredged sediments exist. Therefore, in a recent study, we proposed an alternative sediment treatment using mixing of granular AC (GAC) with the contaminated sediment, followed by subsequent removal of the contaminant loaded GAC as a beneficial reuse approach for dredged or disposed sediments [12]. A central criterion for the

applicability of this technique is sufficient transport of HOCs from the sediment to the GAC during the mixing stage. Consequently, an improved understanding of desorption and adsorption time scales in mixed sediment-GAC systems is required. This includes constraining kinetic parameters for short- and long-term sorption processes for a range of chemicals.

To date, desorption kinetics of HOCs from sediments are usually described using multi-compartment first order models or diffusion models [13-15]. Similar models have been applied to infer sorption rates of HOCs from aqueous solutions to activated carbons having a complex porous structure [16-18]. Many studies usually address desorption from sediment against an infinite sink present in the water phase such as Tenax or XAD beads, present in excess [19-21]. However, in sediment – GAC mixtures with relatively low GAC dose, GAC may not always act as an infinite sink, implying that backward transport from GAC has to be taken into account. Several papers exist on pollutant mass transfer in bed sediments and slowly mixed systems with AC [22-27], HOC release from suspended sediments amended with a low dose of GAC has been studied less extensively [25, 27].

The goal of the present work was to assess and mechanistically understand the exchange kinetics of PAH transfer from sediment using GAC at a relatively low dose as a solid extraction phase. To accomplish this aim, kinetic parameters were obtained by modeling experimental sediment-GAC exchange kinetic data following a two-stage model calibration approach. In the first stage, PAH release from sediment was modeled for systems in which GAC acted as an infinite sink, that is, excluding backward sorption to the sediment. This GAC infinite sink scenario was benchmarked against desorption profiles using Tenax as an infinite sink. In the second stage, PAH release from the sediment was modeled at the actual remediation GAC dosage scenario (4%), including backward transport to sediment. Parameters obtained from the first stage without backward sorption, were used as fixed inputs in the second stage, which increases the accuracy of the parameter estimation. The primary model used for calibration was a first-order multi-compartment model, traditionally used for sediment desorption studies [14, 28, 29]. However, to be able to keep the link with the theory of diffusive transfer, part of the calibrations used a biphasic radial diffusion model as well. The sediment selected was highly contaminated, thus representing a ‘hot spot’ remediation site. This assumes that if 4% GAC extraction efficiencies would suffice for such sediment, they also would for less contaminated sediments.

MATERIALS AND METHODS

Sediment and Activated Carbon

Sediment was obtained from Petroleum Harbor (PH) located in Amsterdam, The Netherlands. Total content of PAHs, petroleum hydrocarbons (TPH), organic carbon (TOC), BC and freely dissolved PAH concentrations were determined in our previous study [12]. A summary of sediment characteristics is provided in Table 1 and Table S1 (Supporting Information). Coal-

based granular activated carbon (GAC 1240W, Norit, Amersfoort, The Netherlands) with a particle size of 0.45-1.75 mm was used in all experiments. Characteristics of GAC were reported previously [12]. Details on other chemicals, materials and analysis are provided as Supporting Information.

Kinetic experiments

Sorption kinetic experiments were performed in parallel for systems comprising a) sediment and Tenax, at 1:1 Tenax:sediment (w:w) ratio, b) GAC-sediment mixtures at 1:1 GAC:sediment (w:w) and c) GAC-sediment mixtures at 1:25 GAC:sediment ratio. Systems a) and b) represent extraction towards an infinite sink, whereas system c) represents a typical *ex situ* remediation GAC dosage [9, 12, 30].

Tenax extractions. Quadruplicate PAH desorption kinetic experiments with PH sediment were performed at 20 ± 1 °C using consecutive Tenax extractions for time periods up to 126 d [14, 20, 31]. In short, the extractions were carried out in separatory funnels, which were filled with 0.75 g PH sediment (d.w.), 50 mL of Mili-Q water containing 100 mg/L NaN_3 and 0.01M CaCl_2 , and 0.75 g of Tenax beads. The separatory funnels were covered with aluminum foil to prevent PAH photolysis and were shaken end-to-end at 160 strokes per minute. At time 1, 2, 3, 4, 8, 14, 28, 42, 84 d the sediment suspension was separated from the sorbent, and the Tenax beads were renewed. After 126 days the sediment was separated from Tenax, centrifuged and dried with Na_2SO_4 for determination of residual concentration of PAHs remaining in the sediment after Tenax extraction. Tenax beads recovered per time point were analyzed for PAHs (see below).

Granular activated carbon extractions at 1:1 GAC:SED ratio. Sediment desorption kinetics of PAHs was assessed through triplicate batch experiments using PH sediment and 50% GAC. In short, a series of 30 brown-colored bottles received 50 mL of the previously described aqueous $\text{NaN}_3/\text{CaCl}_2$ solution, 0.75 g d.w. PH sediment and 0.75 g GAC. The solid-to-liquid ratio was identical to that in the kinetic experiment with Tenax. All bottles were horizontally shaken (160 strokes per minute) at 20°C. At selected time points (same as above) three bottles were sacrificed. The sediment suspensions were separated from the GAC by sieving (250 μm), centrifuged and dried with Na_2SO_4 for determination of residual concentration of PAHs remaining in the sediment after GAC extractions. Further steps were identical as described above. GAC recovery was larger than 90%. To some extent however intensive mixing may have resulted in some erosion of GAC particles.

Granular activated carbon extractions at 1:25 GAC:SED ratio. The desorption kinetics of PAHs from PH sediment was also determined at a GAC dose of 4%, using the same experimental procedure as for GAC:sediment ratio of 1:1 (see above). In short, 30 brown-colored bottles were filled with 200 mL of the $\text{NaN}_3/\text{CaCl}_2$ solution, 3.20 g (d.w.) PH sediment and 0.125 g GAC. Further procedures were identical as described above. In practical

applications, the sediment-to-liquid ratio may be about an order of magnitude higher than these conditions. If mixing is sufficient however, this would not change the results.

Analytical procedures

Before use all glassware was rinsed with acetone and hexane. After removal from the sediment suspensions, the Tenax beads were Soxhlet-extracted with 70 mL hexane/acetone (1:1) for 3 h. Total concentrations of PAHs in PH sediment as well as PAH concentrations remaining in the sediment after Tenax and GAC tests were determined by Soxhlet extraction using 70 mL hexane/acetone (1:1) for 16h [32-34]. Subsequently, all extracts were concentrated to 1 mL using a modified Kuderna-Danish apparatus, and cleaned up over aluminum oxide columns using 25 mL of hexane. Column eluates were reduced to 1 mL, switched to acetonitrile and re-reduced to 6 mL under a gentle flow of nitrogen. Analytes in extracts of sediment and Tenax were separated by reverse-phase HPLC using a C18 column with length 250 mm and diameter 4.6 mm (Vydac, Grace) and a 40-min isothermal (35°C) acetonitrile – water solvent gradient program with a flow of 1 ml min⁻¹. PAHs were quantified with a photodiode array detector UVD340U (Dionex) or programmable fluorescence detection (Hewlett-Packard 1046A).

Quality assurance

Relative standard errors for concentrations in replicated batch systems were between 2 and 11%. Blank and recovery samples were included in the Tenax and sediment extraction procedures. Clean-up recoveries obtained by adding a standard PAH mixture prior to extraction, ranged from 83.6±5.6 (BaP) to 104.7±7.9 (DBA) % ($n = 6$), depending on the compound. Extractions of blank samples showed that no PAH were present in the GAC.

Modeling

Model definition and strategy. To be able to design effective remediation methodologies, kinetic parameters for short- and long-term sorption processes at various GAC dosage levels need to be known. Here, we use a multicompartment model that simulates the transfer of fast and slowly desorbing contaminants from the sediment [14, 20, 29] to the water phase and subsequent adsorption by GAC. A schematic overview of the systems is provided as Supporting Information (Figure S1). The remediation scenario represents the redistribution of PAH from sediment caused by mixing with a GAC dose of only 4%, and therefore has to account for backward sorption. The infinite sink scenario represents a system with 50% GAC, in which backward transport to the sediment is assumed negligible. HOC mass transfer in the remediation scenario can be defined through a series of coupled differential equations (Eq. (1) – (4)). For sediment, PAH exchange between the ‘fast’ sediment compartment (C_{fast}) and water is modeled as:

$$\frac{dC_{fast}}{dt} = k_{fast}(K_{p,fast}C_W - C_{fast}) \quad (1)$$

where C_{fast} ($\mu\text{g/kg}$) and C_W ($\mu\text{g/L}$) are concentrations of chemicals in the fast-desorbing sediment compartment, and in the water phase, respectively, k_{fast} is a desorption rate constant (d^{-1}) and $K_{p,fast}$ (L kg^{-1}) is the partitioning constant of PAHs in the fast reservoir. Similarly, the exchange of PAH from the ‘slow’ sediment compartment is defined as:

$$\frac{dC_{slow}}{dt} = k_{slow}(K_{p,slow}C_W - C_{slow}) \quad (2)$$

where C_{slow} is the concentration of chemicals desorbing slowly (from the ‘slow’ sediment compartment) ($\mu\text{g/kg}$), k_{slow} is the rate constant for slow desorption (d^{-1}) and $K_{p,slow}$ (L kg^{-1}) is the partitioning constant of PAH in the slow sediment compartment, respectively.

For GAC, the equation for PAH exchange is different from those for the fast and slow desorbing sediment-bound PAH, because sorption to GAC is assumed to be non-linear [35]:

$$\frac{dC_{GAC}}{dt} = k_{GAC}(K_{F,GAC}C_W^{n_F-1}C_W - C_{GAC}) \quad (3)$$

where C_{GAC} is the concentration of PAHs in GAC and k_{GAC} is the adsorption rate constant (d^{-1}). In Eq. (3) the GAC partitioning coefficient is replaced by a Freundlich term, with a Freundlich affinity constant, $K_{F,GAC}$ ($\mu\text{g/kg}_{GAC}/(\mu\text{g/L})^n$) and $n_{F,GAC}$, which is the Freundlich exponent for sorption to GAC.

The change of PAH concentration in the water phase (C_W) of mixed sediment-GAC slurry can then be defined as:

$$\begin{aligned} \frac{dC_W}{dt} = & k_{fast} \frac{S_{SED}}{L} (K_{p,fast} C_W - C_{fast}) + k_{slow} \frac{S_{SED}}{L} (K_{p,slow} C_W - C_{slow}) + \\ & k_{GAC} \frac{S_{GAC}}{L} (K_{F,GAC} C_W^{n_F-1} C_W - C_{GAC}) \end{aligned} \quad (4)$$

where $\frac{S_{SED}}{L}$ is the sediment-to-liquid ratio (kg L^{-1}) and $\frac{S_{GAC}}{L}$ is the GAC-to-liquid ratio. For the infinite sink extractions, C_W can be assumed to be close to zero and transport from GAC to the water phase is assumed negligible. Therefore, backward sorption to sediment particles is excluded [31]. This simplifies the equations (1) – (4), such that an analytical solution is available:

$$\frac{C_{SED,t}}{C_{SED,0}} = F_{fast} e^{-k_{fast}t} + (1 - F_{fast}) e^{-k_{slow}t} \quad (5)$$

where $C_{SED,t}$ is the concentration of PAH in the sediment ($\mu\text{g/kg}$) at time t (days), defined as $C_{SED} = C_{fast} + C_{slow}$, $C_{SED,0}$ is the initial concentration of the sorbate, and F_{fast} and $(1 - F_{fast})$ are the fractions of PAH in the fast and slow reservoirs, respectively (dimensionless).

Equation (5) is the equation that is used traditionally to interpret data from sediment desorption experiments with Tenax as an infinite sink [14, 20]. The assumption that 1:1 GAC extraction also is an infinite sink extraction was validated by (a) comparing the parameters obtained from the Tenax and GAC extraction data, and (b) testing the parameters obtained with Eq. (5) and the Tenax and GAC extraction data (50%) with parameter estimates obtained with the full numerical model (Eq. (1)-(4)). The latter approach provided excellent agreement between measured and modeled values (data not shown) and thus confirmed that backward sorption to sediment particles did not play a role.

To interpret the sorption data in the context of diffusion processes, the infinite sink scenario datasets were also evaluated with a biphasic radial diffusion model (SI, Eq. S1). Details of the modelling procedure are provided as Supporting Information.

Parameter estimation. The sorption parameters k_{GAC} and $K_{F,GAC}$ at a GAC dose of 4% of the sediment weight were determined following a two-stage modeling approach. First, Eq. (5) was applied to calculate k_{fast} , k_{slow} and F_{fast} from PAH sediment concentrations as a function of time obtained from the GAC infinite sink extraction (50% GAC), using the solver function in Microsoft Excel (Microsoft Corporation). Subsequently, the same parameters were estimated from the data obtained with excess Tenax infinite sink extraction of the sediment, using the PAH quantities measured in the Tenax. Second, the calibrated parameters were used as fixed input in the modeling of the data from extraction with 4% GAC (resembling the remediation dose), which accounted for backward transport (Eq. (1)-(4)), and in which only the GAC related parameters (k_{GAC} and $K_{F,GAC}$) were optimized. The parameters $n_{F,GAC}$, $K_{p,fast}$ and $K_{p,slow}$ and the initial estimates of $K_{F,GAC}$, were taken from our previous study [12]. This study also provided concentrations of individual PAH in the aqueous phase (C_w) after 28 d ($n=3$) for identical GAC-sediment mixtures and experimental conditions [12]. Consequently, k_{GAC} and $K_{F,GAC}$ parameter estimation was based on the PAH sediment concentration data as a function of time, as well as this 28 d time point for C_w . Eq. 1 to 4 were approximated by a 4th order Runge-Kutta algorithm programmed in Excel, using incremental time steps. The model assumed that at time zero GAC is free of PAH. GAC sorption parameters (k_{GAC} and $K_{F,GAC}$) for 4% GAC were estimated by minimizing the residual sum of squares between experimental and modelled values. Confidence intervals (CI90) for k_{GAC} and $K_{F,GAC}$ were obtained by re-fitting the parameters to meet the criterion [36]:

$$SS_{90} = SS_{min} \left[1 + \frac{p}{n-p} F(p, n-p, 90\%) \right] \quad (6)$$

where SS_{90} is the residual sum of squares at the 90% confidence contour, SS_{min} is the sum of squares at the best estimate of k_{GAC} and $K_{F,GAC}$, n is the number of data points used in the optimization, equal to the number of data points for desorbed PAH in time plus the three pore water concentration data (i.e. $n=13$), p is the number of fitted parameters, and $F(p, n-p, 90\%)$ is the F distribution. The optimized first order rate constant for PAH sorption to GAC at a dose of 4% can be related to parameters for radial diffusion by [37]:

$$k_{GAC} \approx 23 \frac{D_{eff}}{r^2} \quad (7)$$

where D_{eff} is the effective diffusion coefficient (m^2/d) and r is the diffusion path length, which may be approximated by the effective radius of the GAC spheres (0.00065 m). Other data analysis was performed with PASW Statistics 20.0 (SPSS, Chicago, IL).

RESULTS AND DISCUSSION

Sediment characteristics

Measurements of particle size in PH sediment showed two distinct peaks of 8.9 and 176 μm with cumulative volumes of 52 and 44 %, and a smaller peak with particles below 1 μm and cumulative volume of 4 %, respectively (Figure S2). PH sediment was composed primarily of silt-, clay- and fine sand-sized particles. Other sediment characteristics are reported in Table 1.

PAH desorption kinetics from sediment

Desorption parameters obtained with Tenax extractions. Desorption rates for 13 EPA PAHs were obtained by Tenax extraction, which is the most commonly applied method for determination of kinetic parameters for sediments and soils. [31] The simple first-order exponential model i.e. Eq. (5) showed a good fit to the experimental data as can be seen in Figure S3. The fitted values for k_{fast} and k_{slow} ranged from 2.54 to 0.14 d^{-1} and 5.5 to 0.7 $\times 10^{-3} d^{-1}$, respectively, implying a very rapid release of 3- and 4-ring PAHs (Table 1). Approximately, 50 to 70% of the individual 5- and 6-ring PAHs was present in the slowly desorbing sediment compartment (Table 1, Figure S3). The rate constants and fast desorbing fractions declined with increasing $\log K_{OW}$ (Table 1). HOCs associated with amorphous organic carbon are likely to desorb rapidly, whereas desorption from BC phases is slow [2]. High molecular weight PAHs have a higher affinity to BC than the low molecular weight PAHs [2, 38]. Thus, because of the high BC content of 41% TOC as was measured in PH sediment, BC may constitute the main binding phase for high molecular weight compounds (5- and 6-ring), with a lower affinity for 3- and 4-ring PAHs. The latter may be caused by weaker π - π interactions of low molecular weight PAHs with the BC surface [2].

Kinetic data were also evaluated with the biphasic radial diffusion model (SI, Eq. S1). Plots of cumulative mass removed vs. time for each compound are reported as Supporting Information (Figure S3). The rapidly desorbing fractions were large for 3- and 4-ring compounds and were more or less equal to F_{fast} determined by the first-order model except for fluoranthene (FLU), benzo[a]anthracene (BaA) and chrysene (CHR), which showed a difference from 16 to 30% (compare Table 1 and Table S2). The composite parameters D_e^{fast}/r^2 for the labile fraction ranged between 6.240 and 0.004 d^{-1} , and were approximately three orders of magnitude larger than D_e^{slow}/r^2 (5.3×10^{-3} to $2 \times 10^{-6} d^{-1}$) for the slow

compartment. Both $\log D_e^{fast}/r^2$ and $\log D_e^{slow}/r^2$ values decrease linearly with increasing $\log K_{OW}$ of the studied PAHs, similar to k_{slow} estimated with the first order model (Figure S4, S5).

The first-order model (Eq. 5) provided accurate estimates of the kinetic parameters i.e. small standard errors (SE) in F_{fast} (0.9-3.4%), in k_{fast} (5-20%), and in k_{slow} (10-30%) for all PAHs (Figure 1). The root mean square errors (RMSE) were also small, which confirms that Eq. (5) can precisely define the biphasic nature of PAH desorption from PH sediment. Overall, the k_{fast} and k_{slow} parameters comply with literature values [40], whereas D_e^{fast}/r^2 values are up to three orders of magnitude higher than those previously reported for PAHs [14, 28]. However, note that the D_e^{fast}/r^2 parameters are operationally defined. The literature D_e^{fast}/r^2 values related to much smaller F_{fast} values and therefore do not necessarily refer to the same kinetic compartments. High values of D_e^{fast}/r^2 may be caused by the presence of oil, which was visually observed during the experiments, or/and the presence of dissolved or colloidal organic carbon (DOC). It may also be plausible that the actual diffusive path length r was smaller than those of the particles previously studied. We cannot distinguish unambiguously between the true diffusive path length r , oil or DOC related explanations. Although $\log D_e^{fast}/r^2$ vs $\log K_{OW}$ showed a linear relationship, the $\log D_e^{fast}/r^2$ values for 3- and 4-ring compounds i.e. FL, phenanthrene (PHE), ANT, FLU and PYR were more or less constant (Table S2, Figure S4). The linear decrease of $\log D_e^{fast}/r^2$ vs. $\log K_{OW}$ (Figure S4) is much clearer for 5- and 6- ring compounds, which might indicate more pronounced retarded diffusion in intraparticle pores.

The first-order exponential model and the diffusion based model were very similar in their capability to describe desorption profiles showing more than 80 % release of PAHs over 126 days. The diffusion model showed a marginally better fit to the experimental data than the first-order exponential model (Table 1, Table S2). However, the difference is considered too small to prefer either one of the approaches for mechanistic reasons. The current results show that although desorption from sediment probably is a diffusion based process, the first-order approach provides an excellent approximation and with lower calculation complexity.

Desorption parameters obtained with GAC extractions. Desorption parameters k_{fast} , k_{slow} and F_{fast} in the GAC infinite sink scenario were estimated by fitting Eq. (5) to the data of PAH sediment concentration as a function of time. The changes in $C_{SED,t}/C_{SED,0}$ vs. time obtained with GAC are provided as Supporting Information (Figure S6), and show patterns similar to those obtained with Tenax (Figure S3). However, the individual data points are more scattered, which reflects the larger experimental error associated with using independent batches in the desorption experiments and with the heterogeneity of the PH sediment. The first-order model resulted in statistically satisfying fits to the data, with similar or higher RMSE values compared to those obtained with Tenax extractions (Figure S6, Table 1).

Table 1. Sediment characteristics and first-order desorption rate parameters with standard errors (SE) obtained from Tenax and GAC tests at infinite sink condition (Eq. (5)).

[illegible]

Kinetics of hydrophobic organic contaminant extraction from sediment by GAC

GAC:SED 1:1 ratio												
Sorbate	Number of rings	Reduction of C_{SED} , %	F_{fast}	SE	k_{fast} (1/d)	SE	F_{slow}	SE	k_{slow} (10^{-3} 1/d)	SE	R ²	RMSE*
FL	3	93	0.807	0.021	2.757	0.415	0.193	0.010	7.192	1.505	0.998	0.100
PHE	3	84	0.744	0.024	2.225	0.302	0.256	0.011	5.010	1.088	0.997	0.098
ANT	3	77	0.686	0.033	1.165	0.146	0.315	0.017	3.790	1.143	0.994	0.090
FLU	4	79	0.652	0.028	2.164	0.379	0.349	0.013	5.198	0.951	0.995	0.085
PYR	4	78	0.635	0.045	2.075	0.560	0.365	0.020	5.586	1.478	0.988	0.123
BaA	4	64	0.425	0.082	0.778	0.347	0.596	0.047	4.384	1.643	0.949	0.100
CHR	4	52	0.406	0.082	0.573	0.250	0.621	0.050	2.767	1.433	0.940	0.090
BbF	5	53	0.256	0.049	0.486	0.201	0.760	0.033	4.274	0.812	0.976	0.050
BkF	5	55	0.403	0.033	0.566	0.101	0.585	0.020	1.708	0.573	0.986	0.044
BaP	5	37	0.326	0.056	0.548	0.205	0.708	0.033	0.612	0.742	0.935	0.052
DBA	6	29	0.166	0.024	0.228	0.078	0.836	0.020	1.390	0.337	0.983	0.022
BghiP	6	39	0.355	0.035	0.404	0.086	0.674	0.023	0.857	0.522	0.980	0.034
InP	6	43	0.212	0.052	2.942	4.688	0.789	0.022	3.294	0.656	0.950	0.059

RMSE* = Root mean square error, ^a SD between parenthesis, ^b Threshold level for intervention [39]

It appears from Figure S7 that the F_{fast} values for 3- and 4- ringed compounds determined using extractions with Tenax and GAC are very close to each other. However, for BaA, CHR, BbF, benzo[a]pyrene (BaP), dibenzo[*a,h*]anthracene (DBA) and indeno[1,2,3-*cd*]pyrene (InP), desorption from sediment towards GAC yielded lower F_{fast} values (Table 1). Overall, the GAC and Tenax F_{fast} values were not statistically different from each other (t test, $p > 0.05$). The slightly lower F_{fast} values of 5- and 6- ring compounds might be caused by sorption attenuation of GAC by DOC and oil. This is more important for GAC than for Tenax, because Tenax was refreshed during the experiments. The k_{fast} values obtained with Tenax and GAC extractions are not statistically different from each other (paired t -test, $t = -0.783$, $p = 0.448$). This once again confirms that backward transport from GAC did not play a role, because occurrence of backward sorption would have reduced the apparent rate constants for the fast desorbing sorption domain, especially for the low molecular weight PAH [28]. The infinite sink Tenax and GAC extractions resulted in substantial reduction of the concentrations of fast desorbing PAHs. This implies that potential ecological risks have decreased. The remaining fraction of contaminants in PH sediment (Table 1) however, still exceeds generic (tier 1) Dutch threshold level for intervention (Table 1) and classifies the studied sediment as heavily polluted. Case specific assessment of the utilisation of these sediments can be used to determine re-use options.

The diffusion model again showed a marginally better correlation with the experimental data than the first-order exponential model with respect to RMSE (see Table S2). Plots of cumulative mass removed vs. time for individual components are provided as Supporting Information (Figure S6). In summary, these results show that a first order as well as a diffusion model adequately described the desorption data obtained from Tenax and GAC extraction, and that GAC acted as an infinite sink like the Tenax did.

Kinetics of PAH transfer from sediment to 4% GAC. Here we address the main aim of the paper, i.e. the kinetics of PAH mass transfer in a typical sediment remediation scenario with a GAC dose of 4%, which was evaluated with the full numerical model (Eq. (1)-(4)). The simulations used the calibrated parameters k_{fast} , k_{slow} and F_{fast} from the GAC extractions (see above) and measured [12] or fitted initial aqueous phase concentrations. The initial aqueous phase concentrations needed to be fitted mainly for 5- and 6- ring PAHs (Table S3), and were up to three orders of magnitude higher than those obtained with polyoxymethylene (POM) passive sampler measurements [12]. This may be explained from apparent DOC-inclusive aqueous phase concentrations being higher than truly dissolved concentrations as measured by POM samplers [30]. First, we evaluated the model with our previously determined Freundlich exponents for 3- and 4- ring PAHs ($n_F = 0.46 - 0.9$), and a literature value of 0.82 for the 5- and 6- ringed compounds [41].

Table 2. Parameters for sorption of PAH to GAC, present at a dose of 4% of sediment weight, with 90% confidence intervals (CIs) obtained from the first-order numerical model ^a.

Scenario with $n_F = 1$										
Sorbate	k_{GAC} (10^{-2} 1/d)	CI _L ^b 90%	CI _U ^c 90%	$t_{1/2}$ (d)	Log K_{GAC} (L/kg)	CI _L ^b 90%	CI _U ^c 90%	R ²	D_{eff} (m ² /d)	Reduction of C_{SED} , %
FL	44.256	-	-	1.6	5.69	-	-	0.925	8.13×10^{-9}	86
PHE	21.200	-	-	3.3	5.61	-	-	0.877	3.89×10^{-9}	72
ANT	11.207	10.524	11.890	6.2	5.57	5.53	5.61	0.971	2.06×10^{-9}	62
FLU	1.928	1.453	2.402	36.0	5.76	5.69	5.82	0.933	3.54×10^{-10}	49
PYR	0.420	0.401	0.439	164.9	5.98	5.96	5.99	0.987	7.72×10^{-11}	54
BaA	0.611	0.581	0.641	113.4	6.60	6.54	6.66	0.935	1.12×10^{-10}	38
CHR	0.334	0.291	0.377	207.5	6.71	6.64	6.77	0.870	6.14×10^{-11}	43
BbF	0.090	0.084	0.096	770.2	7.90	7.88	7.93	0.862	1.65×10^{-11}	32
BkF	0.090	0.084	0.095	773.0	7.95	7.92	7.97	0.990	1.65×10^{-11}	35
BaP	0.068	0.066	0.070	1022.0	8.00	7.98	8.01	0.882	1.25×10^{-11}	26
DBA	0.050	0.048	0.052	1389.3	8.51	8.49	8.53	0.847	9.16×10^{-12}	16
BghiP	0.059	0.055	0.063	1176.4	8.43	8.40	8.47	0.834	1.08×10^{-11}	19
InP	0.080	-	-	871.2	8.57	-	-	0.746	1.46×10^{-11}	21

^aEq. (1)-(4), ^b CI_L = lower bound, ^c CI_U = upper bound, - high k_{GAC} values caused numerical dispersion, prohibiting calculation of CI boundaries

Sorption parameters k_{GAC} and $K_{F,GAC}$ (Eq. (3)) were estimated from 13 data points i.e. 10 solid phase sediment concentrations (at 1, 2, 3, 4, 8, 14, 28, 42, 84, 126 d) and 3 aqueous phase data points at 28 d. The corresponding parameters for sorption to GAC are reported as Supporting Information (Table S3). The model calibration provided excellent fits to the experimental data, which is expressed through R^2 values close to unity, and narrow ranges of the 90% confidence intervals for k_{GAC} and $K_{F,GAC}$ (for details see Table S3). This implies that sorption to GAC in the presence of sediment, can be adequately described by a first order kinetic model with one GAC compartment, even for prolonged time scales up to 126 d. The n_F values used for 3- and 4- ring PAHs may carry some uncertainty because they relate to sorption isotherms with varying GAC/sediment ratios [12]. Therefore, for comparison, the model was also calibrated to the data using $n_F = 1$, i.e. assuming linear sorption to GAC. This approach is supported by the observation that HOC sorption to fouled charcoal was more linear than to virgin sorbents [42]. Calibrated k_{GAC} values, which were most important because they govern the kinetics, appeared not to be very sensitive to the two approaches to define n_F . The values were approximately the same, except for PHE, ANT and FLU where the difference however, still was a factor of two only (compare Table 2 and Table S3). For $K_{F,GAC}$, the differences were a factor of three on average. For FL, PHE, ANT, FLU and PYR, $K_{F,GAC}$ values were higher in the $n_F < 1$ scenario, whereas the other PAH showed lower $K_{F,GAC}$ values in the $n_F < 1$ scenario. That n_F influences $K_{F,GAC}$ more than k_{GAC} can be understood mechanistically from the fact that n_F affects the shape of the sorption isotherm i.e. sorption strength which is governed by $K_{F,GAC}$, and that therefore n_F is in the unit of $K_{F,GAC}$.

For two example compounds, i.e. ANT and BbF experimental data and model fits ($n_F = 1$) are presented in Figure 1 (a) and (b), respectively. Model fits for all tested compounds are provided as Supporting Information (Figure S9). It appears that confidence intervals for k_{GAC} and K_{GAC} are small (Table 2), which supports the accuracy of the model simulations. The calculations with $n_F = 1$ resulted in marginally better fits to the data (see R^2 values, Table 2) than those with $n_F < 1$ (Table S3). Therefore, and because differences in parameters values were not essentially different as discussed above, further discussion below focuses on the calculations with $n_F = 1$, and ANT and BbF being two representative PAH.

Figure 1 (a, b) shows the modelled ANT and BbF concentration in the fast and slow compartment, the modelled concentration in the aqueous phase (modelled C_w), the calculated sum of modelled concentrations in fast and slow sediment compartments (modelled C_{SED}), the modelled total quantity of PAH adsorbed per unit weight of GAC and the experimental sediment and water concentration data (measured C_{SED} and C_w respectively), as a function of time. For ANT and other 3- ring compounds, i.e. FL and PHE, the initial drop in the aqueous concentration is larger than that of 4-ring PAHs (Figure 1 a and Figure S9). For 5- and 6-ring PAH i.e. BkF, BaP, DBA, BghiP and InP, aqueous concentrations decrease more gradually in time by more than an order of magnitude (Figure S9).

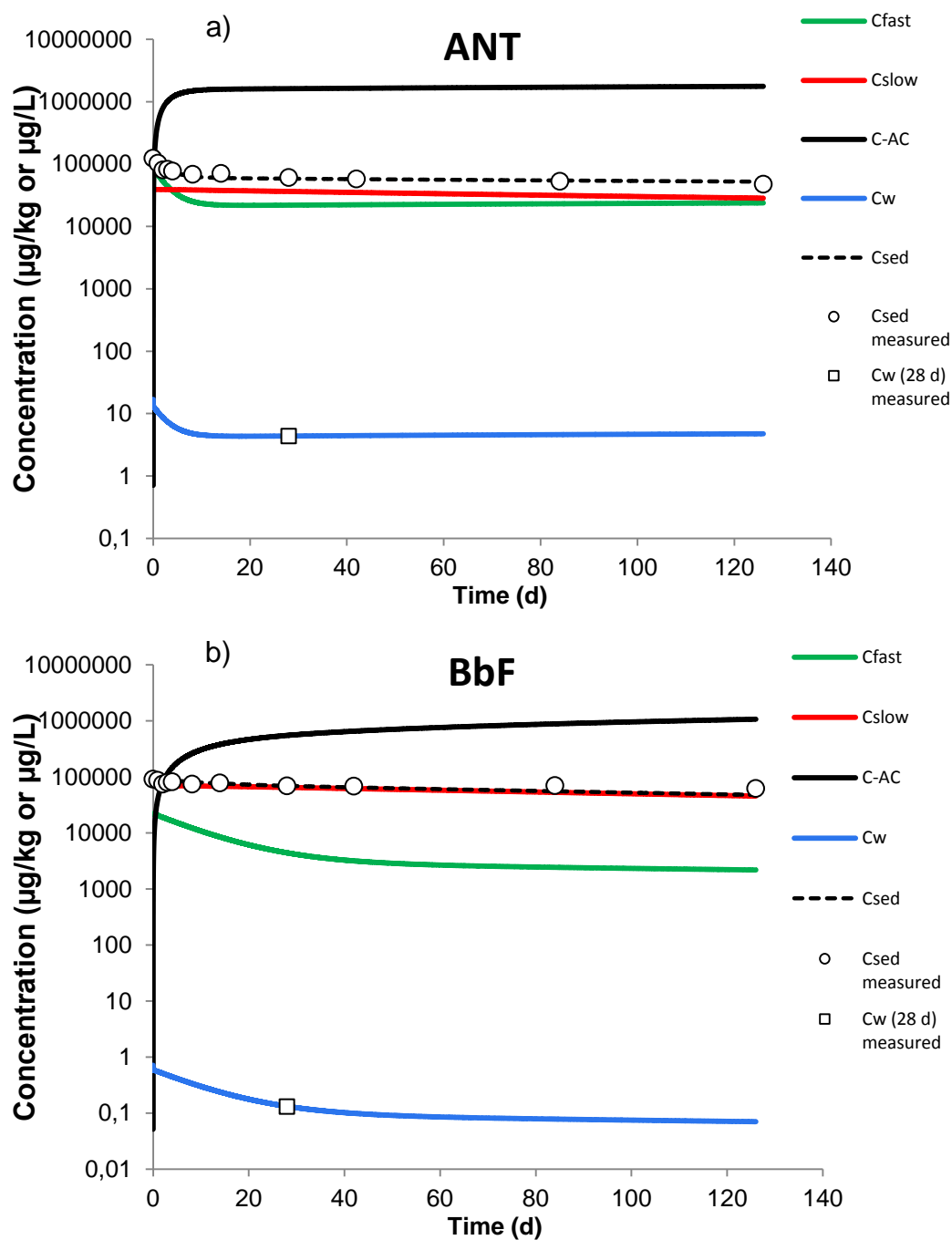


Figure 1. Concentrations of ANT (a) and BbF (b) in PH sediment and GAC (4%) as a function of time. Dashed and solid lines represent modelled values by using Eq. 1-4. ($n_F = 1$), whereas markers represent measured data. The dashed C_{sed} line is calculated as the sum of the modelled C_{fast} and C_{slow} curves. Error bars ($n=3$) for C_w (28 d) relate to standard deviation but are smaller than the markers.

The fact that aqueous concentration is calculated not to be zero, confirms our presumption that 4% GAC does not act as an infinite sink and that indeed backward transport from GAC particles needed to be taken into account. Consequently, the observed sediment to GAC transfer rates depend on all rate and affinity constants derived for GAC and sediment, as well as on the sizes of the fast and slow sediment compartments. For ANT, it can be observed that transfer to GAC proceeds in two steps. First, a rapid stage of a few days is observed, corresponding to release from the fast sediment compartment and adsorption on the external GAC surface. This is followed by a much slower stage, which most probably reflects emptying of the slow sediment compartment. However, sediment slow desorption is not completely limiting because in that case the aqueous concentrations would have decreased over time. Other limiting factors may include intraparticle diffusion in GAC as well as competitive effects. The same behaviour was observed for other 3-ring PAHs, i.e. FL and PHE (for details see Figure S9). In contrast, the initial decline in the BbF aqueous phase concentration is less steep and shows a continued uptake by GAC with time (Figure 1 b).

The GAC adsorption rate constants (k_{GAC}) and approximate equivalent diffusion coefficients (D_{eff} , Eq. 7) varied between 0.44 - 0.0005 (d⁻¹) and 8.13×10^{-9} – 9.16×10^{-12} m² × d⁻¹, respectively (Table 2). Remarkably, the derived k_{GAC} values are approximately two orders of magnitude lower than those reported for pure GAC-water systems [18]. Consequently, we hypothesise that fouling by sediment organic matter attenuates the kinetics of PAH binding to GAC by two orders of magnitude. In contrast, the currently estimated k_{GAC} values are 1-3 orders of magnitude larger than those that can be calculated from the data reported by Hale et al. [25] (for details see Table S4). These authors modeled similar AC-sediment systems, yet using an intraparticle diffusion model, which was applied to data for PAH transfer to powdered AC (2%) mixed with sediment at a less intense mixing regime compared to the present study. Our current data show that apparent rate constants for PAH adsorption to AC can also be obtained very accurately using first-order multi-compartment models. We are not aware of earlier studies that provide measured rate constants for PAH adsorption to GAC in the presence of sediment. The calculated diffusivities are higher for low molecular weight PAHs as compared to those of the high molecular weight PAH (Table 2). The range for high molecular weight compounds complies with reported PHE diffusivities to activated carbon and coke in sediment slurry systems (6.83×10^{-12} – 6.74×10^{-13} m² × d⁻¹ [23]. However, note that these literature diffusivities were derived at much lower aqueous phase concentrations and assuming nonlinear sorption. When plotted against log K_{OW} , log k_{GAC} shows a linear relationship ($R^2=0.858$, Figure S10), with a slope of -1.04 ± 0.93 and intercept 3.67 ± 1.04 , which indicates that PAH sorption rate to GAC correlates with hydrophobicity. Fast desorbing fractions inferred from the infinite sink extractions (1:1) (Table 1) were larger than those desorbed from sediment by extraction with 4% GAC (Figure S9). This implies that at 4% GAC the amount of PAH adsorbed onto the sorbent is controlled by the sorbent side mass transfer rate, whereas at high GAC dose i.e. 50%, PAH transfer is controlled by the sediment PAH releasing domains.

The currently derived PAH sorption affinity constants ($\log K_{GAC}$) for GAC also follow a linear dependence with $\log K_{OW}$ ($R^2=0.876$, Figure S11). The sorption affinity constants reach values reported earlier for pure sorbents [38]. This suggests that fouling may affect the kinetics of the uptake process, but not the eventual equilibrium adsorption affinity of GAC. This also implies that previously reported low apparent GAC or AC sorption affinity coefficients that were explained from fouling, may be partly explained from non-equilibrium or pseudo-equilibrium. For instance, our previous study of PAH sorption to GAC [12] used experimental conditions that were identical to those in the current work, except for a relatively short equilibration time of 28 d. Inspection of the profiles in Figure S9 and Figure 1 indeed shows that 28 d is sufficient for FL, PHE and ANT to reach equilibrium. For FLU, PYR, BaA, CHR, BbF, BkF, BaP, DBA, BghiP and INP, however, equilibration to these GAC particles requires more than 60 – 100 d. The currently fitted K_{GAC} values are infinite time extrapolations based on a time series with 10 data points up to 126 d, and thus may better reflect the actual affinities in the presence of organic matter.

CONCLUSIONS

Ex situ remediation aims at HOC removal by GAC that can be separated after a relatively short mixing period, such that the cleaned sediment can be reused as a construction material or for land application. Hence, the present study provided kinetic and equilibrium sorption parameters for binding of 13 EPA PAHs to GAC in the presence of sediment, representing such an *ex situ* remediation scenario. The optimized first order rate constants k_{GAC} can be translated into GAC uptake half-lives ($t_{1/2}$, see Table 2), by using the relationship $t_{1/2} = \ln 2/k_{GAC}$. As mentioned above, GAC is capable of accumulating FL, PHE, ANT, within a few days, whereas PAHs with higher K_{OW} require more time. This conceptually agrees with the results of our recent field study, which demonstrated that 48 h mixing of sediment and GAC resulted in a reduction of PAH pore water concentration by 97% [9]. Especially FL, PHE, ANT and FLU contribute to pore water PAH concentrations and therefore provide the largest contribution to toxic pressure on benthic communities. The present kinetic data show that GAC at a dose of 4% will effectively reduce the risk of these compounds within days, which is sufficiently fast given the characteristic *ex situ* remediation mixing times of days. Subsequent separation of GAC thus results in cleaner sediments that may be re-used, dependent on local regulations. In designing remediation mixing times or GAC doses, a first order multi-compartment model proved to be a promising predictive tool.

Supporting Information

Modeling details, modeling results and sediment characteristics can be found in Supporting Information.

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Supporting Information for Chapter 4

Materials and Methods

Chemicals for PAH analysis. High performance liquid chromatography (HPLC) standard, EPA 610 PAH Mix containing acenaphthene (ACE), acenaphthylene (ACY), anthracene (ANT), benzo[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbF), benzo[*g,h,i*]perylene (BghiP), benzo[*k*]fluoranthene (BkF), chrysene (CHR), dibenzo[*a,h*]anthracene (DBA), fluoranthene (FLU), fluorene (FL), indeno[*1,2,3-cd*]pyrene (InP), naphthalene (NA), phenanthrene (PHE), and pyrene (PYR) was obtained from Supelco Analytical, USA with purities of >98% except for PYR (purity > 96.6%). Other chemicals used were hexane and acetone (Promochem; picograde), acetonitrile (Lab-Scan, HPLC grade), calcium chloride CaCl₂ (Merck; p.a), sodium azide NaN₃ (Aldrich; 99%), sodium sulphate Na₂SO₄, (Merck, p.a.), aluminum oxide-Super I (ICN Biomedicals). Before use, aluminum oxide was deactivated with 10% (w/w) Nanopure water (Barnstead). Other water preparations used Milli-Q water (Millipore Corporation).

Tenax. The polymer sorbent Tenax TA, 20/35 mesh was purchased from Grace. Prior to use the Tenax beads were rinsed with demineralized water to remove fine particles and further extracted sequentially with acetone (4x) and hexane (4x) on a shaker with horizontal motion at 160 strokes per minute. The sorbent was dried overnight in 80°C and stored in brown colored bottle until use.

Particle size distribution analysis. Petroleum Harbor sediment was characterized for particle size distribution (PSD) using a Beckman Coulter LS 230 (fluid module) laser diffraction particle size analyzer with Polarization Intensity Differential of Scattered Light (PIDS). Sediment samples were brought into suspension in demineralized water and well homogenized prior to particle size analysis. The injected suspension volume was controlled to obtain a total obscuration level of 10±3% and a PIDS obscuration of 50±10% [1].

Table S1. Aqueous phase concentrations determined with POM-SPE [2].

Compound	C_w , ($\mu\text{g/L}$)	Log K_{POM} (L/kg) ^a	Log K_{OW} [REF]
Fluorene (FL)	63.74 (7.42)	3.83	4.2 [3]
Phenanthrene (PHE)	179.99 (15.78)	4.20	4.6 [4]
Anthracene (ANT)	16.76 (1.71)	4.30	4.7 [5]
Fluoranthene (FLU)	23.98 (2.01)	4.56	5.2 [4]
Pyrene (PYR)	13.65 (1.16)	4.57	5.2 [4]
Benzo[a]anthracene (BaA)	0.75 (0.07)	5.46	5.9 [4]
Chrysene (CHR)	0.57 (0.07)	5.43	5.8 [4]
Benzo[b]fluoranthene (BbF)	0.14 (0.02)	5.80	6.0 [3]
Benzo[k]fluoranthene (BkF)	0.04 (0.01)	5.97	6.1 [5]
Benzo[a]pyrene (BaP)	0.10 (0.01)	5.96	6.1 [5]
Dibenzo[a,h]anthracene (DBA)	1.79×10^{-3} (3.65×10^{-4})	6.30	7.0 [4]
Benzo[g,h,i]perylene (BghiP)	1.34×10^{-2} (1.43×10^{-3})	6.09	6.9 [4]
Indeno[1,2,3-cd]pyrene (InP)	8.96×10^{-3} (1.55×10^{-3})	6.26	7.0 [4]

^a Data taken from Hawthorne et al. [6]

Conceptual scheme of PAH exchange kinetics in a remediation scenario and an infinite sink scenario

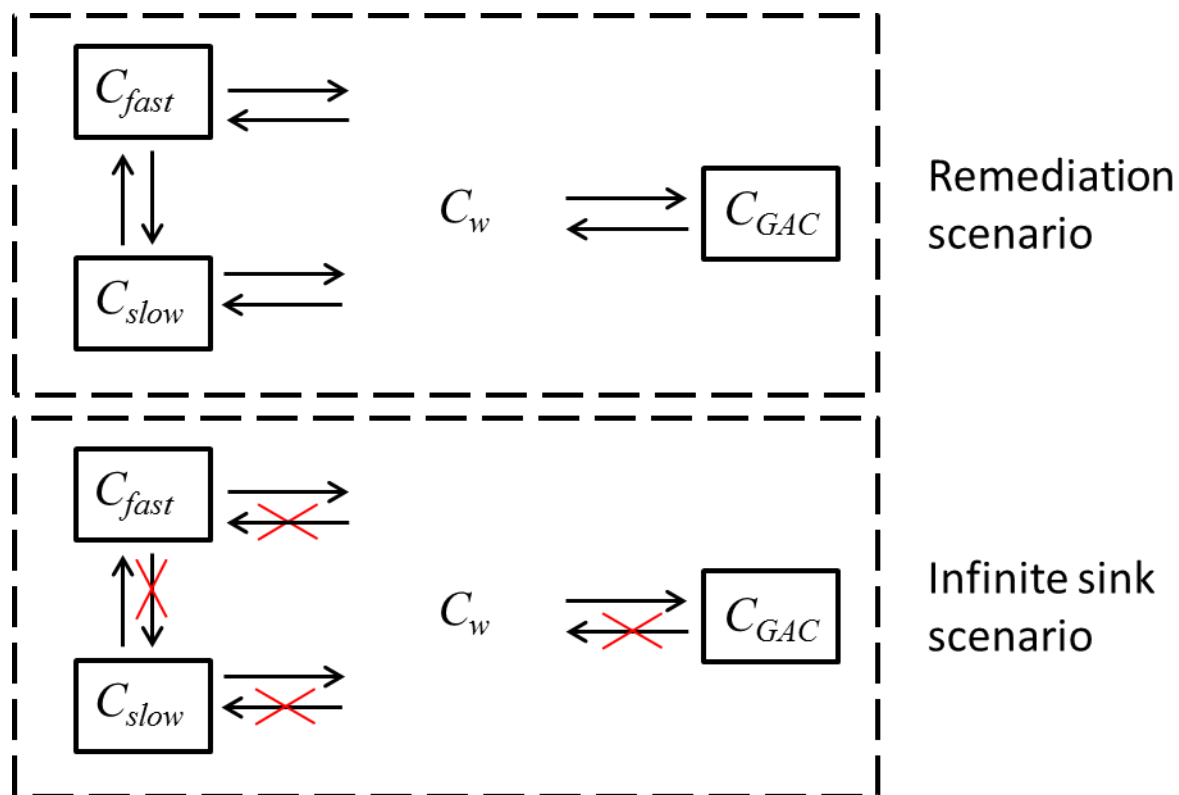


Figure S1. Conceptual scheme of PAH exchange kinetics in a remediation scenario and in the infinite sink scenario.

Modeling diffusion kinetics. Intraparticle diffusion models have been widely applied to determine the kinetics of hydrophobic organic compounds (HOC) mass transfer from or into porous materials [7, 8]. The experimental settings with Tenax and GAC at the infinite-dilution condition (see main text) were also interpreted using Fick's second law of diffusion in radial geometry, which for a bimodal size distribution is given by:

$$\frac{Q_t}{Q_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left(F_{fast}^* \exp \left[\frac{-n^2 \pi^2 D_e^{fast} t}{r_{fast}^2} \right] + (1 - F_{fast}^*) \exp \left[\frac{-n^2 \pi^2 D_e^{slow} t}{r_{slow}^2} \right] \right) \quad (S1)$$

where Q_t/Q_0 is the mass fraction of PAHs that are desorbed at time, t (days), D_e^{fast} and D_e^{slow} are the fast and slow diffusivities and r_{fast} and r_{slow} are the diffusion path lengths for fast and slow diffusion respectively. Because diffusion path lengths are indeterminate [9], Equation S1 was solved for F_{fast}^* , and for the composite parameters D_e^{fast}/r^2 and D_e^{slow}/r^2 , again using the Excel solver tool, and accounting for two thousand terms in the Taylor series [9, 10]. The model assumes that at $t=0$ the pollutant is distributed homogenously within the two sorption domains, each characterized by a distinct diffusion time scale (D_{eff}/r^2). We assume instant, local equilibrium inside the porous particles, based on linear partitioning. Due to vigorous mixing of sediment samples, the external mass transfer resistance was assumed negligible.

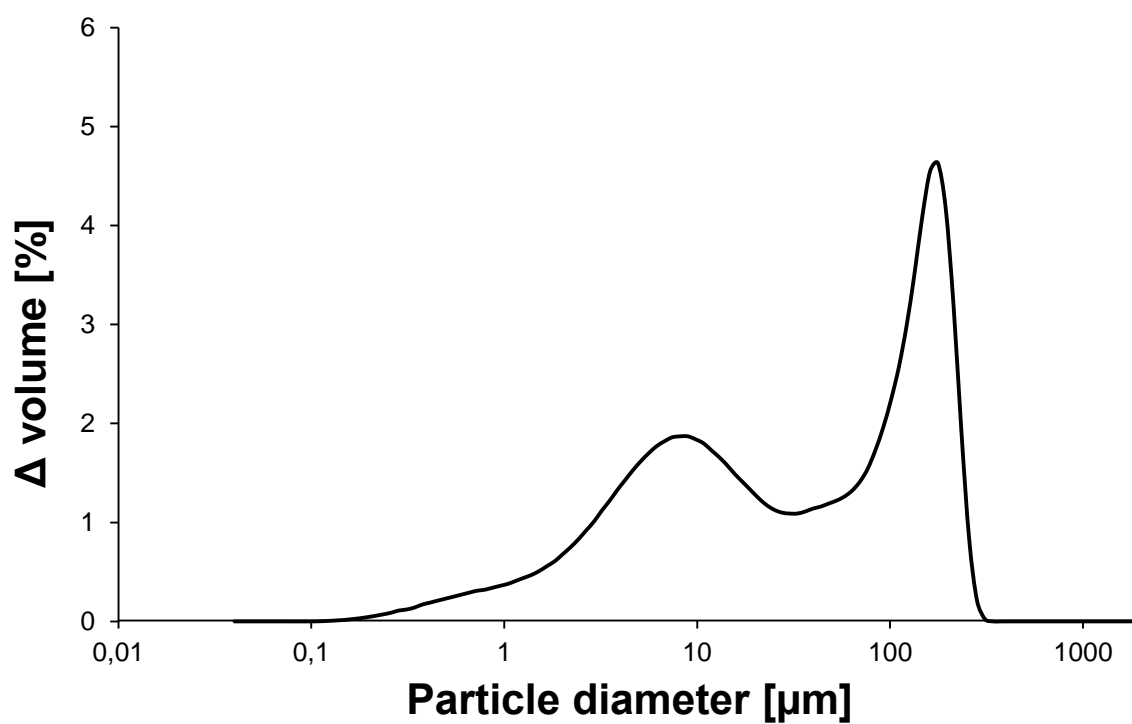


Figure S2. Distribution of particle sizes in PH sediment as determined by laser diffraction. ΔV is the amount of volume related to the discrete particle size range.

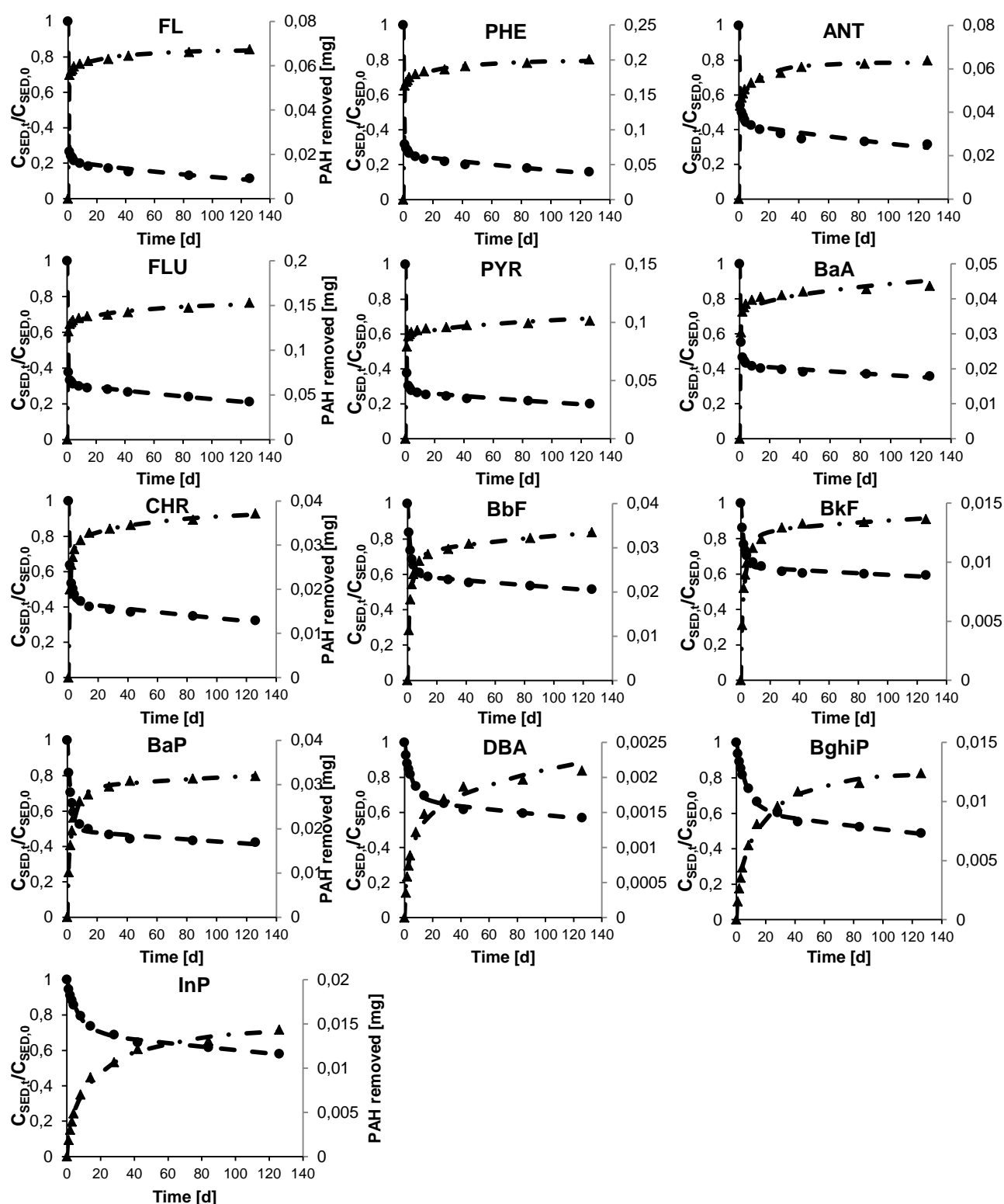


Figure S3. Desorbed mass (mg) (\blacktriangle) and residual fraction ($C_{SED,t}/C_{SED,0}$; unitless) (\bullet) of individual PAHs from PH sediment as determined with Tenax at 1:1 (TA:SED) ratio. Closed markers represent measured data. Dashed lines represent modelled values using first-order, exponential model, whereas dash dotted lines represent modelled values obtained with biphasic diffusion. To increase readability, the different model curves are plotted as mirror images.

Table S2. Desorption rate parameters obtained from the biphasic radial diffusion model.

Tenax:SED 1:1 ratio								
diffusion model parameters								
sorbate	LogK _{OW}	F_{fast}^*	D_e^{fast}/r^2 (1/d)	D_e^{fast} (m ² /d)	D_e^{slow}/r^2 (10 ⁻³ 1/d)	D_e^{slow} (m ² /d)	R ²	RMSE*
FL	4.2	0.816	6.240	1.236×10 ⁻¹⁰	2.906	2.251×10 ⁻¹¹	0.999	0.0006
PHE	4.6	0.799	5.986	1.185×10 ⁻¹⁰	2.936	2.273×10 ⁻¹¹	0.999	0.0019
ANT	4.7	0.621	3.049	6.038×10 ⁻¹¹	5.333	4.130×10 ⁻¹¹	0.999	0.0009
FLU	5.2	0.798	5.021	9.943×10 ⁻¹¹	1.698	1.315×10 ⁻¹¹	0.998	0.0025
PYR	5.2	0.671	3.684	7.296×10 ⁻¹¹	0.410	3.176×10 ⁻¹²	0.994	0.0031
BaA	5.9	0.419	2.512	4.973×10 ⁻¹¹	0.258	1.996×10 ⁻¹²	0.985	0.0021
CHR	5.8	0.745	0.064	1.276×10 ⁻¹²	1.448	1.122×10 ⁻¹¹	0.999	0.0003
BbF	6.0	0.390	0.029	5.736×10 ⁻¹³	0.018	1.375×10 ⁻¹³	0.996	0.0009
BkF	6.1	0.357	0.025	4.902×10 ⁻¹³	0.005	3.761×10 ⁻¹⁴	0.996	0.0004
BaP	6.1	0.505	0.021	4.168×10 ⁻¹³	0.017	1.295×10 ⁻¹³	0.996	0.0009
DBA	7.0	0.323	0.014	2.698×10 ⁻¹³	0.401	3.107×10 ⁻¹²	0.993	0.0001
BghiP	6.9	0.485	0.004	7.503×10 ⁻¹⁴	0.002	1.345×10 ⁻¹⁴	0.996	0.0004
InP	7.0	0.343	0.004	8.118×10 ⁻¹⁴	0.009	7.146×10 ⁻¹⁴	0.997	0.0004
GAC:SED 1:1 ratio								
RMSE* = Root mean square error								
	LogK _{OW}	F_{fast}^*	D_e^{fast}/r^2 (1/d)	D_e^{fast} (m ² /d)	D_e^{slow}/r^2 (10 ⁻⁴ 1/d)	D_e^{slow} (m ² /d)	R ²	RMSE*
FL	4.2	0.771	6.148	1.218×10 ⁻¹⁰	4.455	3.450×10 ⁻¹²	0.898	0.0016
PHE	4.6	0.697	4.748	9.403×10 ⁻¹¹	2.980	2.308×10 ⁻¹²	0.883	0.0061
ANT	4.7	0.577	2.048	4.056×10 ⁻¹¹	3.750	2.904×10 ⁻¹²	0.792	0.0051
FLU	5.2	0.599	4.827	9.558×10 ⁻¹¹	2.733	2.116×10 ⁻¹²	0.911	0.0054
PYR	5.2	0.575	4.722	9.351×10 ⁻¹¹	3.101	2.401×10 ⁻¹²	0.876	0.0048
BaA	5.9	0.260	1.462	2.894×10 ⁻¹¹	3.065	2.374×10 ⁻¹²	0.829	0.0054
CHR	5.8	0.326	0.033	6.595×10 ⁻¹³	0.945	7.316×10 ⁻¹³	0.878	0.0036
BbF	6.0	0.081	0.987	1.955×10 ⁻¹¹	2.848	2.206×10 ⁻¹²	0.952	0.0032
BkF	6.1	0.358	0.043	8.594×10 ⁻¹³	0.541	4.188×10 ⁻¹³	0.967	0.0008
BaP	6.1	0.273	0.031	6.215×10 ⁻¹³	0.064	4.971×10 ⁻¹⁴	0.833	0.0043
DBA	7.0	0.089	0.013	2.567×10 ⁻¹³	0.240	1.859×10 ⁻¹³	0.970	0.0001
BghiP	6.9	0.423	0.015	2.886×10 ⁻¹³	0.172	1.330×10 ⁻¹³	0.928	0.0014
InP	7.0	0.404	0.005	1.044×10 ⁻¹³	0.002	1.266×10 ⁻¹⁵	0.903	0.0020

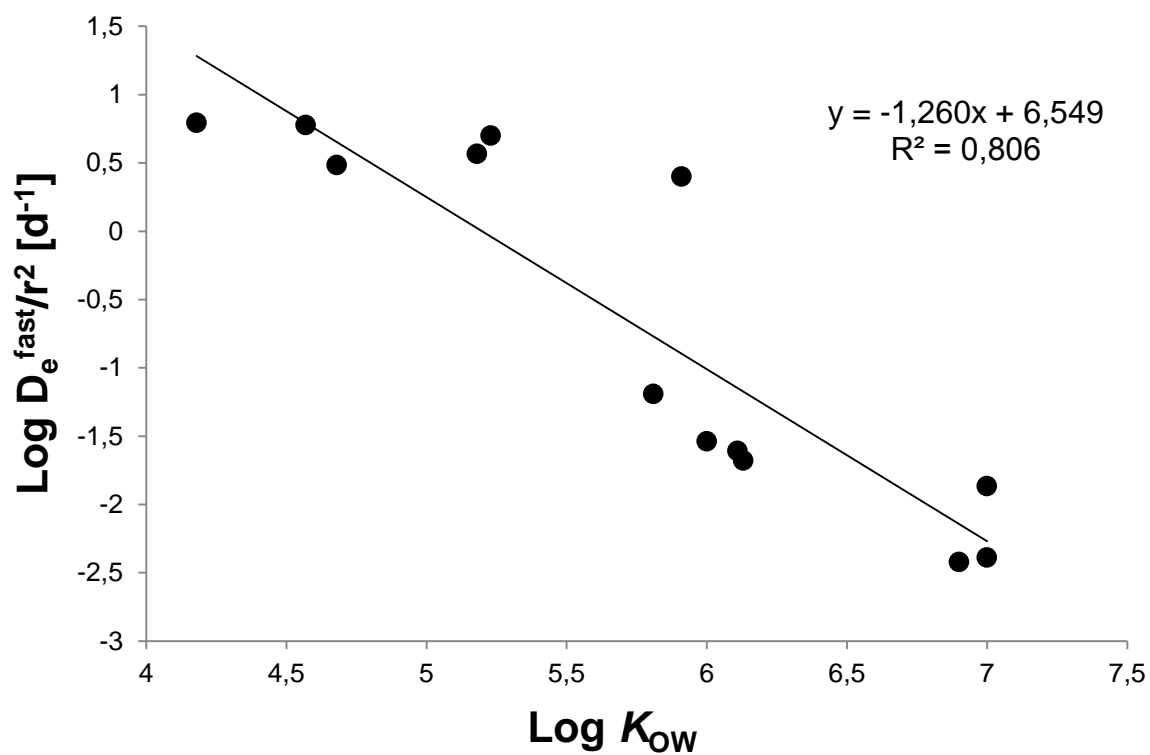


Figure S4. $\text{Log } D_e^{\text{fast}}/r^2$ as a function of $\text{Log } K_{\text{ow}}$ as determined by radial diffusion model.

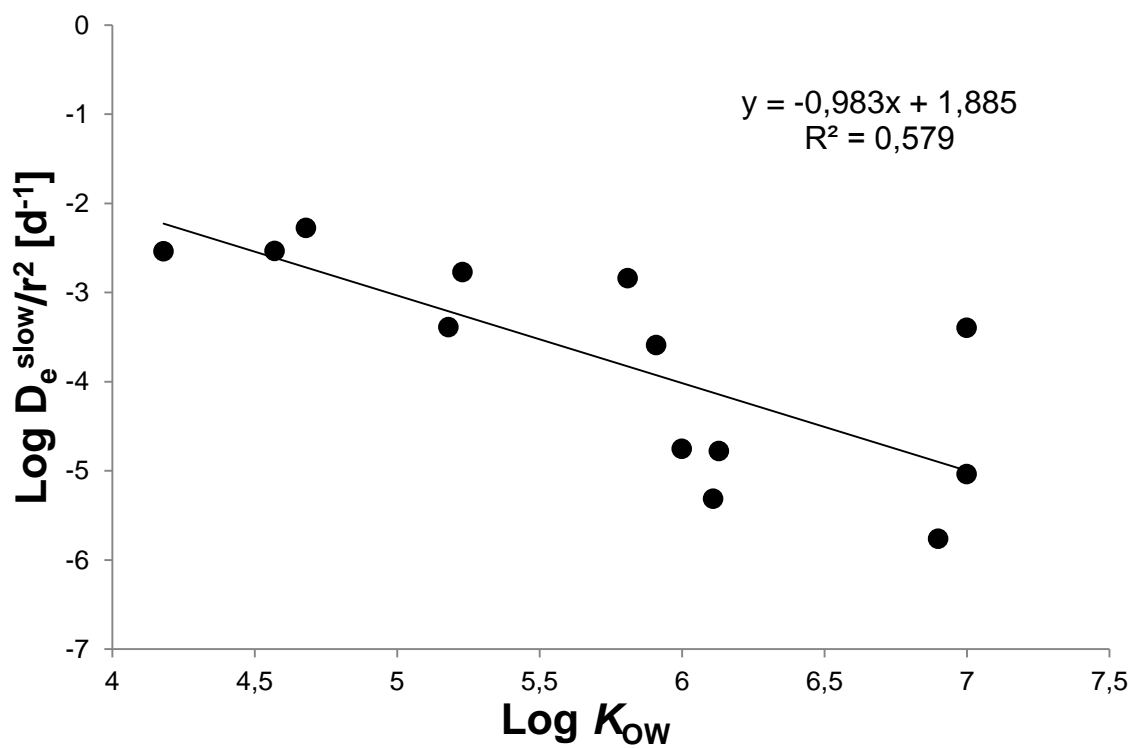


Figure S5. $\text{Log } D_e^{\text{slow}}/r^2$ determined by radial diffusion model as a function of $\text{Log } K_{ow}$.

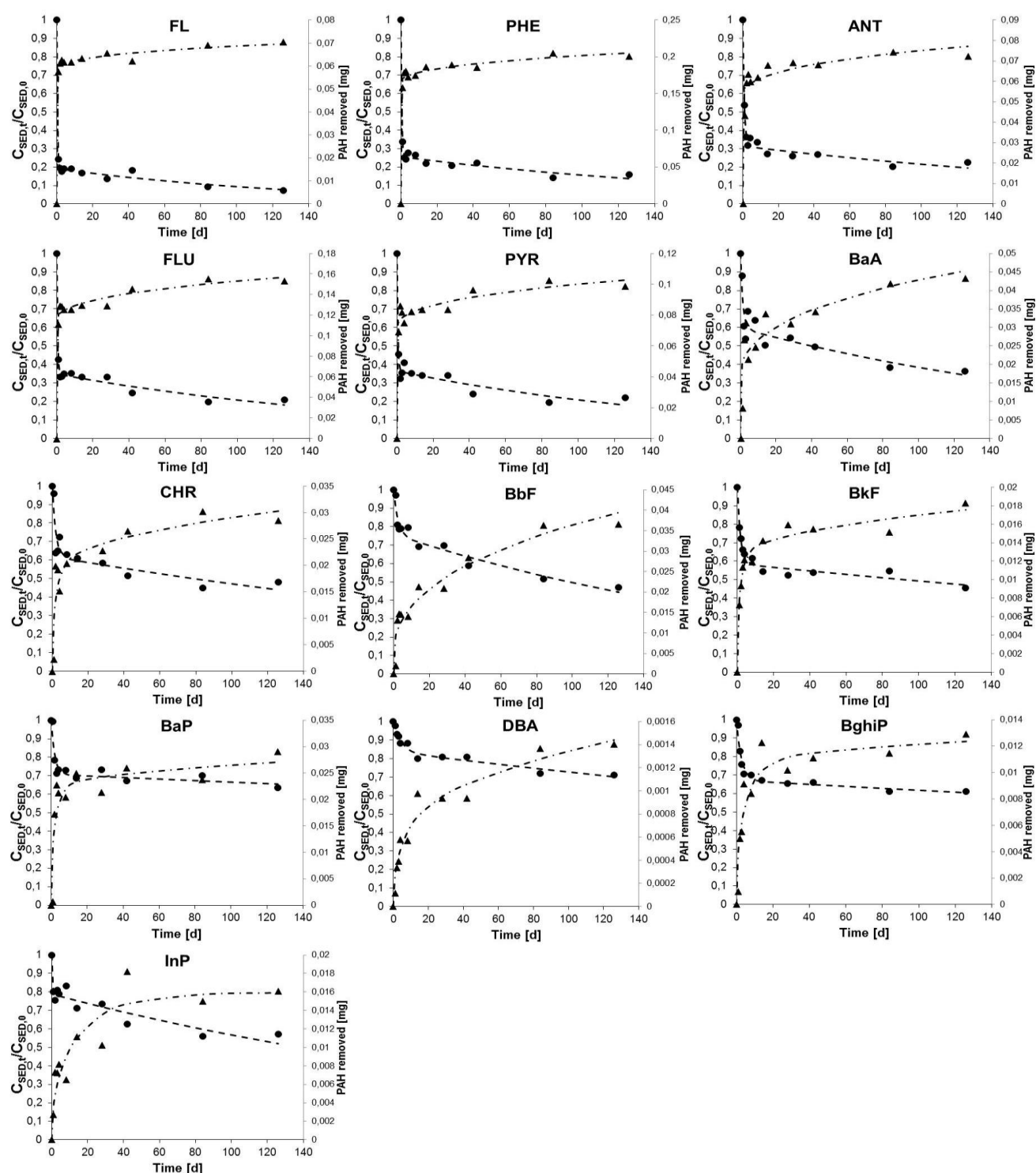


Figure S6. Desorbed mass (mg) (▲) and residual fraction ($C_{SED,t}/C_{SED,0}$; -) (●) of individual PAHs from PH sediment as determined with GAC at 1:1 (GAC:SED) ratio. Closed markers represent measured data. Dashed lines represent modelled values using first-order exponential model, whereas dash dotted lines represent modelled values obtained with biphasic diffusion. To increase readability, the different model curves are plotted as mirror images.

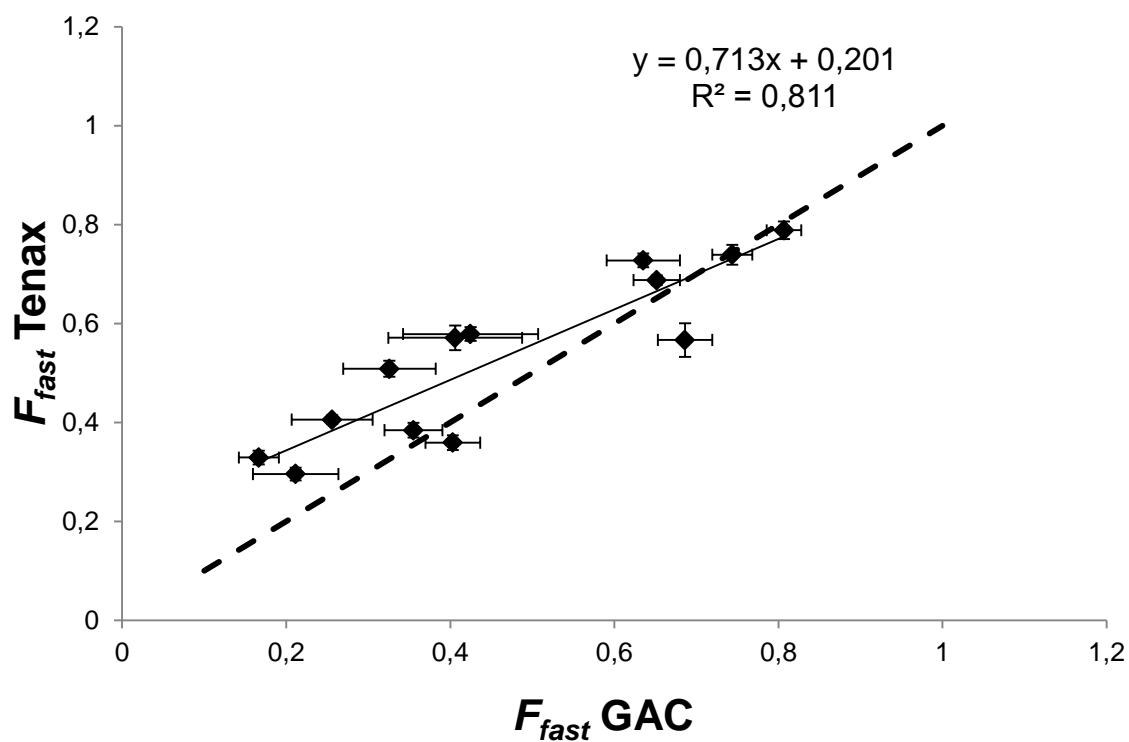


Figure S7. Rapidly desorbing fractions determined with Tenax SPE versus rapidly desorbing fractions as determined with GAC (50%). Solid lines represent linear regression. Dotted lines represent hypothesized 1:1 correlation.

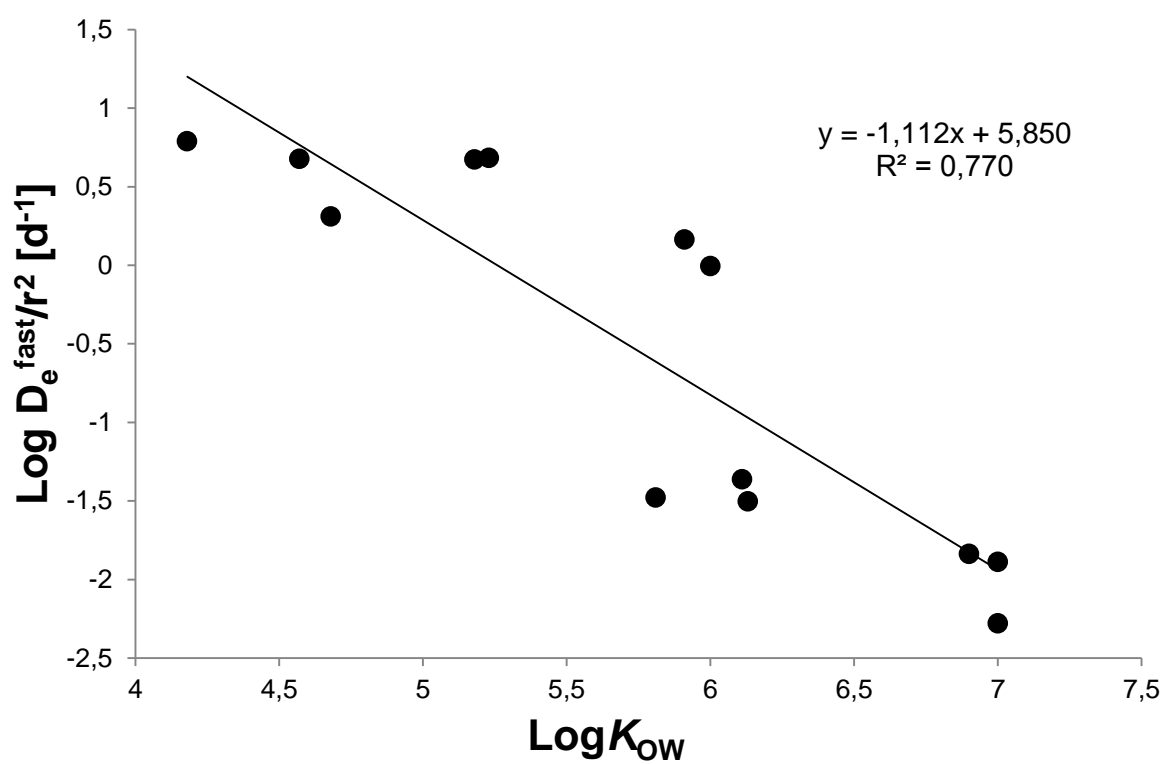
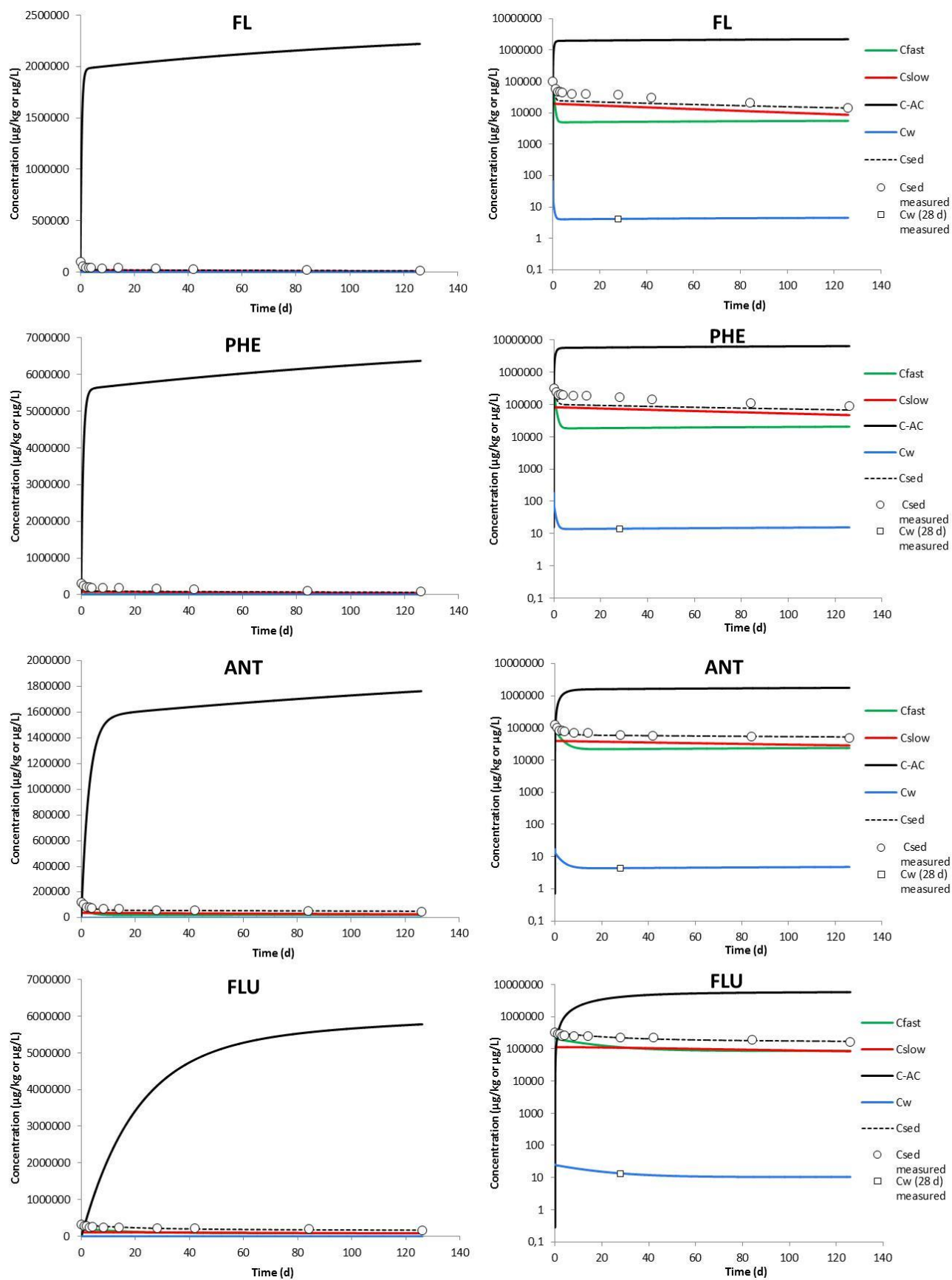


Figure S8. $\text{Log } D_e^{\text{fast}}/r^2$ as a function of $\text{Log } K_{\text{ow}}$ with GAC dose of 50%.

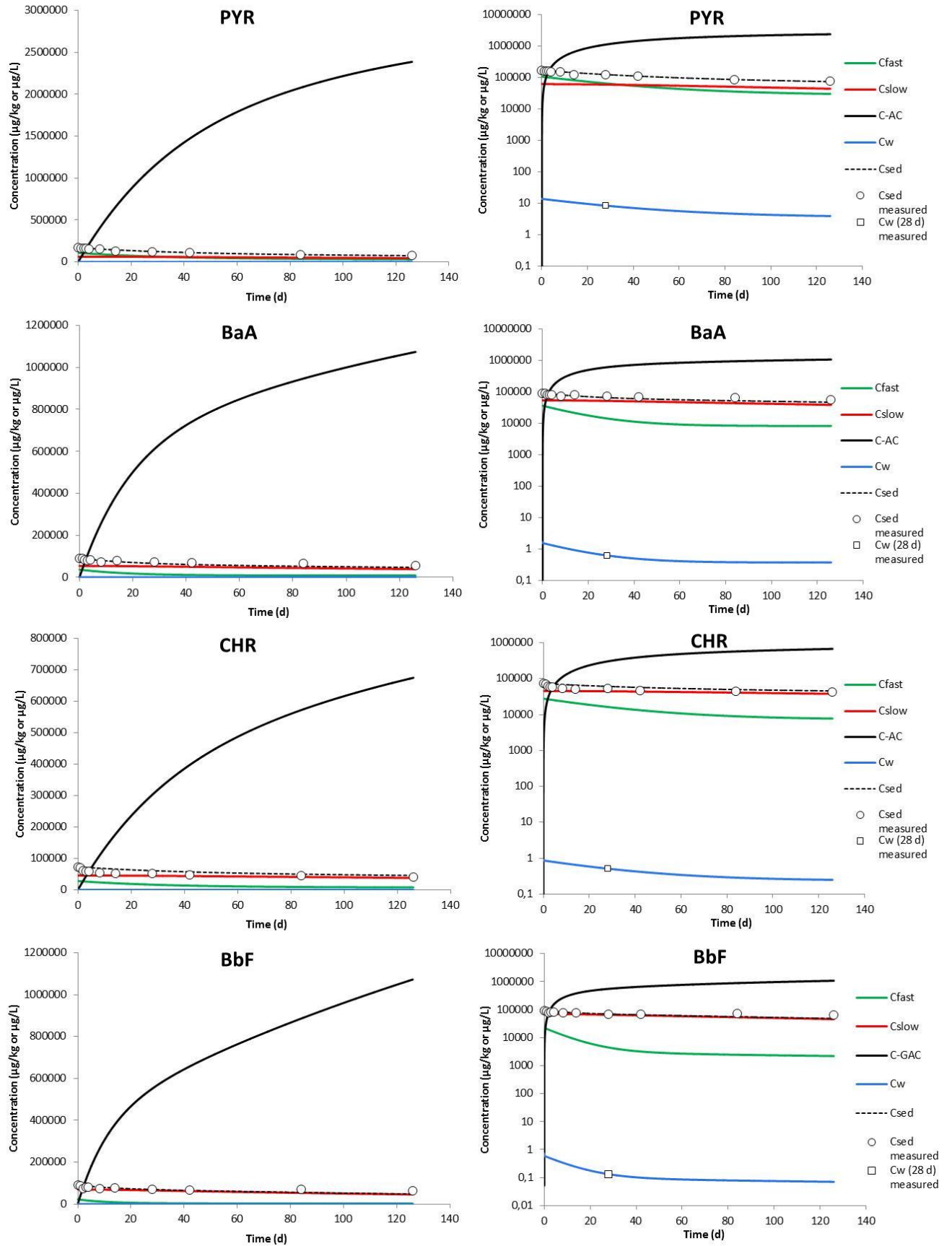
Table S3. GAC sorption parameters at a dose of 4% with 90% confidence intervals obtained from the first-order numerical model (Eq. (1)-(4)).

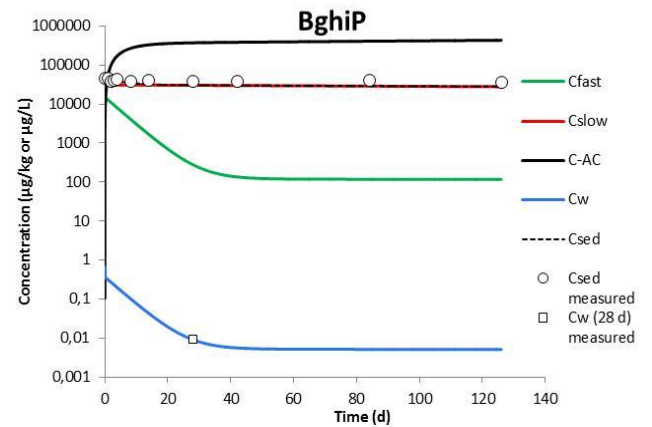
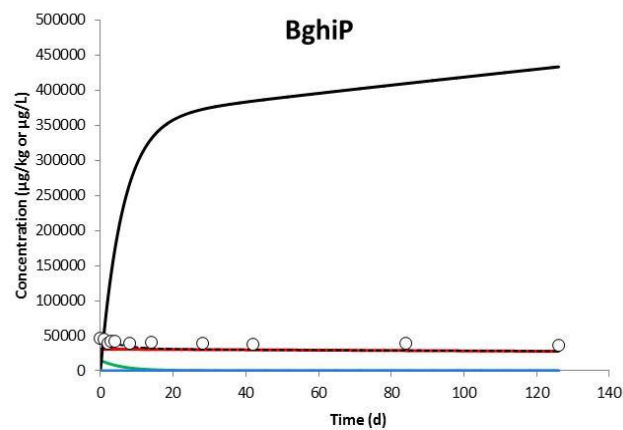
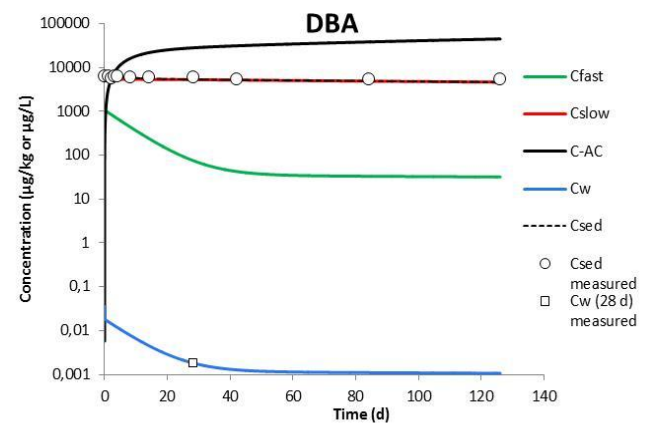
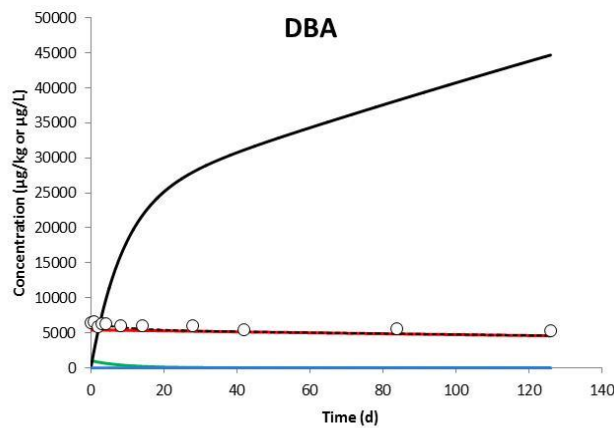
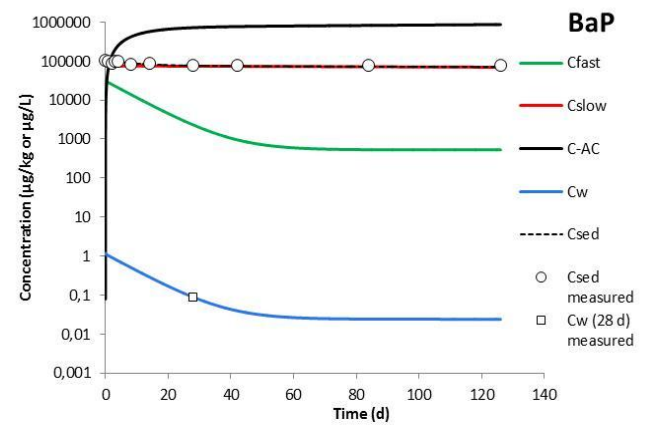
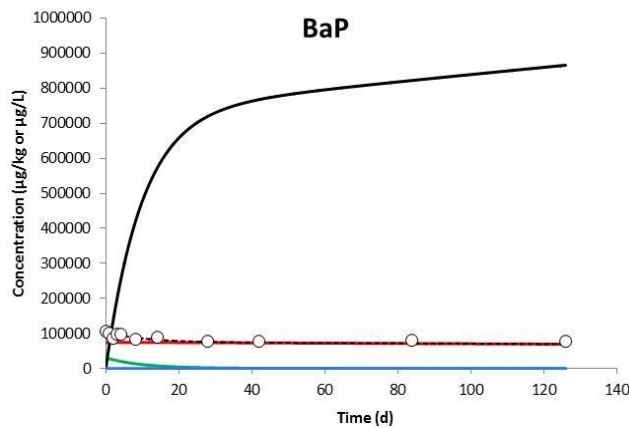
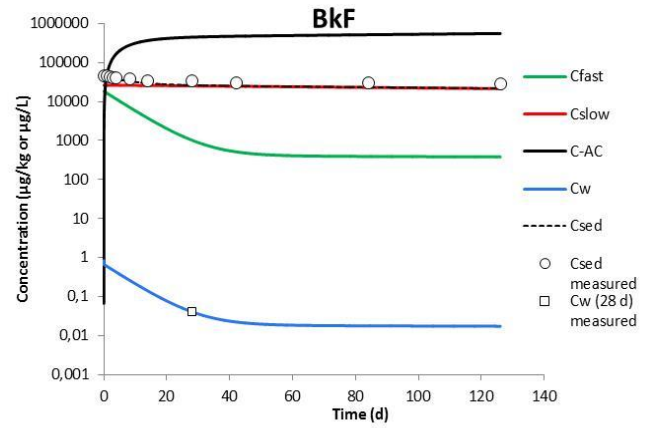
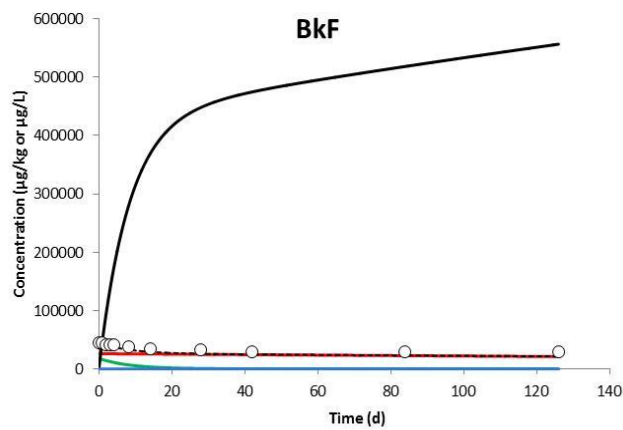
Scenario with $n_F = 0.46-0.91$ [2]													
Sorbate	$\text{Log}K_{OW}$	$n_{F, GAC}$	$k_{GAC} (10^{-2} \text{ 1/d})$	CI_L^a 90%	CI_U^b 90%	$\text{Log}K_{F,GAC}$ $(\mu\text{g/kg}_{GAC})/(\mu\text{g/L})^n$	CI_L^a 90%	CI_U^b 90%	R^2	$K_{p,fast}$ (L/kg)	$K_{p,slow}$ (L/kg)	$D_{eff} (\text{m}^2/\text{d})$	$C_{W,t=0}$ (ug/L)
FL	4.2	0.55	44.112	-	-	5.97	-	-	0.930	3.09	2.47	8.1×10^{-9}	63.736 ^d
PHE	4.6	0.91	39.956	-	-	5.98	-	-	0.868	3.12	2.66	7.34×10^{-9}	179.991 ^d
ANT	4.7	0.58	19.261	19.113	19.409	5.84	5.80	5.88	0.971	3.70	3.36	3.54×10^{-9}	16.958 ^d
FLU	5.2	0.72	0.309	0.109	0.510	6.70	6.69	6.71	0.929	3.92	3.65	5.68×10^{-11}	23.430 ^d
PYR	5.2	0.78	0.420	0.405	0.435	6.21	6.17	6.24	0.986	3.89	3.65	7.72×10^{-11}	13.342 ^d
BaA	5.9	0.43	0.599	0.560	0.639	6.59	6.57	6.62	0.927	4.34	4.55	1.1×10^{-10}	1.652 ^e
CHR	5.8	0.82 ^c	0.309	0.271	0.347	6.70	6.64	6.75	0.848	4.49	4.70	5.68×10^{-11}	0.904 ^e
BbF	6.0	0.82 ^c	0.100	0.094	0.106	7.74	7.72	7.77	0.852	4.49	4.99	1.84×10^{-11}	0.715 ^e
BkF	6.1	0.82 ^c	0.099	0.097	0.101	7.73	7.72	7.74	0.992	4.34	4.50	1.82×10^{-11}	0.833 ^e
BaP	6.1	0.82 ^c	0.090	0.089	0.091	7.80	7.79	7.81	0.872	4.42	4.50	1.65×10^{-11}	1.175 ^e
DBA	7.0	0.82 ^c	0.061	0.059	0.062	7.99	7.98	8.00	0.847	4.48	5.18	1.12×10^{-11}	0.036 ^e
BghiP	6.9	0.82 ^c	0.075	0.072	0.079	8.07	8.05	8.09	0.822	4.36	4.69	1.38×10^{-11}	0.653 ^e
InP	7.0	0.82 ^c	0.100	0.096	0.104	8.12	8.10	8.14	0.737	4.20	4.77	1.84×10^{-11}	0.686 ^e

^a Lower bound. ^b Upper bound. ^c data from Kupryianchyk et al. [11]. ^d measured aqueous phase concentrations and ^e fitted initial aqueous phase concentrations. - high k_{GAC} values caused numerical dispersion, prohibiting calculation of CI boundaries.



Kinetics of hydrophobic organic contaminant extraction from sediment by GAC





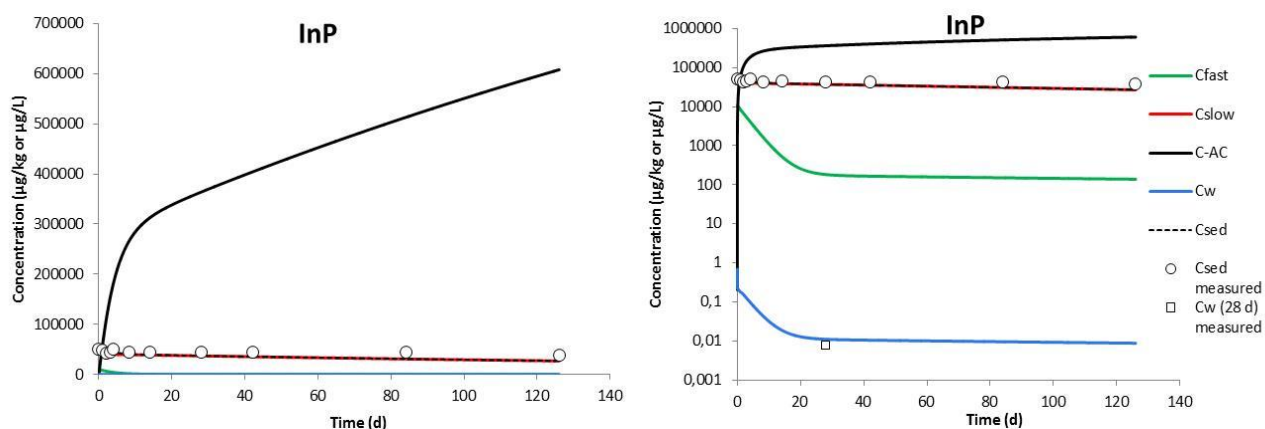


Figure S9. Desorption profiles of individual PAHs from PH sediment and adsorption by GAC at a dose of 4% ($n_F = 1$). The dashed C_{sed} line is calculated as the sum of the modelled C_{fast} and C_{slow} curves. Error bars ($n=3$) for C_w (28 d) relate to standard deviation but are smaller than the markers. For each compound, profiles are provided with linear (left hand side) as well as log transformed (right hand side) concentration scales.

Table S4. AC uptake rate constants calculated from data reported by Hale et al. [12] and using their equation [12].

Sorbate	$\text{Log}K_{AC}$ [cm ³ /g]	k_{AC} (1/d)
NAP*	5.5	0.03776
FL	8.2	0.00008
PHE	7.8	0.00019
ANT	8.2	5.98×10^{-5}
FLU	8.7	1.89×10^{-5}
PYR	8.5	3.0×10^{-5}
CHR	8.7	1.89×10^{-5}
BaA	8.7	1.89×10^{-5}
BbF	8.9	1.19×10^{-5}
BkF	8.7	1.89×10^{-5}
BaP	8.6	1.89×10^{-5}
InP	9.2	4.75×10^{-6}

* NAP = naphthalene

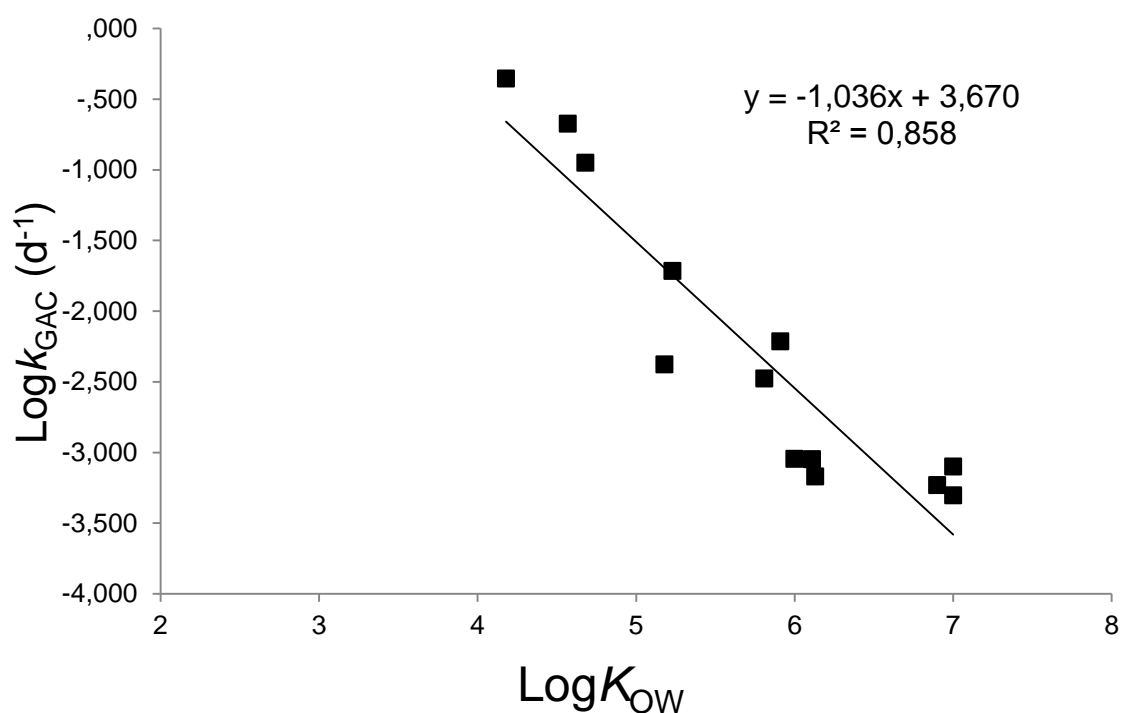


Figure S10. PAH adsorption rate constants ($\text{Log} k_{\text{GAC}}$) at $n_F = 1$ for sorption to 4% GAC in the presence of sediment plotted against $\text{Log} K_{\text{OW}}$. Sorption parameters are determined with Eq. (1) – (4).

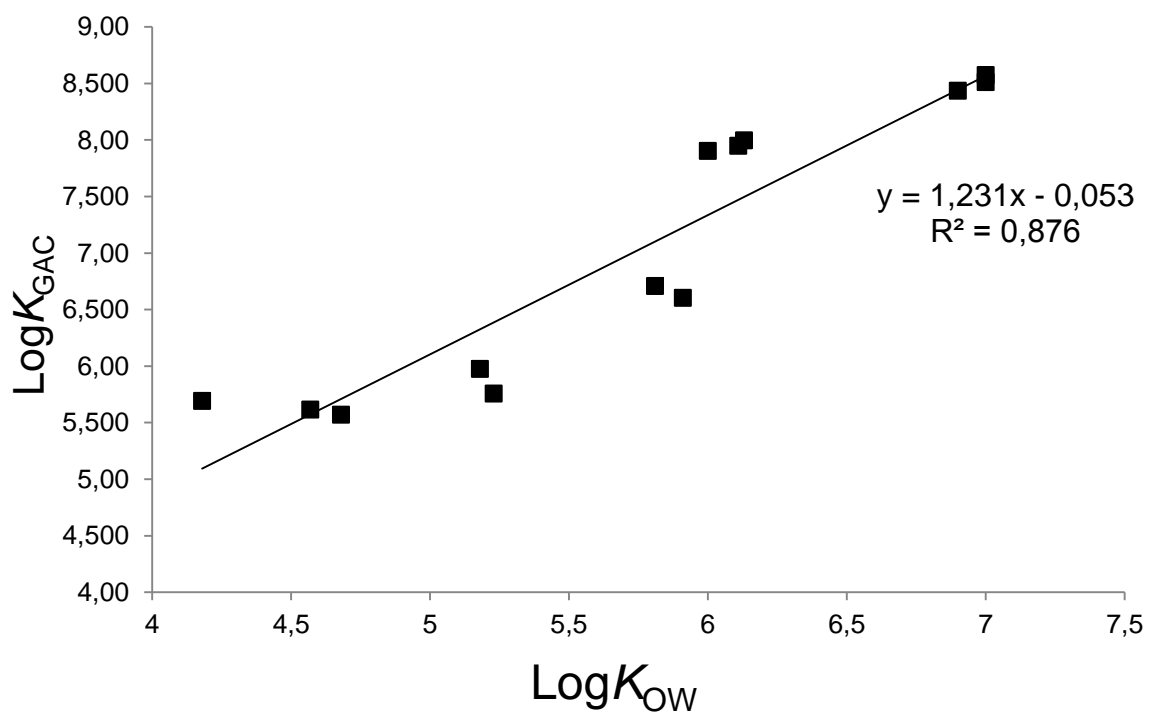


Figure S11. PAH sorption affinity constants ($\text{Log}K_{\text{GAC}}$) at $n_{\text{F}} = 1$ for sorption to 4% GAC in the presence of sediment plotted against $\text{Log}K_{\text{OW}}$. Sorption parameters are determined with Eq. (1) – (4).

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CHAPTER 5

Turbulent mixing accelerates PAH desorption due to fragmentation of particle aggregates

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ABSTRACT

Sediment stripping with granular activated carbon (GAC) is a promising remediation technique of which the efficiency depends on the rate of contaminant extraction from the sediment by the GAC. The present study therefore investigated the effect of mixing intensity on the short term extraction rate of PAHs from contaminated sediment. Desorption data were interpreted using a radial diffusion model. Fast desorption rate constants D_e/r^2 with D_e the effective diffusion coefficient and r the particle radius, ranged from 3.7×10^{-3} to $1.1 \times 10^{-1} \text{ d}^{-1}$ (PHE) and 6×10^{-6} to $1.9 \times 10^{-4} \text{ d}^{-1}$ (CHR), respectively, and increased with the intensity of mixing. The D_e/r^2 values would correspond to D_e ranges of $1.8 \times 10^{-14} - 1.2 \times 10^{-16} \text{ m}^2 \times \text{d}^{-1}$ and $1.8 \times 10^{-12} - 3.7 \times 10^{-15} \text{ m}^2 \times \text{d}^{-1}$, assuming fast desorption from the measured smallest particle size classes at 200 and 600 rpm, respectively. It appeared that desorption of PAHs was significantly accelerated by a reduction of particle aggregate size caused by shear forces that were induced by mixing. The effective intraparticle diffusion coefficients, D_e , were larger at higher mixing rates.

INTRODUCTION

Desorption of hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) from sediments to the water column is often described as a bi- or tri-phasic process where each of the phases follows an exponential decrease in time [1-4]. The extent of desorption from sediment particles is an important factor affecting the fate, transport behavior and risks of organic contaminants in aquatic ecosystems. Over the past two decades it has been shown that especially the fast desorbing fraction is relevant for risks to aquatic biota, as this fraction rapidly equilibrates to the freely dissolved concentration in the pore water, which in turn is the relevant concentration for bioaccumulation. At the same time, the mass of contaminants desorbed predicts the efficiency of potential remediation strategies [5]. Desorption kinetics of hydrophobic organic compounds in contaminated sediments are determined by chemical and physical properties of the sorbents, such as amorphous and condensed organic matter content, particle porosity, surface area-to-volume ratio, as well as by mixing conditions and refreshment rate. It is hypothesized that mixing and turbulence may affect laminar boundary layers around sediment particles and thus contaminant mass transfer [6]. Although a number of studies have reported on the adsorption/desorption processes of HOCs on a variety of natural sediments or soils [7-13], not many have focused on evaluating the effects of mixing conditions on particle size distribution and desorption kinetics [13-15].

Sorption processes also play a key role in reducing mobility and risks of sediment-bound contaminants in aquatic environments. Recently, *in situ* sorbent amendments such as activated carbon (AC) to contaminated sediments have been proposed as a suitable remediation technology [16-21]. In laboratory as well as pilot-scale field studies, AC amendments to sediments have been shown to reduce HOC aqueous-phase concentrations,

and thus bioaccumulation in benthic invertebrates and fish [16, 17, 19, 21, 22], (**Chapter 7**). Alternatively, sorbent amendments may involve active *ex situ* treatment methods such as mixing of granular AC (GAC) with the contaminated sediment, followed by subsequent removal of the contaminant loaded GAC (sediment stripping) [21, 23, 24]. Active sediment stripping with GAC can be the method of choice if the cleaned sediment can be reused as construction material or for land application. A prerequisite for the application of active stripping with GAC in contaminated sediment remediation is effective transport of pollutants from the sediment to the GAC during the mixing stage. Earlier studies have emphasized the importance of mixing conditions on the mass transfer of HOCs in AC-sediment systems [25]. It has been also shown that higher refreshment rate of water increased the mass transfer of HOCs from suspended sediments [12, 26]. However, it is unclear how the GAC/sediment mixing step affects desorption kinetics of HOCs for instance by changing the sediment particle size distributions, and whether these factors may influence the effectiveness of *ex situ* GAC extraction technology. Consequently, an improved understanding of HOC desorption time-scales in mixed sediment-GAC systems at various mixing regimes is required in order to design effective stripping reactors.

The purpose of this study was to determine the kinetics of PAH desorption from sediment at a wide range of rotational speeds (min^{-1}) (rpm) monitored by uptake in Tenax polymeric resins using a completely mixed batch reactor [26]. To accomplish this aim kinetic parameters were estimated using a radial diffusion model. In order to evaluate the effect of mixing on particle disintegration, particle size distributions were measured for undisturbed sediment samples and sediment samples after mixing at 600 rpm. Desorption parameters obtained with the radial diffusion model were correlated with particle size measurements and interpreted mechanistically.

MATERIALS AND METHODS

Chemicals

HPLC standard EPA 610 PAH Mix containing acenaphthene (ACE), acenaphthylene (ACY), anthracene (ANT), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[g,h,i]perylene (BghiP), benzo[k]fluoranthene (BkF), chrysene (CHR), dibenzo[a,h]anthracene (DBA), fluoranthene (FLU), fluorene (FL), indeno[1,2,3-cd]pyrene (InP), naphthalene (NA), phenanthrene (PHE), and pyrene (PYR) with purities of >98% except for PYR (purity >96.6%) was obtained from Supelco Analytical. Picograde organic solvents were obtained from Promochem (hexane and acetone) and HPLC grade acetonitrile from Lab-Scan. Other chemicals and materials used were: calcium chloride CaCl_2 (Merck; p.a), sodium azide NaN_3 (Aldrich; 99%), sodium sulphate Na_2SO_4 (Merck, p.a.), Tenax TA (20/35 mesh; Grace), stainless steel filters (pore size $2\mu\text{m}$, Supelco), pump (Watson Marlow 502S) and PTFE tubing. All water preparations used Milli-Q water (Millipore Corporation). Prior to use the Tenax beads were rinsed with water to remove fine particles and further

extracted sequentially with acetone (4x) and hexane (4x) on a shaker with horizontal motion at 160 strokes per minute, after which they were dried overnight at 80°C.

Sediment

Sediment was obtained from Petroleum Harbor (Amsterdam, The Netherlands) and characterized for total content of PAHs, petroleum hydrocarbons (TPH), organic carbon (TOC) and BC. Freely dissolved PAH concentrations were determined by polyoxymethylene (POM) passive samplers as reported in our previous study [23], (**Chapter 3**). A summary of sediment characteristics is provided as Supporting Information (Table S1).

Desorption experiments

Desorption from sediment at different mixing regimes. The experimental setup of Smit et al. [26] was used (Figure S1). Experiments were performed at 20 ± 1 °C in 500 ml modified Schott flasks mounted with flat-blade rotating discs and columns of Tenax beads (2g) to trap compounds desorbed from Petroleum Harbor (PH) sediment. The flasks were filled with 2 g PH sediment (d.w.), 300 mL of Mili-Q water containing 100 mg/L NaN_3 and 0.01M CaCl_2 . The suspension was led over two stainless steel filters and pumped to the Tenax column leading to a hydraulic retention time in the flasks of 15 min. After extraction of HOC in the Tenax column, the water was recycled into the flasks. At fixed times throughout the experiment Tenax columns were replaced with clean sorbent and loaded Tenax recovered per time point was analyzed for PAHs (see below). At the same times, the stainless steel filters were replaced with new filters to minimize changes in the flow rate due to clogging. After 9.5 hours the sediment-water suspension was centrifuged and dried with Na_2SO_4 for determination of residual concentration of PAHs remaining in the sediment after desorption. The studied mixing rates were 200, 400, 500, 600 and 700 rpm (rotations per minute), where 200 and 700 rpm resembled bed and suspended sediment conditions, respectively. All desorption experiments were carried out in duplicate. Prior to the experiments the flow rate was optimized in the system. Typically, after 15 to 20 minutes the steel filters were covered with light density organic matter.

Analytical procedures

Before use all glassware was rinsed with acetone and hexane. After removal from the columns, the Tenax beads with preconcentrated PAHs and residual sediment samples were extracted in 30 mL hexane/acetone (1:1) with microwave assisted extraction (MAE) for 1.5 h at 120°C [27]. Subsequently, hexane/acetone extracts were concentrated with a rotary evaporator, further reduced to 1 mL under a gentle stream of nitrogen and exchanged to acetonitrile for PAH analysis. Analytes in extracts of Tenax and sediment were separated by reverse-phase HPLC using a C18 column with length 250 mm and diameter 4.6 mm (Vydac, Grace) and a 40-min isothermal (35°C) acetonitrile – water solvent gradient program with a

flow of 1 ml min⁻¹. PAHs were quantified with a photodiode array detector UVD340U (Dionex) or programmable fluorescence detection (Hewlett-Packard 1046A).

Particle size distribution analysis. To evaluate the effect of mixing conditions on particle size distribution, additional experiments were conducted at 600 rpm. The duplicate sediment-water suspensions were stirred continuously at 600 rpm for an identical time period as described above. Immediately after sampling the particle size distribution (PSD) of stirred sediment suspensions as well as fresh sediment (without stirring) were measured using a Beckman Coulter LS 230 (fluid module) laser diffraction particle size analyzer with Polarization Intensity Differential of Scattered Light (PIDS). The injected suspension volume was controlled to obtain a total obscuration level of 10±3% and a PIDS obscuration of 50±10%, respectively.

Quality assurance

Mass balance analysis showed that the sums of the PAH quantities desorbed (extracted by Tenax) and those remaining in the sediment after the desorption experiments ranged between 83-91 % compared to the initial mass in the sediment, except for BbF which was 78±9 %. Differences between duplicates of each experiment were always between 10 and 15%.

Data analysis

The removal rate (k_r) in the experimental system calculated as flow rate/water volume was high i.e. $k_r > 10$ (d⁻¹). Therefore, desorption from PH sediment was rate limiting. The rate limitation may originate from the resistance for transport across the water-side boundary layer (WSBL), from intraparticle diffusion, or from both. To evaluate whether the WSBL has influence on the desorption kinetics, the current data were interpreted using a method provided by Schwarzenbach et al. [28] (calculation provided as Supporting Information, Eq. S1-S2). In these calculations, particle radius ranges of the smallest size fractions were used. After all, the PSD analysis showed that the volume fraction of the higher peak at 600 rpm (i.e. at 9 µm) is 74%, whereas the 9 µm peak in the non-mixed system relates to 47% of sediment volume (Figure 1). The volume fraction of the higher peak at 600 rpm agrees very well with the percentage of PAH desorbed from PH sediment. Moreover, that peak relates to the smallest particles i.e. having short diffusion path lengths. It can therefore be safely assumed that the particles in that peak dominate the fast desorbing sediment compartment.

The calculation showed that the WSBL has no significant influence on the flux across the particles (i.e. $D_{bl}\delta \gg 10^{-14}$) calculated for non-stirred and stirred systems at 600 rpm with $r = 4.5$ µm and boundary layer thicknesses ranging from 10⁻⁵ – 10⁻⁸ m (Table S2, Supporting Information). We therefore conclude that desorption is not limited by the WSBL and can be described using a diffusion model. Because of the short desorption time span studied, desorption from one kinetic pool is assumed to suffice such that a one compartment diffusion model can be used.

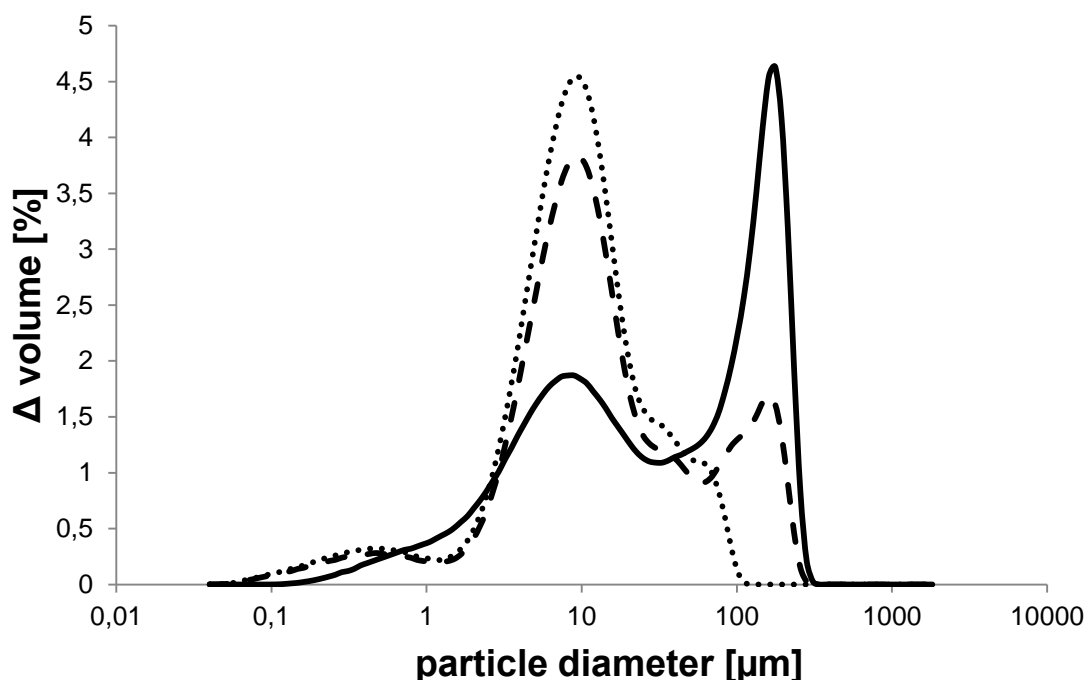


Figure 1. Distribution of particle sizes in unmixed (solid line) and mixed PH sediment at 600 rpm in duplicate (dashed lines). ΔV is the amount of volume related to the discrete particle size range.

Intraparticle diffusion models have been widely applied to determine the kinetics of hydrophobic organic compounds (HOC) mass transfer from or into porous materials in aqueous media [12, 29, 30]. The changes of PAH concentrations in sediment as inferred from the Tenax extraction data were evaluated with a radial diffusion model, which for a single kinetic sediment compartment is given by [31, 32]:

$$\frac{Q_t}{Q_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left(\exp \left[\frac{-n^2 \pi^2 D_e t}{r^2} \right] \right) \quad (1)$$

Eq. (1) expresses the mass fraction of PAHs (Q_t/Q_0) that is desorbed at time, t (days). D_e is the apparent diffusion coefficient and r is the equivalent particle radius. Eq. (1) was solved for D_e/r^2 , using the Excel solver tool, and accounting for 2000 terms in the Taylor series [31, 32].

RESULTS AND DISCUSSION

Sediment characteristics. Petroleum Harbor (PH) sediment had a TOC of 4.46 ± 0.51 % and a black carbon content of 1.85 ± 0.19 % ($n=3$). Total PAH $_{\Sigma 13}$ and petroleum hydrocarbon (TPH) concentration measured in PH sediment were 1604 ± 90 mg/kg ($n=4$) and 5.37 ± 0.41 g/kg ($n=3$), respectively. Other PH sediment characteristics have been published before [23].

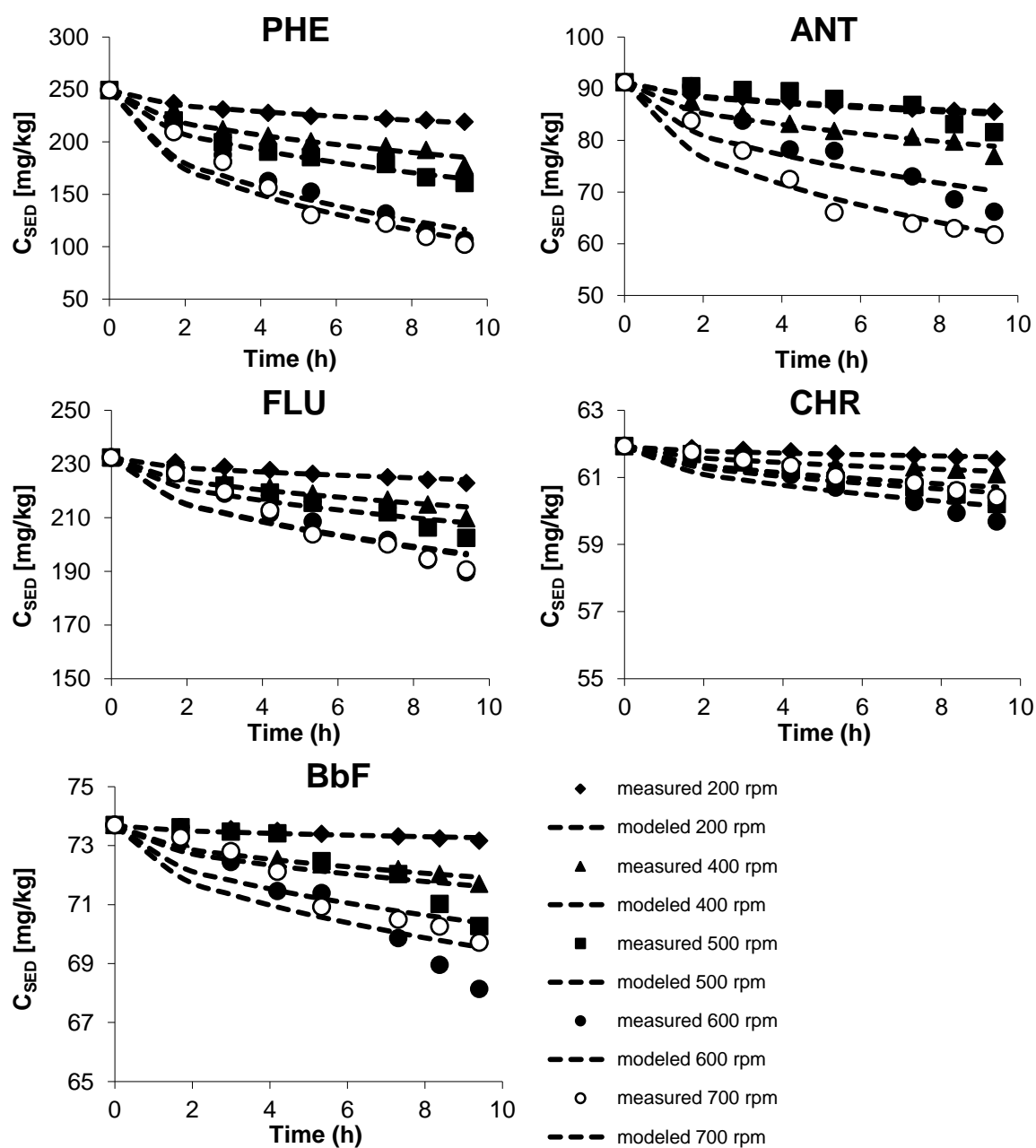


Figure 2. Desorption profiles of individual PAHs from PH sediment at various mixing regimes. Closed markers represent measured data. Dashed lines represent modelled values using the radial diffusion model as condensed in Eq. (1).

PAH desorption from sediment at different mixing regimes. The influence of mixing conditions on PAH desorption from PH sediment was determined by varying the rotor speed (200-700 rpm). Results of five experiments at different mixing intensities in combination with modeled data according to Eq. (1) are presented in Figure 2. Because of the short desorption time of about 9.5 h, the observed desorption rate relates to fast desorption, which typically has

a desorption half-life of 10 h [4]. Here we focus on five PAHs i.e. PHE, ANT, FLU, CHR and BbF representing 3-, 4- and 5- ring compounds. In general, the experimental sediment concentration data for all compounds agree very well with the modelled values of C_{SED} , with R^2 values close to unity, although some discrepancies can be observed between measured and modeled data at 600 and 700 rpm. Desorption is faster with increasing mixing intensity (Figure 2). At the lowest mixing rate i.e. 200 rpm, PHE and ANT concentrations in the sediment decline with 12 and 6%, respectively after 9.5 h mixing compared to the initial concentration. At the maximum mixing rate of 700 rpm, PHE and ANT concentrations in the sediment decline with 59 and 32 %, respectively. In case of FLU, CHR and BbF the C_{SED} at 200 rpm is only 0.7 - 4% lower after 9.5 h compared to the initial concentration ($C_{SED,0}$). At 700 rpm the concentrations of FLU, CHR and BbF further decrease by 18, 4 and 7%, respectively.

Table 1. Desorption rate parameters obtained from the radial diffusion model.

Sorbate	LogK _{OW}	Number of rings	RPM	D_e/r^2 (d ⁻¹)	R ²
PHE	4.57	3	200	3.70×10^{-3}	0.997
			400	1.71×10^{-2}	0.977
			500	3.15×10^{-2}	0.990
			600	9.12×10^{-2}	0.966
			700	1.08×10^{-1}	0.974
ANT	4.68	3	200	9.00×10^{-4}	0.968
			400	4.42×10^{-3}	0.961
			500	1.05×10^{-3}	0.951
			600	1.35×10^{-2}	0.944
			700	2.76×10^{-2}	0.947
FLU	5.23	4	200	2.83×10^{-4}	0.996
			400	1.46×10^{-3}	0.980
			500	2.58×10^{-3}	0.827
			600	5.73×10^{-3}	0.922
			700	5.91×10^{-3}	0.971
CHR	5.81	4	200	6.00×10^{-6}	0.959
			400	3.31×10^{-5}	0.983
			500	1.13×10^{-4}	0.945
			600	1.88×10^{-4}	0.926
			700	8.76×10^{-5}	0.937
BbF	6	5	200	7.58×10^{-6}	0.952
			400	1.30×10^{-4}	0.982
			500	1.79×10^{-4}	0.813
			600	7.24×10^{-4}	0.902
			700	4.60×10^{-4}	0.928

At all mixing speeds, highly hydrophobic PAHs (CHR and BbF) were desorbed slower and to a lesser extent than low molecular weight compounds (PHE and ANT). This is in line with expectations, since the effective diffusion coefficients are lower due to stronger sorption of the more hydrophobic compounds to the sediment [9, 33]. We therefore conclude that intensive mixing allows for a substantial enhancement of the mobilization and redistribution of PAHs from the studied sediment. This may be used beneficially to accelerate the short-term effectiveness of remediation approaches involving AC addition, but also indicates enhanced risks of spreading HOC into the water of PAH loaded sediments entering turbulent waterways.

Mechanistic interpretation of the size dependence of the sorption kinetic data. The radial diffusion model i.e. Eq. (1) was used to estimate PAH desorption parameters. Desorption rates differed substantially among the compounds and mixing regimes. The composite parameter D_e/r^2 ranged between $3.7 \times 10^{-3} - 1.1 \times 10^{-1}$ (PHE), and $6 \times 10^{-6} - 1.9 \times 10^{-4}$ d⁻¹ (CHR) and appeared to increase with rpm as a proxy for turbulence, and to decrease with increasing PAH hydrophobicity (Table 1, Figure 3). The decrease of D_e/r^2 with increasing hydrophobicity (Figure 3) strongly supports the assumption that desorption was intra-particle diffusion controlled [28, 32]. The increase with increasing turbulence can also be explained by intraparticle diffusion being rate limiting, that is, by the parameter D_e/r^2 which depends on r and becomes higher if r would be reduced by particle disintegration due to turbulence.

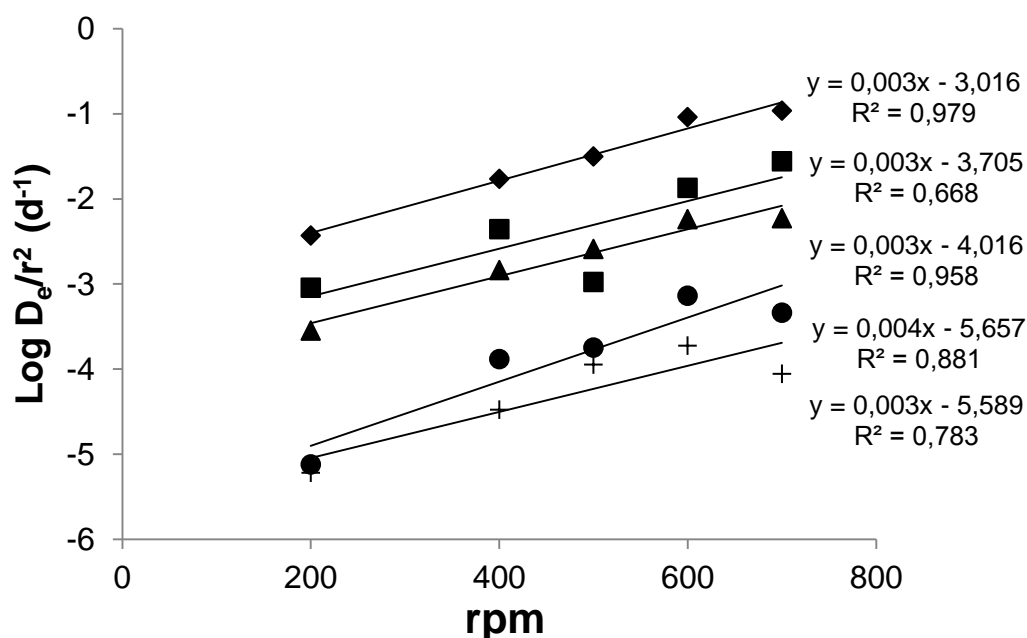


Figure 3. Log D_e/r^2 vs rpm for PHE (♦), ANT (■), FLU (▲), CHR (+) and BbF (●).

The particle size distributions of PH sediment were examined after stirring at 200 as well as at 600 rpm. The results show that the particle size distribution indeed shifted considerably to smaller sizes (Figure 1). The decrease in particle size is paralleled with the increase of desorption rates with increasing mixing speed. The volume fraction of the smaller peak at 9 μm in the non-mixed system also increased from 47% to 74% at 600 rpm, percentages that agree with the percentages of PAH desorbed. Altogether this suggests that the fast desorbing PAHs are mainly associated with small particles. Desorption from small particles is known to be a fast process due to larger surface area and short diffusion path lengths [28]. In order to investigate the trends of the observed values of D_e/r^2 with particle radius and hydrophobicity, the $\log D_e/r^2$ values for 200 and 600 rpm were plotted against $\log K_{OW}$ (Figure 4). These plots show a negative dependence of D_e/r^2 on PAH hydrophobicity because the more hydrophobic, i.e. larger solutes, diffuse more slowly through the organic matter, as can be expressed by the effective diffusion coefficient (D_e) equation [13]:

$$D_e = \frac{D_m p}{(1-p)dK_{SED}} \quad (2)$$

in which the sediment-pore water partitioning coefficient K_{SED} (L/kg) is proportional to the octanol–water partitioning coefficient (K_{OW}) [28]. In Eq. (2), D_m is the free aqueous diffusivity (cm^2/s) of the PAH, p is the sediment intra-aggregate porosity (dimensionless) and d is density (g/cm^3).

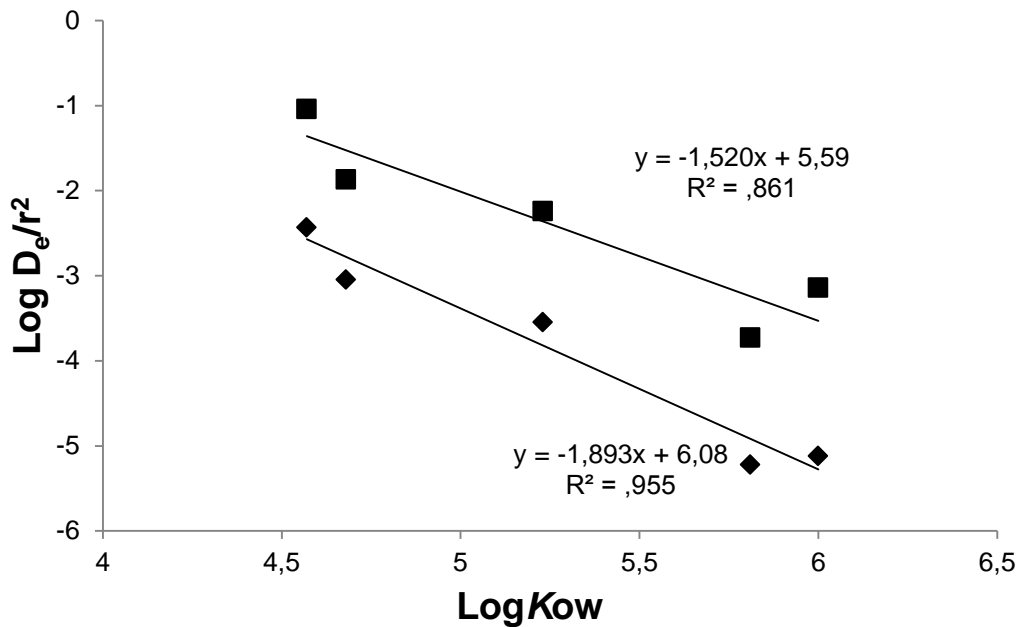


Figure 4. $\log D_e/r^2$ vs $\log K_{OW}$ at 200 rpm (♦) and 600 rpm (■).

The $\log D_e/r^2$ - $\log K_{OW}$ regression lines differ approximately 1.5 log units (Figure 4), which means that D_e/r^2 differs by a factor of $10^{1.5}$ between 200 and 600 rpm. It is with these results

not possible to unambiguously distinguish between effects of r or of D_e on intra-particle dominated desorption at varying mixing intensity. This includes uncertainty in r , which would require integrated modeling over the full particle radius range i.e. 10nm-100um and D_e affected by tortuosity of the pores and micro- and macro-pore distributions. However, assuming that for instance, D_e values are equal for the particles at 200 and 600 rpm, the effective particle radius r at 600 rpm would be 5.6 times lower than at 200 rpm.

Alternatively, other explanations of the observed enhancement of desorption at intensified mixing rates in especially turbulent systems are still possible, and need to be taken into account in interpreting the experimental and modelling results. One of these could be DOC accelerated transfer at higher mixing rates. It is well known that turbulence leads to extraction of DOM or organic colloids from sediments [34, 35]. In the present experimental setup, these organic matter colloids were released and removed from the system, because steel filters were used in order to prevent clogging of the flow through system. This DOM leaching proceeds in time and is not accounted for in our model. Furthermore, it is plausible that the particle size reduces as an effect of shear and inter-particle forces in turbulent systems, thus leading to progressively smaller particles in the 9.5 h experimental period. The model also does not account for such a change in r over time. Both these effects may explain the apparent lack of fit observed at 600 and 700 rpm after 8 h (Figure 2). Here, the model appears to underestimate desorption, which is consistent with particles being smaller than at $t < 8$ h. Because sorption retarded intra-particle diffusion is the rate limiting process, the more hydrophobic PAH would be most sensitive to such an experimental artifact. The lack of fit indeed is larger for more hydrophobic PAHs (Figure 2).

From this analysis we indicate that turbulence enhanced desorption of PAH may be due to fragmentation of aggregates and particles, and possibly a result of probably including the formation of DOC. Because the sediment-water partition coefficient is in the denominator of D_e (Eq. 2), the slopes of the $\log D_e/r^2$ plots against $\log K_{OW}$ (Figure 4) and those of $\log K_{SED} - \log K_{OW}$ regressions should be the same in absolute value but opposite in sign. The negative value of the slope at 200 rpm relating to the original non-fragmented sediment particles, is 1.52 ± 0.35 and agrees very well with the slope of the $\log K_{SED} - \log K_{OW}$ regression previously measured for the same sediment of 1.37 ± 0.079 [23]. The higher slope of 1.89 ± 0.24 at 600 rpm relates to the smaller fragmented particles. We explain the higher slope from a higher affinity of the PAH for the smaller particles.

IMPLICATIONS

In the GAC stripping remediation technique, the mixing stage is important because contact between sediment and GAC and a uniform distribution of the GAC stimulate mass transfer of PAH from the sediment to the GAC. This study showed that turbulence also significantly accelerated desorption of PAH from contaminated sediment by decreasing the size of the sediment particles. In practice, this may reduce the time required for mixing during remediation by sediment stripping. The reduction of particle size however, may also change the characteristics of the sediment particles, creating particle size fractions with different

properties in composition and sorption/desorption behavior. This means that the accelerating effect may differ among sediments, dependent on their size distribution and other properties. These results also imply potentially enhanced exposure of biota to HOCs desorbing from HOC loaded sediments when rivers change from low discharge non turbulent systems to high discharge turbulent systems [36].

Supporting Information

The experimental design and WSBL calculations can be found in Supporting Information.

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Supporting Information for Chapter 5

Table S1. Characteristics of Petroleum Harbor sediment; concentrations of PAH in the sediment and aqueous phase concentrations determined with POM-SPE [1].

Sorbate	Log K_{OW}	C_{SED} (mg/kg)	C_w (μ g/L)
Fluorene (FL)	4.2 ^a	99.8 (6.5)	63.74 (7.42)
Phenanthrene (PHE)	4.6 ^b	304.8 (16.9)	179.99 (15.78)
Anthracene (ANT)	4.7 ^c	116.7 (5.3)	16.76 (1.71)
Fluoranthene (FLU)	5.2 ^b	323.5 (14.6)	23.98 (2.01)
Pyrene (PYR)	5.2 ^b	199.5 (5.9)	13.65 (1.16)
Benzo[<i>a</i>]anthracene (BaA)	5.9 ^b	106.9 (9.2)	0.75 (0.07)
Chrysene (CHR)	5.8 ^b	96.6 (11.4)	0.57 (0.07)
Benzo[<i>b</i>]fluoranthene (BbF)	6.0 ^a	92.0 (11.9)	0.14 (0.02)
Benzo[<i>k</i>]fluoranthene (BkF)	6.1 ^c	40.7 (4.1)	0.04 (0.01)
Benzo[<i>a</i>]pyrene (BaP)	6.1 ^c	105.9 (15.3)	0.10 (0.01)
Dibenzo[<i>a,h</i>]anthracene (DBA)	7.0 ^b	10.0 (3.2)	1.79×10^{-3} (3.65×10^{-4})
Benzo[<i>g,h,i</i>]perylene (BghiP)	6.9 ^b	45.9 (4.4)	1.34×10^{-2} (1.43×10^{-3})
Indeno[1,2,3- <i>cd</i>]pyrene (InP)	7.0 ^b	51.3 (4.2)	8.96×10^{-3} (1.55×10^{-3})
$\Sigma 13$ EPA PAHs		1604.3 (90.2)	
TOC [%]		4.46	
OC [%]		2.61	
BC [%]		1.85	
BC/TOC		0.415	

^a Data taken from Maruya et al.[2]

^b Data reported by Jonker & Smedes [3]

^c Data from de Maagd et al. [4]

^d Data taken from Hawthorne et al. [5]



Figure S1. Duplicated experimental system used in desorption studies.

Calculation of water-side boundary layer across the particle surface (Table S2)

The influence of water-side boundary layer on the flux across the particle surface is negligible when the following condition is fulfilled [6] :

$$D_{bl}\delta \gg \frac{1}{3}r_0^3 k\varphi(K_d r_{sw} + 1)e^{-k} \quad (S1)$$

where D_{bl} is the diffusion in the boundary layer with thickness δ (m), spherical particle aggregate with radius r , $r_{sw} = \rho(1-\phi)/\phi$ is the solid-to-water-phase ratio of the particle aggregate, ϕ is particle porosity, K_d is the distribution coefficient (L/kg) and k in the desorption rate constant (d^{-1}) and t is time (d).

DOC facilitation will increase D_{bl} according to [7]:

$$D_{bl} = D_m(1 + 0.025K_{DOC}[DOC]) \quad (S2)$$

where D_m is molecular diffusivity in the water and K_{DOC} is the DOC-water partition coefficient (L/kg) and $[DOC]$ is the concentration of DOC in the aqueous phase (L/kg). The K_{DOC} and $[DOC]$ values were taken from Kupryianchyk et al. [7].

Results of the calculations are provided in Table S2.

Table S2. Parameters for WSBL transport in the non-mixed system.

		scenario				
		δ (m)	δ (m)	δ (m)	δ (m)	
Compound		0,00001	0,000001	0,0000001	0,00000001	
	D_{bl}	$D_{bl}\delta$	$D_{bl}\delta$	$D_{bl}\delta$	$D_{bl}\delta$	right side term
FLU	5.72×10^{-5}	5.72×10^{-10}	5.72×10^{-11}	5.72×10^{-12}	5.72×10^{-13}	2.27×10^{-14}
CHR	6.92×10^{-5}	6.92×10^{-10}	6.92×10^{-11}	6.92×10^{-12}	6.92×10^{-13}	3.94×10^{-14}
BbF	7.82×10^{-5}	7.82×10^{-10}	7.82×10^{-11}	7.82×10^{-12}	7.82×10^{-13}	2.99×10^{-13}

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CHAPTER 6

Equilibrium and kinetic modeling of contaminant immobilization by activated carbon amended to sediments in the field

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ABSTRACT

Addition of activated carbons (AC) to polluted sediments and soils is an attractive remediation technique aiming at reducing pore water concentrations of hydrophobic organic contaminants (HOCs). In this study, we present (pseudo-)equilibrium as well as kinetic parameters for *in situ* sorption of a series of PAHs and PCBs to powdered and granular activated carbons (AC) after three different sediment treatments: sediment mixed with powdered AC (PAC), sediment mixed with granular AC (GAC), and addition of GAC followed by 2 d mixing and subsequent removal ('sediment stripping'). Remediation efficiency was assessed by quantifying fluxes towards SPME passive samplers inserted in the sediment top layer, which showed that efficiency decreased in the order of PAC > GAC stripping > GAC addition. Sorption was very strong to PAC, with $\log K_{AC}$ (L/kg) values up to 10.5. $\log K_{AC}$ values for GAC ranged from 6.3 - 7.1 and 4.8 - 6.2 for PAHs and PCBs, respectively. $\log K_{AC}$ values for GAC in the stripped sediment were 7.4 - 8.6 and 5.8 - 7.7 for PAH and PCB. Apparent first order adsorption rate constants for GAC (k_{GAC}) in the stripping scenario were calculated with a first-order kinetic model and ranged from 1.6×10^{-2} (PHE) to $1.7 \times 10^{-5} \text{ d}^{-1}$ (InP). Sorption affinity parameters did not change within 9 months post treatment, confirming the longer term effectiveness of AC in field applications for PAC and GAC.

INTRODUCTION

Currently, there is much interest in activated carbon (AC) and biochar amendment strategies to reduce the exposure of organisms to sediment- and soil- associated hydrophobic organic chemicals (HOCs) [1-4]. Carbonaceous materials are strong sorbents for polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs) and chlorinated pesticides and thus offer alternatives for risk reduction in contaminated soils and sediments and open possibilities for site redevelopment and material reuse [1, 3, 4]. The potential of sorbent amendments has been successfully verified in a number of field studies, which demonstrated that AC can significantly influence the fate and behavior of sediment- and soil- bound organic contaminants with respect to their transport, bioavailability and biodegradation. Several field trials showed the high effectiveness and functionality of AC deployments in reducing aqueous phase concentrations [5-8], fluxes and thus mobility of HOCs [1, 9]. Further benefits are reduced bioaccumulation of PCBs into benthic invertebrates and fish [1, 5, 10-12], and reduced toxicity of contaminated sediments [13-15]. Consequently, AC may serve as an effective tool in risk mitigation and remediation of contaminated sediments.

AC amendment strategies may vary depending on the sediments' environment and thus may involve *in situ* deployment methods, such as mixing into the biologically active zone or capping, and *ex situ* treatment methods, such as sediment stripping [16]. For a recent field scale remediation trial we demonstrated that 48 h mixing of sediment and granular AC (GAC) resulted in a reduction of PAH pore water concentration by 97% in the short term, whereas addition of powdered AC (PAC) to the sediment reduced bioaccumulation of PCBs

by benthic invertebrates, zooplankton, fish, and macrophytes even by 95 % [12]. In spite of these promising results it is still uncertain to what extent these reduced pore water concentrations change over time and how they differ for chemicals and for different AC remediation scenarios. It is important to know whether field conditions change mass transfer of PAHs in sediment that has been treated by addition and subsequent removal of GAC. Treatment efficiency and sorption parameters under actual remediation i.e. field conditions still are less well studied than under controlled laboratory conditions.

To date, HOC sorption to AC has been studied by different sorption models and isotherms. Multi-domain empirical models have been used to quantify the adsorption of HOCs to AC in AC-amended sediments [17, 18], and to a priori estimate an effective AC dosage for sediment remediation [17]. This approach is supported by the observations that besides added AC, sediments contain considerable fractions of amorphous organic carbon and ‘black’ carbon (BC) phase, i.e. soot and coal, that exhibit strongly nonlinear sorption for hydrophobic organic pollutants [19, 20]. While refractory phases in the sediment such as BC or weathered oil may significantly limit desorption of HOCs to AC [21, 22], other phases, such as dissolved organic carbon (DOC) may compete with target HOCs for AC sorption sites [18, 23]. Therefore, it is highly relevant to identify affinity parameters for sorption of organic contaminants to AC under field conditions, in different sediment treatment scenarios.

The objective of the present study was to determine the temporal variation and chemical dependence of treatment efficiency for three AC treatments: a) mixing sediment with PAC, b) mixing with GAC, and c) sediment stripping with GAC. SPME fibers were inserted in the sediments at predesigned time intervals and reductions of fluxes towards SPME fibers were used as a novel metric for treatment efficiency. The second aim was to assess the kinetics of PAH mass transfer in the GAC stripping scenario. To accomplish this aim, we applied a previously published multi-compartment first-order model to interpret the pore water concentrations during the first weeks after GAC treatment. Third aim was to determine the *in situ* (pseudo-)equilibrium sorption constants of PAHs as well as PCBs to AC in all treatment scenarios by using the concept of multiple domain sorption modeling [17, 22] and to evaluate the applicability of such conceptual models under field conditions.

MATERIALS AND METHODS

Details of the activated carbon remediation field experiment have been published in our previous paper that addressed treatment effects on bioaccumulation [12, 24] and are provided as Supporting Information. Here, a brief summary is given and model details are described.

Sediment and Activated Carbon

In short, twenty five cubic meters of sediment (d.w. 53%, bulk density 1.7 t/m^3) were dredged from The Biesbosch National Park in December 2011 and transported to the experimental field station ‘the Sinderhoeve’ (Renkum, The Netherlands), where the sediment remediation

experiment was conducted. A summary of sediment characteristics is provided as Supporting Information (Table S1). Coal-based powdered activated carbon SAE Super (particle size 1-150 μm) and granular activated carbon GAC 1240W (450-1750 μm) were kindly supplied by Norit (The Netherlands). PAC and GAC characteristics were reported previously [15, 16]. Details on other chemicals, materials and analysis are provided as Supporting Information.

Field Study

The field study comprised four identical ditches (15 m length, 1.5-2 m width, 1 m depth) that received untreated sediment (control) and three different treatments with AC. The sediment was processed in two containers (34 m^3 each) at the site. An excavator and two electric submersible pumps, i.e. Tsurumi Pump KTV2-80 (400V, 50Hz, 3-phase 80 mm hose coupling) were used for direct mixing. Industrial sieves (1.6x1.0 m, mesh size 20 and 1 mm) were used for sediment pretreatment [12, 24].

Biesbosch sediment was diluted with groundwater to 20% d.w., sieved over a 20 mm sieve and homogenized for 4 h, after which one-fourth of the sediment slurry was pumped into ditch 1 (control sediment) and one-fourth of the sediment into ditch 2. Powdered activated carbon (PAC, 170 kg) was added to sediment in ditch 2, to obtain 4% d.w. of total sediment volume, which was denoted as PAC-sediment treatment. Thereafter, GAC was added to the remaining 50% of the sediment slurry at a dose of 4% (340 kg), and mixed for 3 h. Half of this GAC-sediment mixture (25% of the original sediment quantity) was pumped into ditch 3 (GAC treatment). The remaining GAC-sediment slurry was mixed for 48 h, after which the GAC was separated from the sediment by means of sequential sieving (1 mm). Subsequently, the stripped sediment was pumped into ditch 4 (stripped sediment). Approximately 63% of GAC particles was removed from the treated sediment. The remainder of GAC particles (< 1000 μm), and which constituted 1.5% d.w. in the total volume of the sediment, was transferred with the sediment to the ditch.

After 4 months each ditch was split into three equal compartments by inserting non-permeable EPDM (*ethylene propylene diene monomer*) rubber curtains. The rubber curtains will adsorb the PCB and PAH but the curtain surface area was calculated to be negligible compared to the GAC and PAC surface areas present in the systems i.e. $3.7 \times 10^8 \text{ m}^2$. Biota was added for bioaccumulation assessments as described before by Kupryianchyk et al. [12]. The ditches were monitored from December 2011 to September 2012 during regular sampling events.

Sampling

Samples were taken six times: at start ($t=0$) and after 1, 3, 4, 6, and 9 months [12]. The samples were used for analysis of total organic carbon (TOC) contents of sediment, total sediment PAH and PCB concentrations, petroleum hydrocarbon (TPH) and metal concentrations, passive sampler based pore water PAH and PCB concentrations (POM-SPE,

[25]), *in situ* (SPME) pore water concentrations, and PCB concentrations in fish, invertebrate, zooplankton and macrophytes. Details on the latter biota samples were reported in [12], whereas POM-SPE and SPME methodologies and analysis are provided as Supporting Information. Biesbosch sediment had a TOC of 5.86 ± 0.51 % ($n=3$) and a black carbon content of 1.15 ± 0.19 %. Total PAH_{Σ13}, PCB_{Σ7} and petroleum hydrocarbon (TPH) concentration measured in Biesbosch sediment were 11 mg/kg, 0.70 mg/kg and 700 mg/kg, respectively. Individual PAH, PCB and heavy metal concentrations are summarized as Supporting Information (Table S1).

Analytical procedures

GAC analysis. The morphology of recovered GAC particles was investigated with scanning electron microscopy (SEM). Samples were dried and then glued on a copper sample holder using conductive silver tape and sputter coated with 20 nm platinum (JFC 1200, JEOL, Japan). Samples were analyzed at 2 kV, 50 pA, WD 4 at ambient temperature in a Field Emission Scanning Electron Microscope (Magellan 400, FEI, Eindhoven, The Netherlands). Virgin GAC was used as a reference material.

Particle size distribution analysis. Biesbosch sediment was characterized for particle size distribution (PSD) using a Beckman Coulter LS 230 (fluid module) laser diffraction particle size analyzer with Polarization Intensity Differential of Scattered Light (PIDS). PSD analysis showed that Biesbosch sediment had silt-, clay- and fine sand-sized particles (for details see Figure S1, Supporting Information).

Data analysis

Flux calculation. The *in situ* PAH concentrations detected by solid phase micro extraction (SPME) passive samplers were used to estimate the apparent average flux of contaminants across the SPME samplers in untreated and AC treated sediment. The flux ϕ ($\text{ng} \times \text{m}^{-2} \times \text{d}^{-1}$) for a specific PAH can be defined as:

$$\phi = \frac{Q_{SPME}}{A_{SPME} t_{SPME}} \quad (1)$$

where Q_{SPME} is the quantity of PAH in the SPME fibre (ng), A_{SPME} is the surface area of the fiber (m^2) and t_{SPME} is the fibre deployment time (d). The flux of contaminants into the samplers was calculated for all monitoring stages i.e. after 1, 3, 4, 6, and 9 months of AC amendment to contaminated sediment. The SPME fibers may or may not act as an infinite sink extractor dependent on chemical and system properties, rendering the flux data incomparable. Therefore, the flux data were normalized to flux reduction ratios, i.e. the ratio of the flux in the AC treated sediments divided by that in the unamended control. Because the apparent flux is proportional to pore water concentration in all cases, the flux reduction ratios

can be interpreted as pore water concentration reductions due to AC treatment. A detailed explanation is provided as Supporting Information (Eq. (S1)-(S5)).

Mass transfer kinetic modeling of PAH extraction by GAC in the sediment stripping treatment. The initial changes of aqueous-phase PAH concentrations in the GAC stripping treatment measured by POM passive samplers were evaluated with a previously published first-order multicompartment mass transfer model (Chapter 4) [26]. These PAH concentrations relate to a first phase of 2 d mass transfer from sediment to pore water and AC during sediment stripping by GAC, followed by a second phase of 28 d mass transfer in the laboratory after sampling of the treated sediment. The second phase relates to the standard 28 d equilibration period used for 76 μm POM passive samplers, after which equilibrium is established [25, 27, 28]. After the 2 d mixing period, GAC particles are removed by a 1 mm mesh sieve. Therefore the 28 d mass transfer in the laboratory accounts for a fraction of the original GAC with smaller particles. The model simulated the release of contaminants from the fast and slow desorption sediment compartments in the sediment to the water phase and subsequent uptake by GAC. PAH mass transfer in the stripped scenario is described as in Eq. (S6)-(S9) (Supporting Information). Eq. (S6)-(S9) were approximated by a 4th order Runge-Kutta algorithm programmed in Excel, using incremental time steps. Further details of the modeling strategy were explained in our previous study [26]. Modeling of mass transfer during the original and sieved GAC fractions accounted for the differences in PSD caused by the sieving.

Parameter optimization. Sorption parameters were fitted using Eq. (S6)-(S9) for all PAHs simultaneously using the Microsoft Excel solver tool (Microsoft Corporation). To obtain rigor in parameter estimation, the slopes and intercepts of the $\text{Log}k_{\text{GAC}}\text{--}\text{Log}K_{\text{OW}}$ and $\text{Log}K_{\text{GAC}}\text{--}\text{Log}K_{\text{OW}}$ linear regressions were optimized, rather than fitting separate values for k_{GAC} and K_{GAC} . This reduced the number of optimization parameters from eighteen to four. That $\text{Log}k_{\text{GAC}}$ and $\text{Log}K_{\text{GAC}}$ can be assumed to depend linearly on $\text{Log}K_{\text{OW}}$ was shown in our previous work that used the same AC types [26]. Optimization was based on pore water concentration data in treated sediment and sediment concentration data after 28 d, for nine PAHs ($n=18$). Parameter values for k_{fast} , k_{slow} and F_{fast} were calculated from regressions against $\text{Log}K_{\text{OW}}$ taken from the literature [29]. Fast desorbing fractions F_{fast} values for Biesbosch sediment were obtained from De Lange et al. [30].

Equilibrium sorption modeling. Sorption of HOCs to AC was evaluated with the Freundlich equation. Assuming equilibrium and presence of three sorption domains i.e. amorphous organic matter, black carbon (BC) and AC, the apparent *in situ* K_{AC} values can be estimated using [17]:

$$K_{\text{AC}} = \frac{f_{\text{OC}}K_{\text{OC}}(C_{\text{W}}^0 - C_{\text{W}}^1) + f_{\text{BC}}K_{\text{BC}}[(C_{\text{W}}^0)^{n_{\text{F,BC}}} - (C_{\text{W}}^1)^{n_{\text{F,BC}}}]}{f_{\text{AC}}(C_{\text{W}}^1)^{n_{\text{F,AC}}}} \quad (2)$$

where C_w^0 and C_w^1 are the HOC pore water concentration before and after AC amendment as determined with POM passive samplers ($\mu\text{g/L}$), f_{OC} , f_{BC} and f_{AC} , are the organic carbon, black carbon (BC) and AC fractions ($\text{kg}_{\text{CARBON}}/\text{kg}_{\text{SED}}$), respectively. K_{OC} is the organic carbon-normalized distribution coefficient for OC (L/kg_{OC}), K_{BC} is the Freundlich adsorption coefficient for BC ($\mu\text{g/kg}_{BC}/(\mu\text{g/L})^{n_{F,BC}}$) and $K_{F,AC}$ is the Freundlich affinity constant, ($\mu\text{g/kg}_{AC}/(\mu\text{g/L})^n$), $n_{F,BC}$ and $n_{F,AC}$ are the Freundlich exponents that enable nonlinear sorption modeling to BC and to AC. For AC however, a linear sorption model was assumed ($n_F=1$). The K_{OC} values for amorphous carbon were calculated from compound-class specific regressions with $\text{Log}K_{OW}$ i.e. quantitative structure property relationships (QSPRs), which were taken from van Noort et al. [31, 32]. The affinity constants for sorption to BC were estimated from the pore water concentration data of untreated sediment (control) and a dual sorption domain model equation [17]:

$$K_{BC} = \frac{C_{SED} - f_{OC} K_{OC} C_w^0}{f_{AC} (C_w^0)^{n_{F,BC}}} \quad (3)$$

where C_{SED} is PAH or PCB concentration in sediment ($\mu\text{g/kg}$) d.w. Note that K_{AC} , K_{BC} , are conditional constants reflecting the influences of DOC fouling and pseudo- or non-equilibrium.

RESULTS AND DISCUSSION

Remediation efficiency as indicated with apparent flux reductions to SPME. The apparent fluxes of PAHs across the SPME fiber were calculated with Eq. (1) for all treatment scenarios after 1, 3, 4, 6, and 9 months of AC amendment to contaminated sediment. Because PCBs were either not quantified or below detection limits, flux data were only obtained for PAH. Based on absolute values, we observed a decline of PHE and ANT fluxes, probably due to degradation. During the course of the field study the fluxes of PAHs in all AC treatments were reduced compared to the untreated sediment (Figure 1, all $\text{Log}(\phi_t / \phi_c) < 0$). The metric $\text{Log}(\phi_t / \phi_c)$ represents the flux of PAH in the AC treatment scenarios (ϕ_t) normalized to the flux in the unamended control (ϕ_c), which eliminates non-equilibrium artifacts (see the Supporting Information). In general, PAC treatment was most effective in reducing fluxes of all PAHs i.e. showed the lowest $\log \phi_t/\phi_c$ ratios among all remediation scenarios (Figure 1; Figure S2). Sediment stripping with GAC decreased fluxes up to 1.4 log units, and GAC amendment to a lesser extent i.e. 0.5 log unit (Figure 1, Figure S2). The higher effectiveness of PAC compared to other treatments is likely due to larger total surface area of the sorbent [33] and the fine dispersion of the AC particles resulting in shorter diffusion path lengths. GAC addition resulted in high flux reductions for PHE and ANT after 1 month, however an increase in ϕ_t/ϕ_c ratios was observed with time (Figure 1 a, Figure S2). The low molecular weight PAH showed increasing normalized fluxes, which most likely is caused by faster degradation in the control than in the AC treatments.

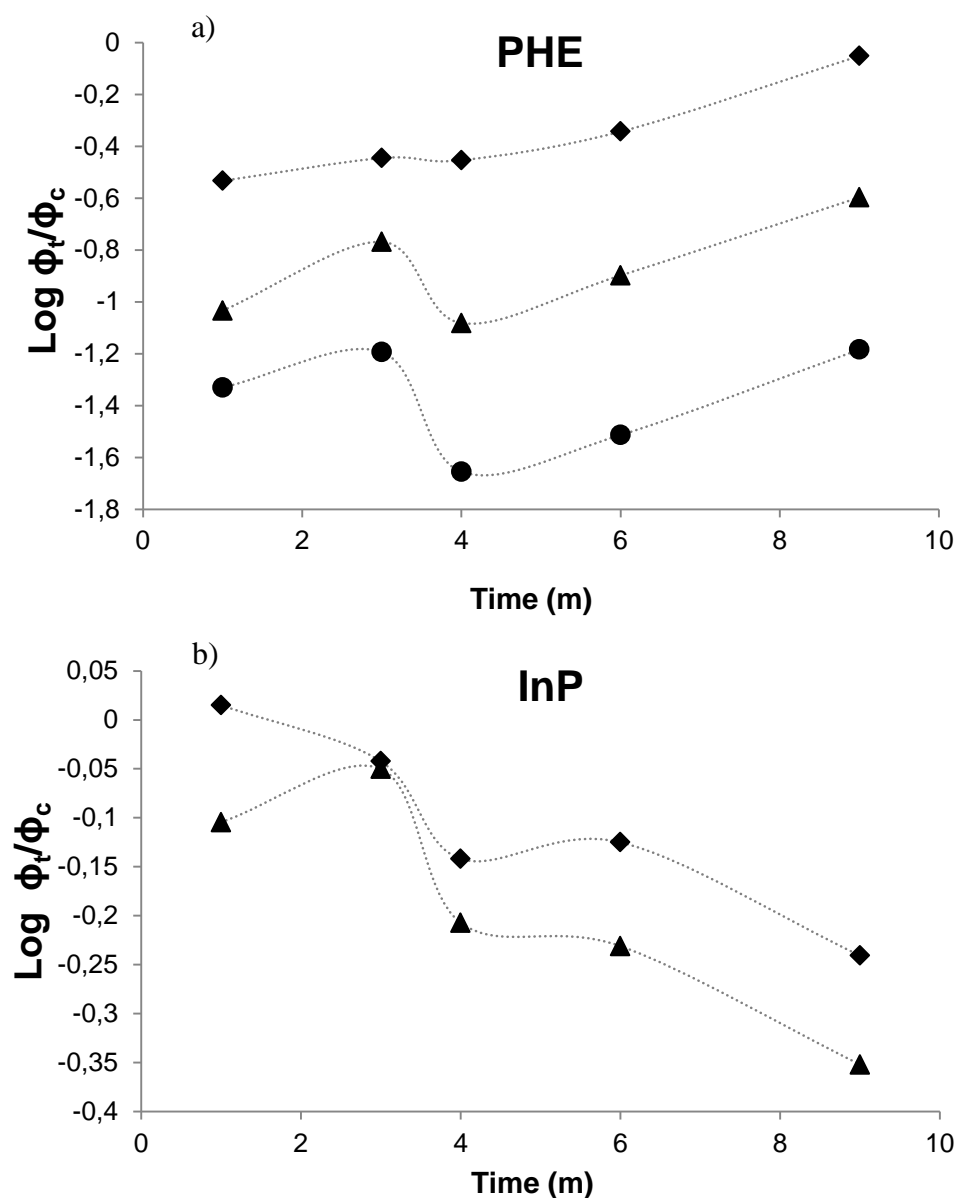


Figure 1. PHE and InP flux ratios as a function of time in the PAC (●), GAC (♦) and stripped (▲) sediment. Interpolated curves are meant to guide the eye.

Similar behavior was noted for PAC amended sediment and stripped sediment, the only difference being that the largest flux reduction occurred after 4 months (Figure 1, Figure S2).

In case of FLU, PYR, BaA, CHR, BeP, BbF, BkF, BaP and BghiP, a gradual decline was observed in the GAC amendment with maximum flux reduction after 4 months, but elevated fluxes occurred after 6 months, which leveled off again after 9 months (Figure S2). PAC amendment and sediment stripping yielded maximum flux reductions after 4 months for the aforementioned compounds, and a slightly lower increase in flux in later time points

compared to GAC scenario. In case of InP, both GAC amendment and stripping resulted in a gradual decline of InP flux with time (Figure 1 b). We hypothesize that the increase of the flux ratio towards 6 months may be affected by addition of biota at month 4, which initiated bioturbation and bioturbation-induced fluxes [24, 34]. It is plausible that biota activity, biodegradation, growth of macrophytes, as well as dissolved organic carbon (DOC) concentrations affected the transport across the SPME-water interface. The decrease of fluxes for low molecular weight compounds was more pronounced in the control ditch, which may relate to enhanced biodegradation of PAH in sediment without AC addition.

Mass transfer kinetic modeling. The mass transfer of PHE, ANT, FLU, BaA, CHR, BkF, BaP, BghiP and InP during 2 d sediment stripping by GAC, followed by a second phase of 28 d mass transfer in the laboratory during equilibration with POM was modeled by using Eq. (S1)-(S4) (Supporting Information). Model fits were based on PAH pore water concentrations ($n=9$) as well as PAH sediment concentration data after 28 d ($n=9$), and used literature-based k_{fast} , k_{slow} and F_{fast} parameters. First, we evaluated the model with our previously derived $\log k_{GAC} - \log K_{OW}$ and $\log K_{GAC} - \log K_{OW}$ regression parameters [26] (Figure S3, S4), which were used as fixed input in model simulations. However, these default parameters were too high and thus resulted in only limited agreement between modeled and measured data. Note that the present sediment had another source than the sediment used in our previous study which may explain that other parameter values are required. Consequently, regression parameters were optimized, which provided a $\log k_{GAC} - \log K_{OW}$ regression slope of -1.23 and intercept of 3.81 (Figure S3). This slope is marginally lower (i.e. 19%) than in our previous study, but the intercept agrees with the previously reported value within error limits (3.66 ± 0.73) [26]. Optimization of the $\log K_{GAC} - \log K_{OW}$ regression parameters resulted in a slope of 1.01 but a significantly higher intercept i.e. 0.81, compared to our earlier reported value of -0.05 (Figure S4). The present results represent average sediment contamination levels, whereas our previous study concerned a highly contaminated ‘hot spot’ sediment [26]. Therefore, the higher intercept might reflect that GAC is less prone to fouling in Biesbosch sediment due to the lower oil content compared to that in Petroleum Harbour sediment. Adsorption rate constants (k_{GAC}) were approximately up to two orders of magnitude lower than k_{GAC} values derived for Petroleum Harbour sediment (Figure S3), whereas sorption coefficients ($\log K_{GAC}$) for PHE, ANT, FLU, BaA and CHR, i.e. $\log K_{OW} < 6$ are up to one order of magnitude higher compared to default parameters. The currently obtained k_{GAC} values comply with those that can be calculated from the data reported by Hale and co-authors [35].

The modelled changes of PAH concentrations in the aqueous phase, in the fast and slow sediment compartments, in the GAC and in the experimental sediment and water concentration data (measured C_{SED} and C_W) show how mass transfer occurs in time (Figure S5, Supporting Information). A representative example is provided as Figure 2.

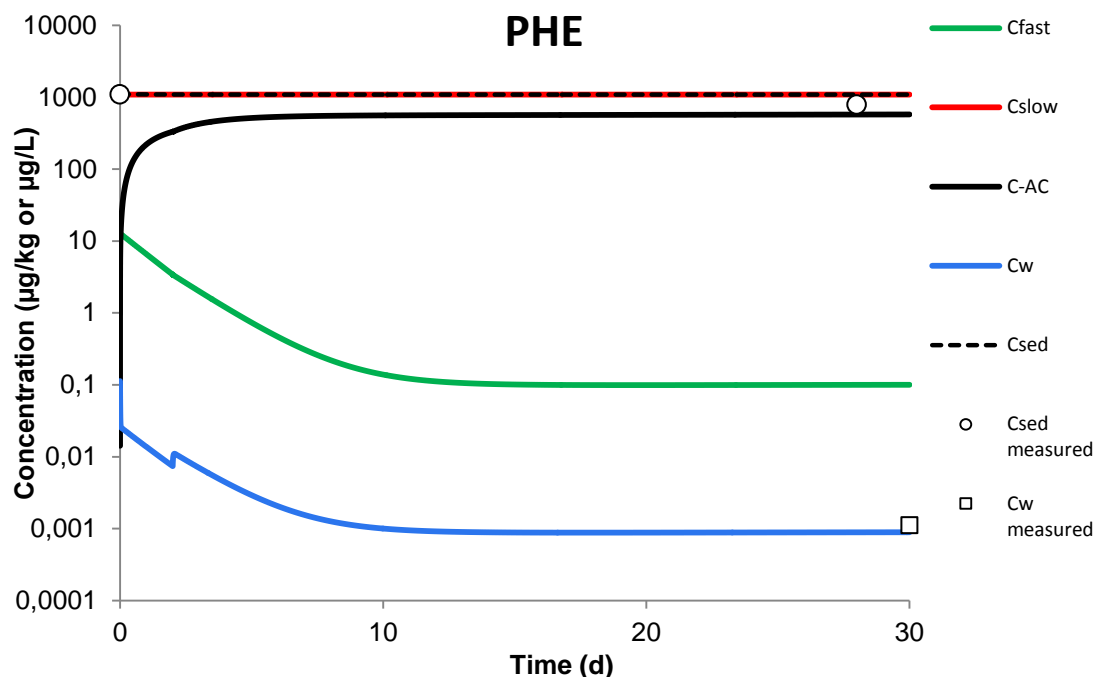


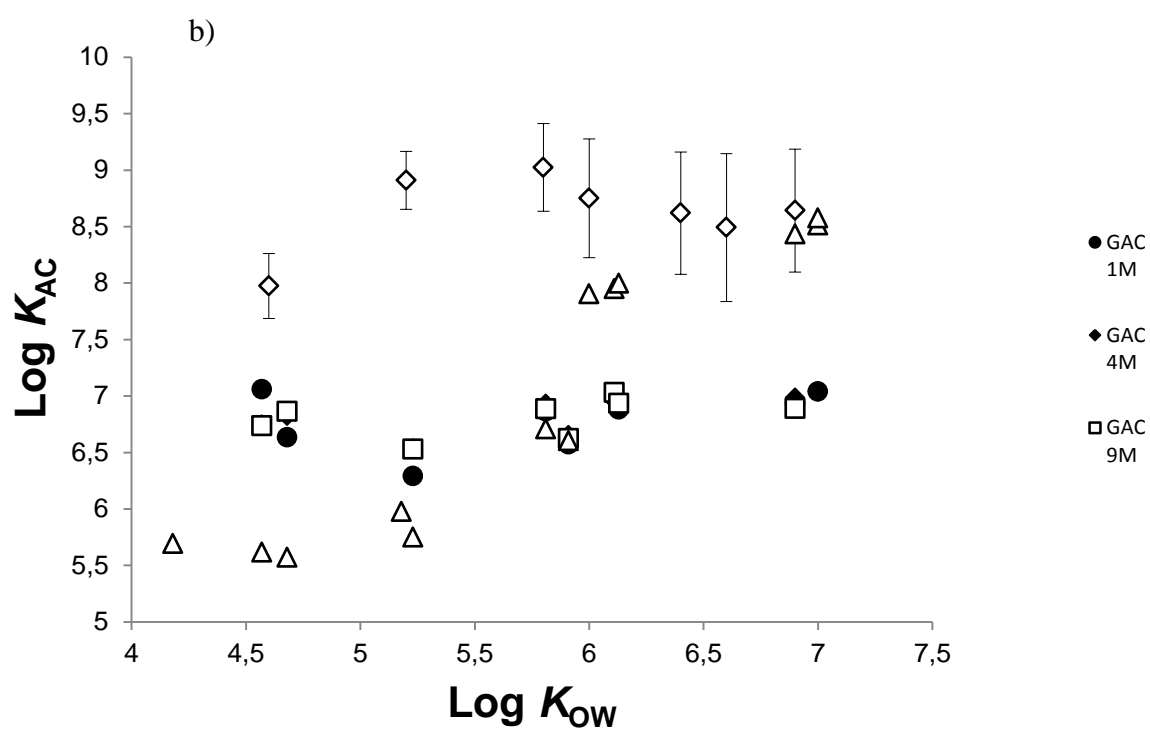
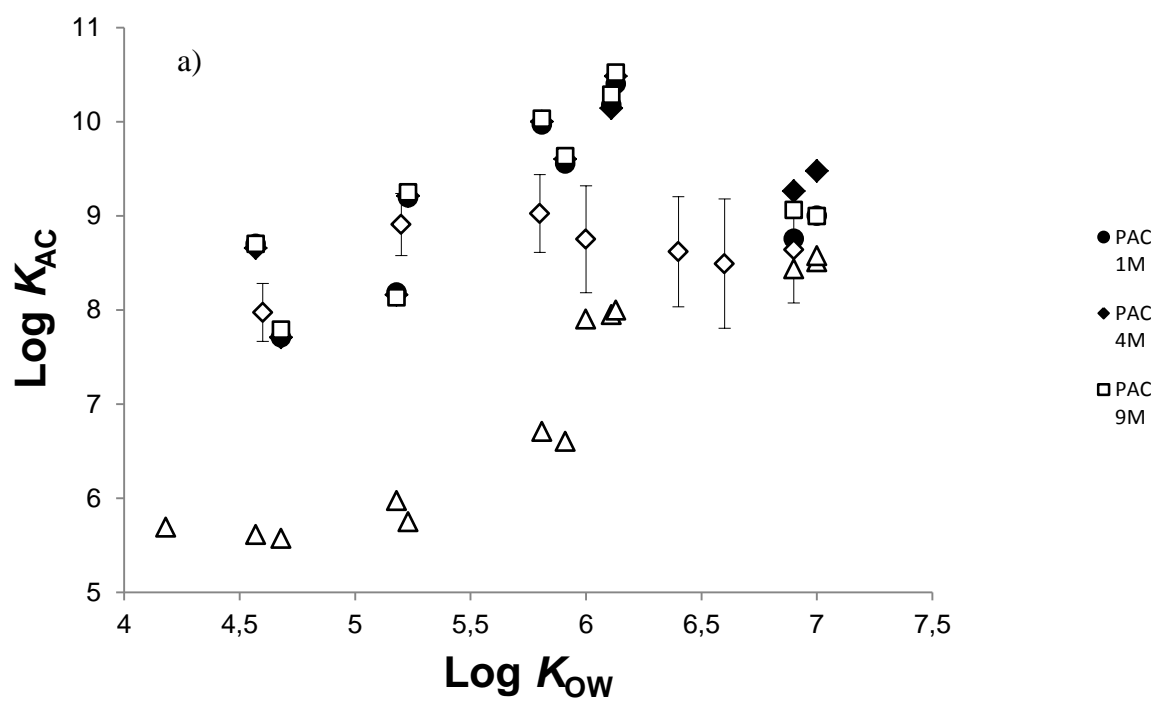
Figure 2. Concentrations of PHE in Biesbosch sediment and GAC (4%) as a function of time in the first month of treatment. Dashed lines represent modelled values by using Eq. S1-S4. ($n_F = 1$), whereas markers represent measured data. The dashed C_{sed} line is calculated as the sum of the modelled C_{fast} and C_{slow} curves.

The modelled aqueous concentrations agree very well with the measured values of C_W (Figure S5) for all compounds except ANT, which confirms the model accuracy. All graphs show an apparent discontinuity at 2 d, which in fact relates to a change of solid to liquid ratio due to the transfer of the solids from the field to the laboratory systems, after which mass transfer proceeds at this new ratio. During the 2-d mixing stage, aqueous phase concentrations of PHE, ANT and FLU decline by up to one order of magnitude and show a further decrease within 10 days (Figure 2, Figure S5). In case of BaA, CHR, BkF, BaP, BghiP and InP the C_W is only a factor of 2-4 lower after 2 d but decreases gradually by two orders of magnitude during the 28 d laboratory mixing stage in the presence of the POM samplers (Figure S5). The high reductions of PAH aqueous concentrations within the 28 d post-treatment period can be explained by the presence of GAC particles $< 1000 \mu\text{m}$ and thus faster mass transfer [36]. Overall, the initial reduction of C_W by GAC in the stripping scenario is more pronounced for low molecular weight compounds, which is consistent with our previous laboratory results [26]. High molecular weight compounds require more time to reach the GAC surface and may suffer more from sorption competition or pore blocking by DOM fouling. In summary, less intense mixing, sediment properties and fouling by sediment organic matter may effectively reduce PAH uptake rate constants (k_{GAC}) by GAC under field conditions.

Equilibrium sorption modeling. Apparent sorption of native PAHs and PCBs to AC in all treatment scenarios was calculated with Freundlich isotherms (Eq. 2). The K_{AC} values were estimated assuming $n_{F,AC} = 1$. This approach is supported by previous observations that HOC sorption to fouled carbonaceous materials was more linear than to clean sorbents [37].

PAC amendment. The corresponding binding constants were calculated from measured aqueous concentrations only for ANT, BghiP, InP and PCBs (CB-28, 101, 138, 153, 180). In case of PHE, FLU, BaA, CHR, BkF and BaP minimum K_{AC} values were calculated from detection limit data, which served as a proxy for pore water concentration after amendment. The Log K_{AC} values for sorption to PAC ($n_{F,AC} = 1$) after one month, range between 7.70 and 10.40 depending on PAH hydrophobicity and increase 0.01-0.5 log unit except for PHE within 4 months after amendment (Figure 3 a). After 9 months, sorption coefficients for 3-, 4- and 5- ring PAHs ($\text{Log}K_{OW} = 5.23\text{-}6.13$) marginally increased, whereas K_{AC} values for BghiP and InP slightly declined (Figure 3 a). Log K_{AC} for PCBs ($n_{F,AC} = 1$) ranged from 9.0 to 10.5 after 1 month and remained more or less constant during the time frame of the field study (Figure 4). Overall, these observations show that AC affinity persists in the longer term (9 months), which means that AC amendment technology can be considered as a sustainable approach. In contrast to the earlier study by Oen et al [18], who reported higher K_{AC} values for freshly added AC than those of field-aged AC, we did not observe a substantial decline of apparent sorption coefficients in time. The Log K_{AC} parameters appear to increase linearly with increasing PAH hydrophobicity up to a Log K_{OW} value of 6.13 (Figure 3 a), whereas Log K_{AC} values for PCBs in the PAC ditch show a strong correlation with Log K_{OW} ($R^2=0.98$; Figure 4). These results suggest that slower sorption kinetics of more hydrophobic PCBs or/and steric effects are less important for sorption to very fine PAC (1-150 μm). The calculated Log K_{AC} values for PAC are up to one order of magnitude higher than the affinity constants derived from previous AC amendment studies [17, 18, 38] with coarser sorbent particles. Consequently, the currently obtained K_{AC} values are the highest ever reported and support the superiority of PAC in sediment remediation.

GAC amendment. In the GAC remediation scenario the apparent sorption constants ($\text{Log}K_{AC}$) ranged from 6.30 - 7.06 and 4.8 - 6.2 for PAHs and PCBs, respectively (Figure 3 b and Figure 4). These results are in line with previous studies, which reported higher sorption effectiveness of AC towards more planar PAHs compared to PCBs [4, 39]. The apparent K_{AC} values increased 0.25 log unit during 4 months for all PCBs and PAHs with $\text{Log}K_{OW}$ between 4.7 and 5.8. For PAHs with $\text{log}K_{OW} > 5.8$ the K_{AC} remain constant in time (Figure 3 b). This again shows that even a short initial mixing period i.e. 3 h allows for a redistribution of the most mobile HOCs from the sediment to the GAC, whereas the sequestration of high molecular weight compounds by GAC requires more time.



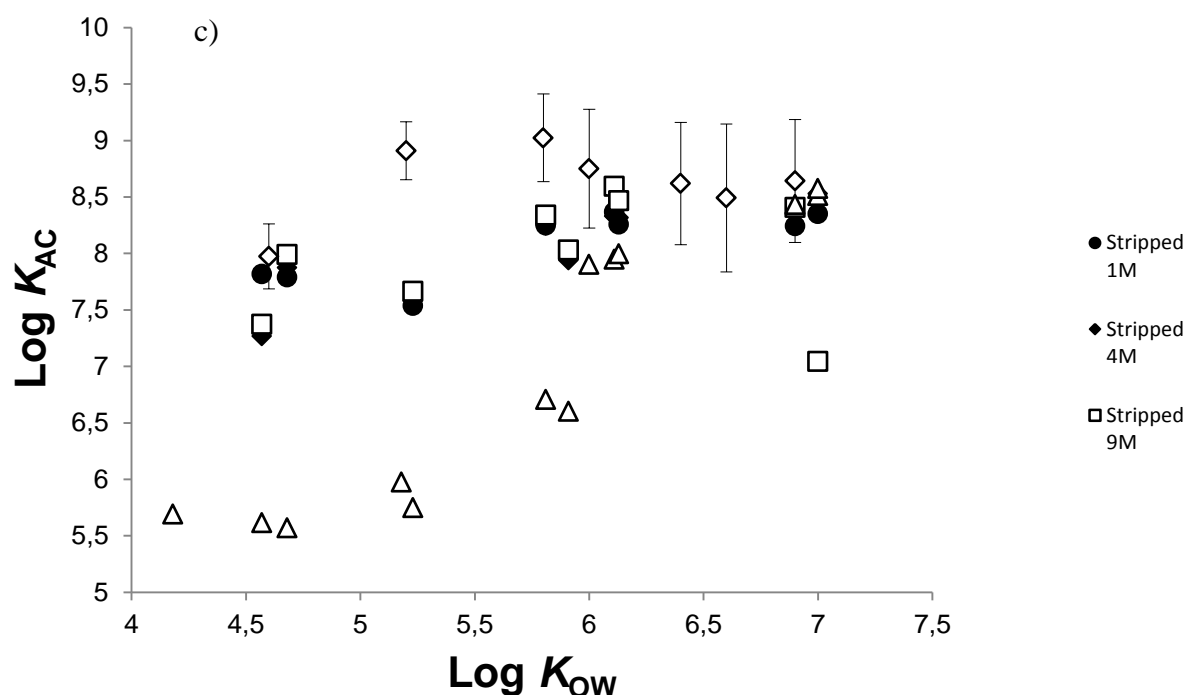


Figure 3. Apparent sorption coefficients ($\text{Log} K_{AC}$; L/kg) for PAHs as a function of $\text{Log} K_{OW}$ in a) PAC-treated sediment; b) GAC-treated sediment and c) stripped sediment. Open diamonds and open triangles are literature Freundlich affinity constants taken from [17] (obtained from multi-domain modeling) and [26] (obtained from mass transfer modeling), respectively.

However, after 9 months a decline in $\log K_{AC}$ was observed especially for PHE and PCBs with $\log K_{OW} > 6.38$ (Figure 3 b and Figure 4). This suggests that the least hydrophobic PAHs and bulky PCBs are more prone to organic matter fouling and competitive effects [37]. Based on SEM micrographs of the internal structure of GAC we did not observe differences in morphology between virgin and used GAC (after sediment stripping) (Figure S6). Both pictures show a condensed and coarse nature of GAC, which agrees with earlier observations reported by Jonker and Koelmans [39]. However, after sediment stripping plant detritus was visually observed on the outer surface of GAC. $\text{Log} K_{AC}$ values for GAC-treated sediment are 1 to 3.5 orders of magnitude lower than those of the PAC-treated sediment and approximately up to 2 orders of magnitude lower than the Freundlich affinity parameters reported for AC particles (75-300 μm) by Kupryianchyk et al. [17] (Figure 3 b). Note that these authors calculated binding constants for different and smaller sized sorbents (including PAC), which were applied to a variety of natural sediments. The lower sorption affinities for GAC can be explained by lower surface areas, small particle sizes of AC used in aforementioned literature studies, and sorption non-equilibrium, despite uniform distribution of GAC particles after mixing. The state of non-equilibrium can be derived from Figure S2, showing equilibrium for most PAH, with clearly declining fluxes (i.e. pore water concentration ratios against the control) only for BghiP and InP. Unexpectedly, the K_{AC} values for GAC did not correlate with

PAH hydrophobicity i.e. $\text{Log}K_{\text{OW}}$, which again suggests that heavy molecular weight compounds may reach GAC surface in extended time frames.

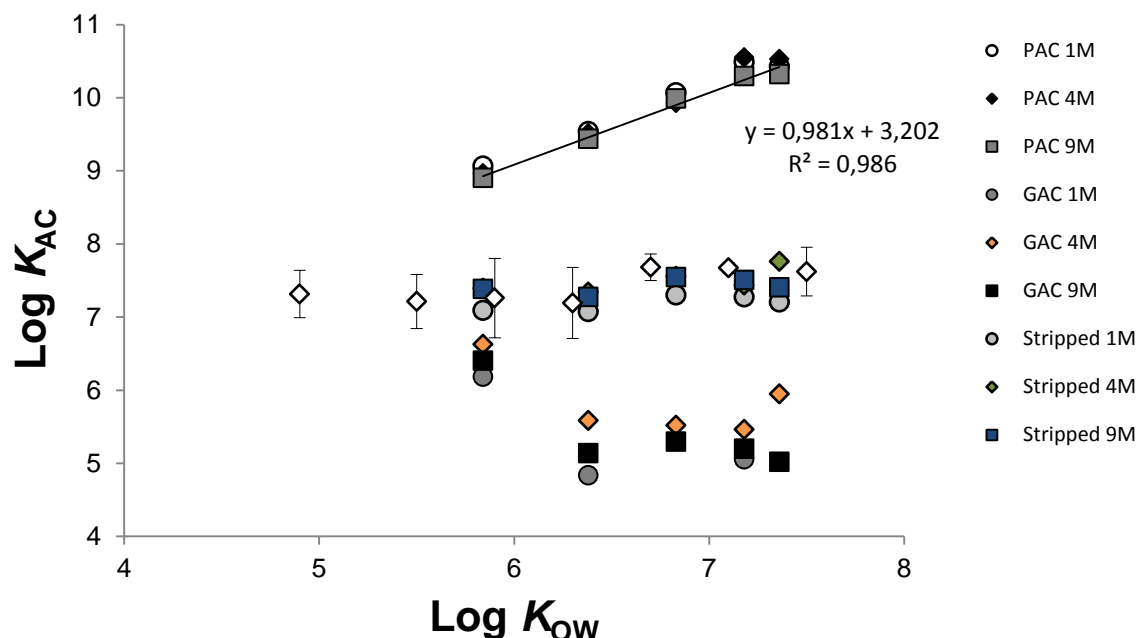


Figure 4. Apparent sorption coefficients ($\text{Log}K_{\text{AC}}$; L/kg) for PCBs as a function of $\text{Log}K_{\text{OW}}$ in PAC-treated sediment; GAC-treated sediment and stripped sediment. Open diamonds are literature Freundlich affinity constants taken from [17] (multi-domain modeling).

Sediment stripping with GAC. After one month post-treatment, the apparent $\text{Log} K_{\text{AC}}$ values for PAH and PCB sorption to GAC in the stripped sediment were up to 2 orders of magnitude higher than those in the GAC-treated sediment (Figure 3 c, Figure 4). The $\text{log} K_{\text{AC}}$ for PAHs with $\text{Log}K_{\text{OW}} > 4.68$ increase gradually by 0.2 log unit during 9 months (Figure 3 c), whereas sorption coefficients for PCBs increased 0.2-0.5 log units after 4 months and remained more or less constant within 9 months (Figure 4). This can be attributed to the fact that stripped sediment still contained GAC particles smaller than $1000 \mu\text{m}$, which would yield higher surface area, shorter diffusive path lengths and faster uptake of 4-, 5- and 6- ring PAHs compared to the GAC treatment. This again shows that the efficiency of sediment stripping with GAC was retained for an extended period.

The $\text{log} K_{\text{AC}}$ values appear to increase linearly with $\text{log} K_{\text{OW}}$ between 4.5 and 6.1 and then level off at a $\text{Log}K_{\text{OW}} = 6.1\text{--}7.0$ (Figure 3 c). From this figure it appears that after sediment stripping, the *in situ* $\text{log} K_{\text{AC}}$ values for high molecular weight compounds i.e. $\text{log} K_{\text{OW}} > 6$ coincide well with recent literature data [17, 18, 26]. The $\text{log} K_{\text{AC}}$ values for compounds with $\text{log} K_{\text{OW}} < 6$ are up to 2.5 orders of magnitude higher than those calculated with a mass transfer model for PAH sorption to GAC in Petroleum Harbor sediment [26] (see Figure 3 c). Again, these differences may be explained by the differences in sediment properties. It is

known that oil contributes to fouling of carbonaceous materials [22] and degradation of PAH [40], and oil concentrations in petroleum harbor sediment were five times higher than in the present sediment. Furthermore, our previous sorption constants were derived at aqueous phase concentrations in the $\mu\text{g/L}$ range, whereas the current values are calculated for C_W in the ng/L range. The observed sigmoidal relationships between $\log K_{AC}$ values and $\log K_{OW}$ are in line with observations reported in our earlier work [26], and are explained from competitive effects at the sorbent surface [41], such as dissolved organic matter loadings [42].

CONCLUSIONS

The present study showed that sediment treatment with PAC is most effective and less prone to organic matter fouling and ongoing natural processes in the field. The effectiveness of GAC is higher in the 48h sediment stripping scenario than in the GAC amendment approach. Stripping still leaves a small GAC size fraction in the sediment, which however may be considered beneficial as a chemical immobilizer in case of sediment reuse. Sorption parameters generally agree with literature values but also show variability among sediments. In terms of in situ sorption coefficients, the three treatments can be rated and ranked in the order PAC addition > sediment stripping > GAC addition. Affinity parameters do not seem to change in the long term, which is an important prerequisite for the longer term sustainability of the improved state of the treated sediments.

Supporting Information

The supporting information includes sediment characteristics, flux calculation, modeling details and modeling results.

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Supporting Information for Chapter 6

Methods

Chemicals and materials

Polyoxymethylene sheets (POM; thickness 76 μm) were purchased from CS Hyde Company, Lake Villa, IL, USA. Before use, coupons of desired weight (approximately 30-100 mg) were cut, washed with hexane, acetonitrile, and methanol, and air-dried. Anthracene (ANT), benzo[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbF), benzo[*e*]pyrene (BeP), benzo[*ghi*]perylene (BghiP), benzo[*k*]fluoranthene (BkF), chrysene (CHR), dibenzo[*a,h*]anthracene (DBA), fluoranthene (FLU), indeno[1,2,3-*cd*]pyrene (InP), naphthalene (NAP), phenanthrene (PHE), and pyrene (PYR) were obtained from Sigma-Aldrich or Acros Organics, The Netherlands, all with a purity of >98%. Internal standard 2-methylchrysene (99.2% pure) was supplied by the Community Bureau of Reference (BCR), Geel, Belgium. Other chemicals used were hexane and acetone (Promochem; picograde), methanol (Mallinckrodt Baker, Deventer, The Netherlands; HPLC gradient grade), acetonitrile (Lab-Scan, Dublin, Ireland; HPLC grade), 2,2,4-trimethylpentane (Mallinckrodt Baker, Deventer, The Netherlands), Barnstead Nanopure water (Sybron-Barnstead, Dubuque, IA, USA), calcium chloride (Merck; p.a), aluminum oxide-Super I (ICN Biomedicals, Eschwege, Germany), and silica gel 60 (Merck; 70-230 mesh). Prior to use, silica gel was activated at 180 °C for 16 h, and aluminum oxide was deactivated with 10% (w/w) Nanopure water.

Analytical procedures

Total contaminant concentrations in the sediment. Metals, TPH, PAH and PCB were analysed by the certified laboratory OMEGAM (Amsterdam, The Netherlands).

Determination of PAH and PCB concentrations in pore water. PAH and PCB concentrations in sediment pore water were determined *ex situ* using the POM-SPE method [1] and *in situ* using a solid phase micro extraction (SPME) method [2].

POM-SPE measurements. The 76 μm POM strips were extracted using a cold extraction method and analysed for PCBs using GC and for PAHs using HPLC. An amount of wet sediment corresponding to about 10 g of dry weight was brought into a full glass 50 mL bottle, which was filled with an aqueous solution of sodium azide (50 mg/L) and calcium chloride (0.01 M) in Nanopure water. After the addition of POM with a known weight, the bottles were shaken on a shaker table at 20 °C and 150 rpm for 28 d, which is sufficient to obtain equilibrium of the HOCs with the POM sampler [1, 3, 4]. Then, the pieces of POM

were recovered, cleaned with wet tissue, and extracted with acetonitrile. Finally, internal standards (CB-209 and 2-methylchrysene) were added. PAH and PCB aqueous concentrations were calculated from equilibrium concentrations measured in POM (C_{POM}) using previously published POM-water partitioning coefficients (K_{POM}) [3, 4].

SPME measurements. Additionally, PAH concentrations in pore water were determined *in situ* using solid phase micro extraction (SPME) fibers [2], containing a 30 μm thick coating of polyacrylate. These fibers were exposed statically in sediment cores that had been taken by a Jenkins core sampler (\varnothing 6 cm). Cores were carefully transferred to the lab in order not to disturb the core integrity. In the lab, 7 SPME fibers with a length of 3 cm each were added to stainless steel envelopes [2, 5], which were then inserted into the upper 4.5 cm layer of the sediment cores. The envelopes were left fully undisturbed in the cores for 30 days at 20 °C. Prior to insertion, the fibers had been washed 3 x 30 min with 1:1 methanol:Millipore water and 3 x 30 min with Millipore water, respectively. Upon finishing the exposures, the envelopes were withdrawn from the cores one by one and the fibers were recovered, cleaned with wet tissues, and put in autosampler vials, fit with an insert containing acetonitrile. All fibers from one envelope were pooled in one vial. 2-Methylchrysene was finally added as internal standard.

Particle size distribution analysis. Biesbosch sediment was characterized for particle size distribution (PSD) using a Beckman Coulter LS 230 (fluid module) laser diffraction particle size analyzer with Polarization Intensity Differential of Scattered Light (PIDS). Sediment samples were brought into suspension in demineralized water and well homogenized prior to particle size analysis. The injected suspension volume was controlled to obtain a total obscuration level of $10\pm 3\%$ and a PIDS obscuration of $50\pm 10\%$. [6]

Estimation of porewater concentration reduction based on reduction of apparent fluxes to SPME fibers

The flux ($\text{ng} \times \text{m}^{-2} \times \text{d}^{-1}$) of PAHs from the water to the SPME fiber in the cores is defined by [7]:

$$\Phi = (K_L A_{SPME}) \left(C_W - \frac{C_{SPME}}{K_{SPME}} \right) \quad (\text{S1})$$

where K_L ($\text{m} \times \text{d}^{-1}$) is the mass transfer coefficient for PAH transfer to the SPME fiber, A_{SPME} is the surface area of the fiber (m^2), C_W is the aqueous phase concentration (ng/L), C_{SPME} is PAH concentration in the SPME sampler (ng/kg) and K_{SPME} is the SPME – water partitioning coefficient (L/Kg).

The concentration change in SPME fiber can be calculated by expressing Eq. S1 in terms of the change of concentration in the fiber volume V_{SPME} (m^3)

$$\frac{dC_{SPME}}{dt} = \left(K_L \frac{A_{SPME}}{V_{SPME}} \right) \left(C_W - \frac{C_{SPME}}{K_{SPME}} \right) \quad (\text{S2})$$

Because of the very small fiber volume, the sediment is present in excess and thus acts as an infinite source to the fiber. Consequently, C_W can be assumed constant during deployment time t (d). Then the analytical solution to Eq. S2 is:

$$C_{SPME} = K_{SPME} C_W \left(1 - \exp \left[- \left(K_L \frac{A_{SPME}}{V_{SPME}} \right) t \right] \right) \quad (\text{S3})$$

For low molecular weight compounds that have a relatively high K_L , the term $1 - \exp \left[- \left(K_L \frac{A_{SPME}}{V_{SPME}} \right) t \right]$ is equal to 1 so that Eq. S3 simplifies to:

$$C_{SMPE} = K_{SPME} C_W \quad (\text{S4})$$

Subsequently, in calculating the ratio of the fluxes in the treated and the control systems the K_{SPME} term cancels out and the ratio of the fluxes equates to $C_{W, \text{ treated}} / C_{W, \text{ untreated}}$

For high molecular weight compounds i.e. very low K_L , the fiber acts as an infinite sink. Consequently, backward transport from the fiber does not play a role and equation S1 becomes:

$$\phi = K_L A_{SMPE} C_W \quad (\text{S5})$$

Subsequently, in calculating the ratio of the fluxes in the treated and the control systems the $K_L A_{SPME}$ terms cancel out and the ratio of the fluxes again equates to $C_{W, \text{ treated}} / C_{W, \text{ untreated}}$.

For PAH with intermediate hydrophobicity there may not be equilibrium with the sampler, but the sampler might not act as an infinite sink either. Consequently, the exponential term has a certain value, which however can be assumed to depend on exposure time, chemical and sampler properties only. Per chemical, these properties are equal for control and treated sediment. Consequently, the terms: $K_{SPME} \left(1 - \exp \left[- \left(K_L \frac{A_{SPME}}{V_{SPME}} \right) t \right] \right)$ cancel out and the ratio of the apparent flux between treated system and untreated control system still is equal to $C_{W, \text{ treated}} / C_{W, \text{ untreated}}$.

Mass transfer modeling

The sorption parameters k_{GAC} and $K_{F,GAC}$ for the intensive addition-removal scenario at a GAC dose of 4% of the sediment weight were determined by using a multicompartment model that simulates the release of contaminants from the fast and slow sediment compartments to the water phase and subsequent adsorption by GAC [8]. For sediment, PAH exchange between the ‘fast’ compartment (C_{fast}) and water is modeled as:

$$\frac{dC_{fast}}{dt} = k_{fast}(K_{p,fast}C_W - C_{fast}) \quad (S6)$$

where C_{fast} ($\mu\text{g/kg}$) and C_W ($\mu\text{g/L}$) are concentrations of chemicals in the fast sediment compartment, and in the water phase, respectively, k_{fast} is a desorption rate constant (d^{-1}) and $K_{p,fast}$ (L/kg) is the partitioning constant of PAHs in the fast reservoir. Similarly, the exchange of PAH from the ‘slow’ compartment is defined as:

$$\frac{dC_{slow}}{dt} = k_{slow}(K_{p,slow}C_W - C_{slow}) \quad (S7)$$

where C_{slow} is the concentration of chemicals desorbing slowly (from the ‘slow’ sediment compartment) ($\mu\text{g/kg}$), k_{slow} is the rate constant for slow desorption (d^{-1}) and $K_{p,slow}$ (L/kg) is the partitioning constant of PAH in the slow compartment, respectively.

For GAC, the equation for PAH exchange is different from those for the fast and slow desorbing sediment-bound PAH, because sorption to GAC is assumed to be non-linear:

$$\frac{dC_{GAC}}{dt} = k_{GAC}(K_{F,GAC}C_W^{n_F-1}C_W - C_{GAC}) \quad (S8)$$

where C_{GAC} is the concentration of PAHs in GAC and k_{GAC} is the adsorption rate constant (d^{-1}). In Eq. 3 the GAC partitioning coefficient is replaced by a Freundlich term, with a Freundlich affinity constant, $K_{F,GAC}$ ($\mu\text{g/kg}_{GAC}/(\mu\text{g/L})^n$) and $n_{F,GAC}$, which is the Freundlich exponent for sorption to GAC.

The change of PAH concentration in the water phase (C_W) of mixed sediment-GAC slurry can be defined as:

$$\begin{aligned} \frac{dC_W}{dt} = & k_{fast} \frac{S_{SED}}{L} (K_{p,fast} C_W - C_{fast}) + k_{slow} \frac{S_{SED}}{L} (K_{p,slow} C_W - C_{slow}) + \\ & k_{GAC} \frac{S_{GAC}}{L} (K_{F,GAC} C_W^{n_F-1} C_W - C_{GAC}) \end{aligned} \quad (S9)$$

where $\frac{S_{SED}}{L}$ is the sediment to liquid ratio (kg L^{-1}) and $\frac{S_{GAC}}{L}$ is the GAC to liquid ratio.

Table S1. Total concentrations of PCBs, PAHs, metals, mineral oil and DDT in Biesbosch sediment.

PAHs	C, mg/kg	Threshold effect level ^a , mg/kg	PCBs	C, µg/kg	Threshold effect level ^a , µg/kg
Naphthalene (NAP)	0.51	0.03	CB-18	14 (0.7)	
Phenanthrene (PHE)	1.1	0.09	CB-20	10 (0.3)	
Anthracene (ANT)	0.87	0.05	CB-28	74 (1.9)	
Fluoranthene (FLU)	2.2	0.11	CB-29	1.0 (0.01)	
Benzo[<i>a</i>]anthracene (BaA)	1.2	0.07	CB-31	43 (1.2)	
Chrysene (CHR)	1.4	0.11	CB-44	14 (0.7)	
Benzo[<i>k</i>]fluoranthene (BkF)	1.0	0.06	CB-52	82 (1.2)	
Benzo[<i>a</i>]pyrene (BaP)	1.1	0.09	CB-101	75 (4.1)	
Benzo[<i>ghi</i>]perylene (BghiP)	0.78		CB-105	17 (0.8)	
Indeno[1,2,3- <i>cd</i>]pyrene (InP)	0.64		CB-118	29 (0.7)	
ΣPAHs	11	0.87	CB-138	69 (3.2)	
Metals			CB-149	80 (2.3)	
As	50	7.2	CB-153	95 (2.9)	
Cd	6.5	0.68	CB-155	3.0 (0.1)	
Cr	190	52	CB-170	19 (0.7)	
Cu	120	19	CB-180	40 (1.2)	
Hg	5.1	0.13	CB-194	7 (0.3)	
Pb	170	30	CB-204	4 (0.1)	
Ni	26	16	CB-209	22 (1.0)	
Zn	920	124	ΣPCBs	700 (28)	22
Mineral oil	700		TOC, %	5.86 (0.51)	-
ΣDDT/DDE/DDD	0.22	0.0045	BC, %	1.15 (0.19)	-

^a[9]

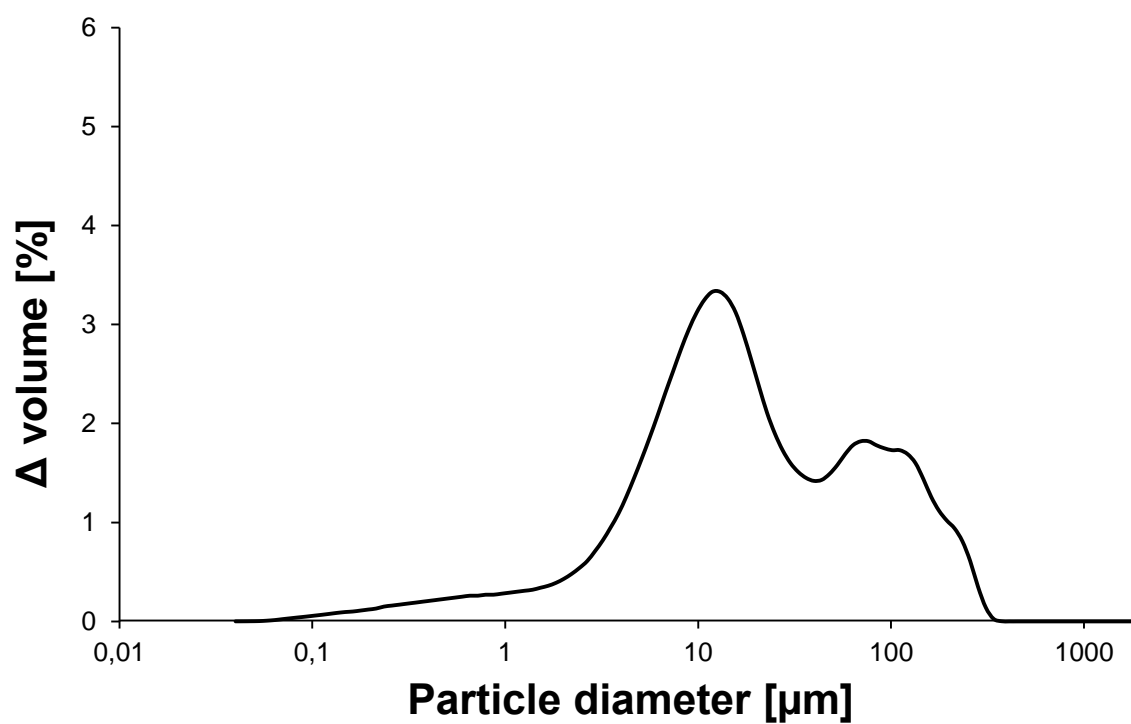
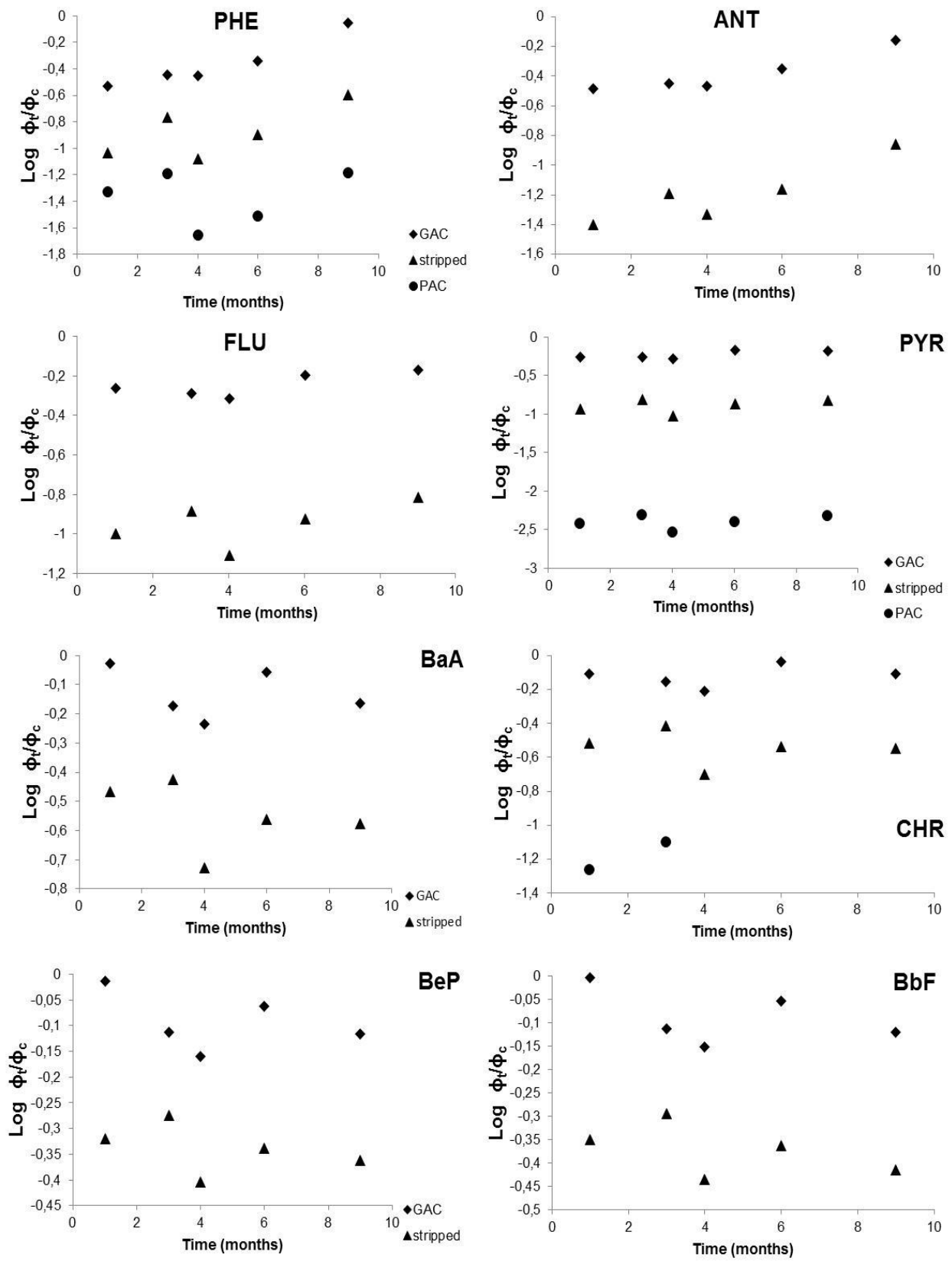


Figure S1. Distribution of particle sizes in Biesbosch sediment as determined by laser diffraction where ΔV is the amount of volume related to the discrete particle size range.



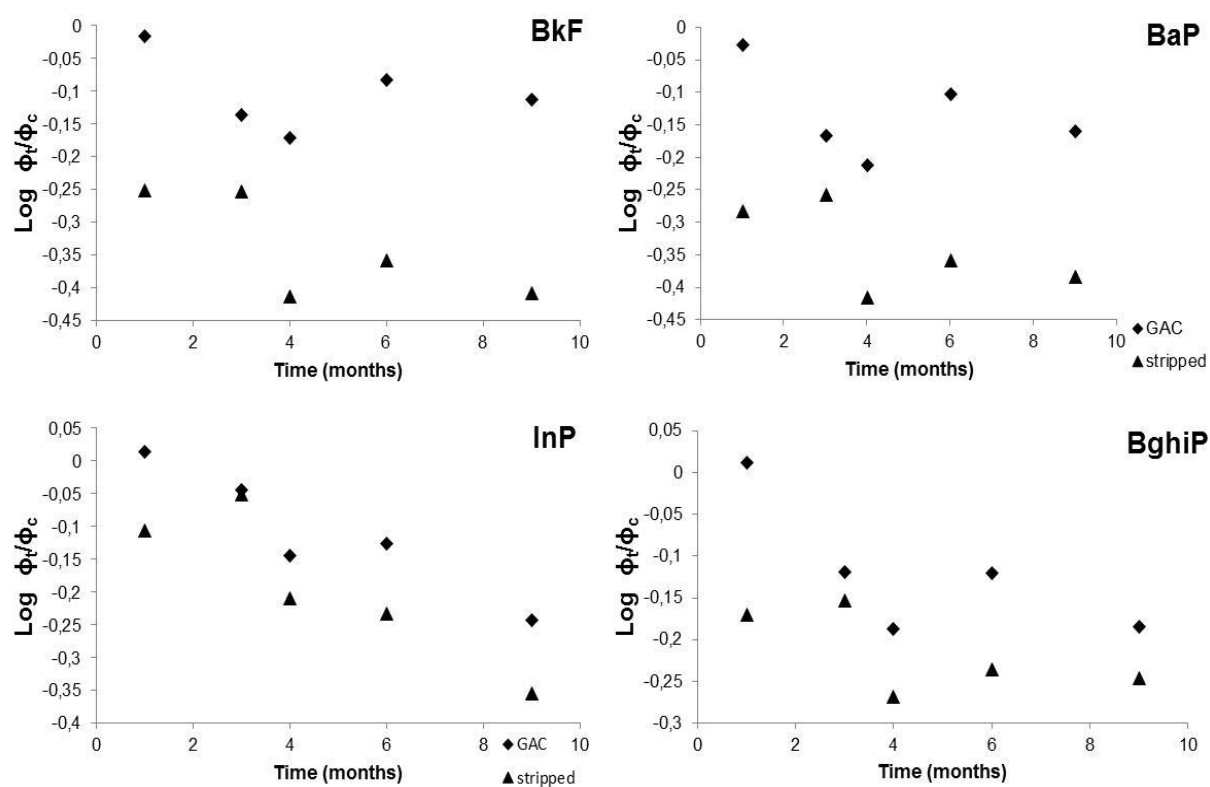


Figure S2. PAH $\log \phi_t/\phi_c$ ratios (flux in the AC treated sediment ϕ_t divided by the flux in the non-amended control ϕ_c) plotted as a function of time in the PAC (●), GAC (◆) and stripped (▲) sediment. Missing data for PAC relate to non-detects caused by strong PAH sorption to PAC.

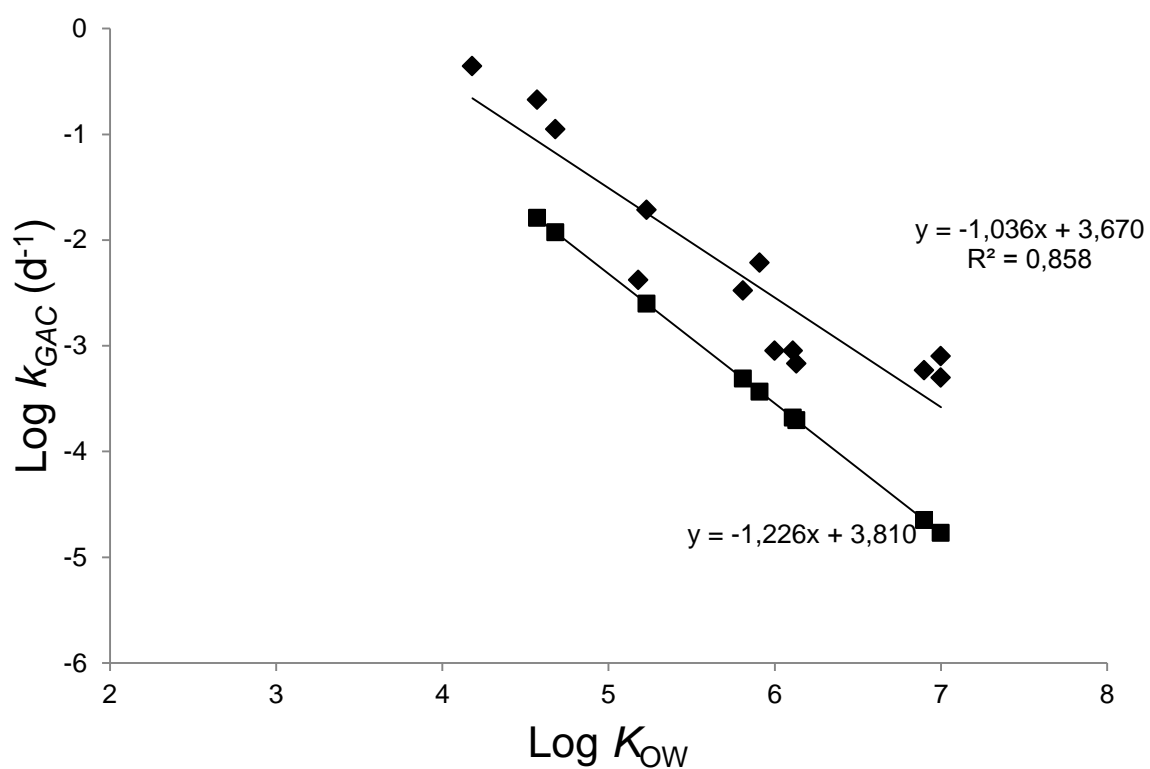


Figure S3. Comparison of the fitted dependence of PAH adsorption rate constants ($\text{Log } k_{\text{GAC}}$) at $n_F = 1$ for sorption to GAC in the presence of Biesbosch sediment with $\text{log } K_{\text{OW}}$ (■) and previously reported data for Petroleum Harbor sediment (◆) [8].

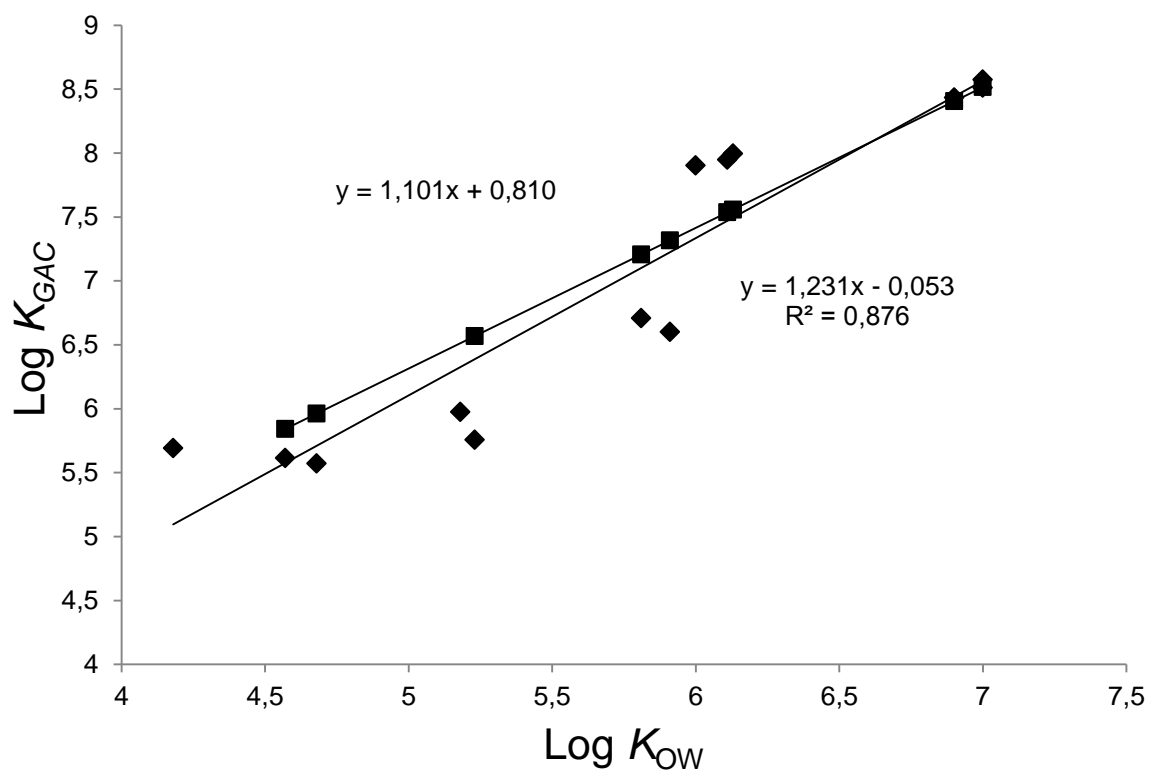
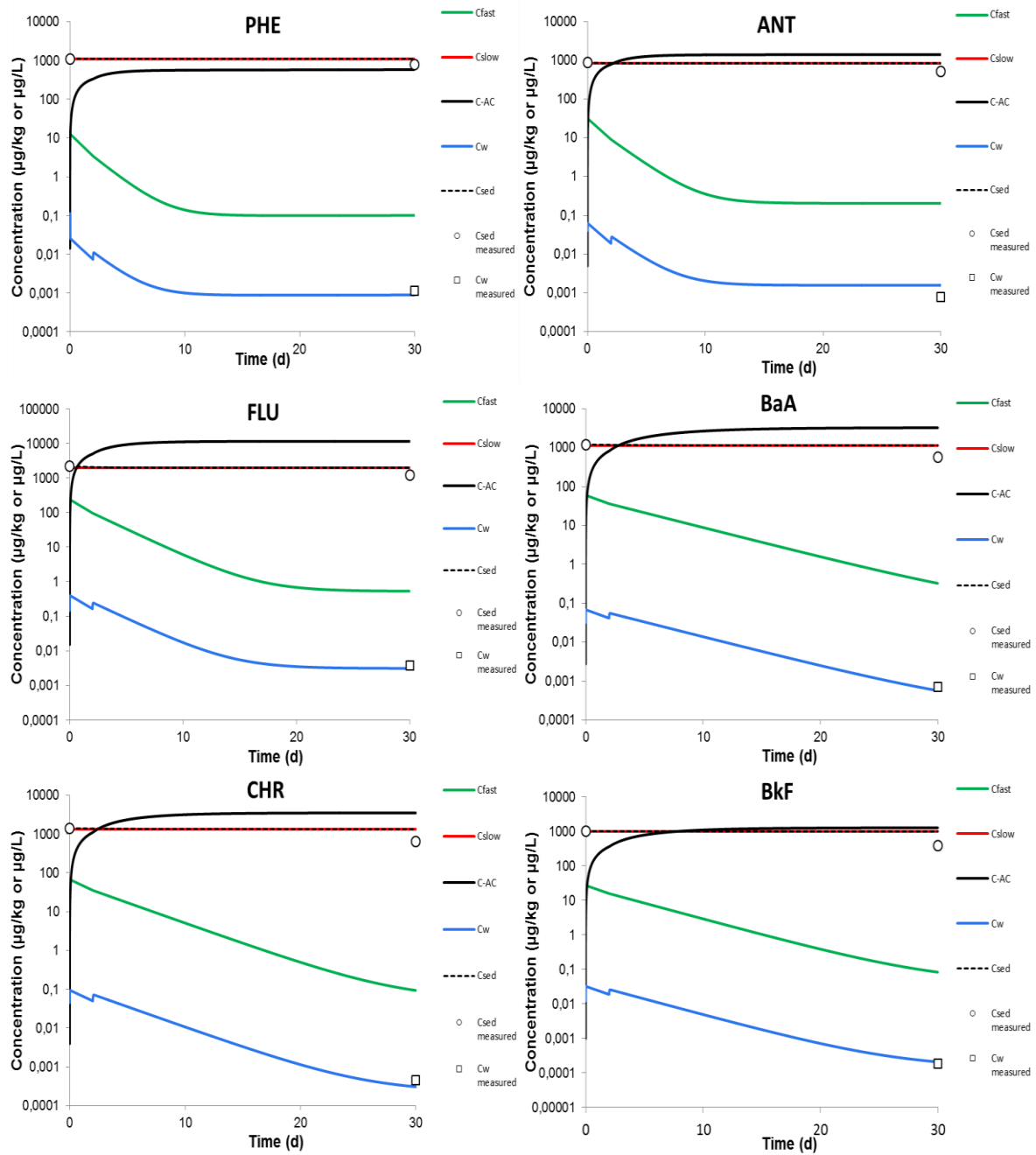


Figure S4. Comparison of the fitted dependence of PAH adsorption affinity constants ($\text{Log } K_{\text{GAC}}$) at $n_{\text{F}} = 1$ for sorption to GAC in the presence of Biesbosch sediment with $\text{log } K_{\text{OW}}$ (■) and previously reported data for Petroleum Harbor sediment (♦) [8].



Equilibrium and kinetic modeling of contaminant immobilization by AC amended to sediments

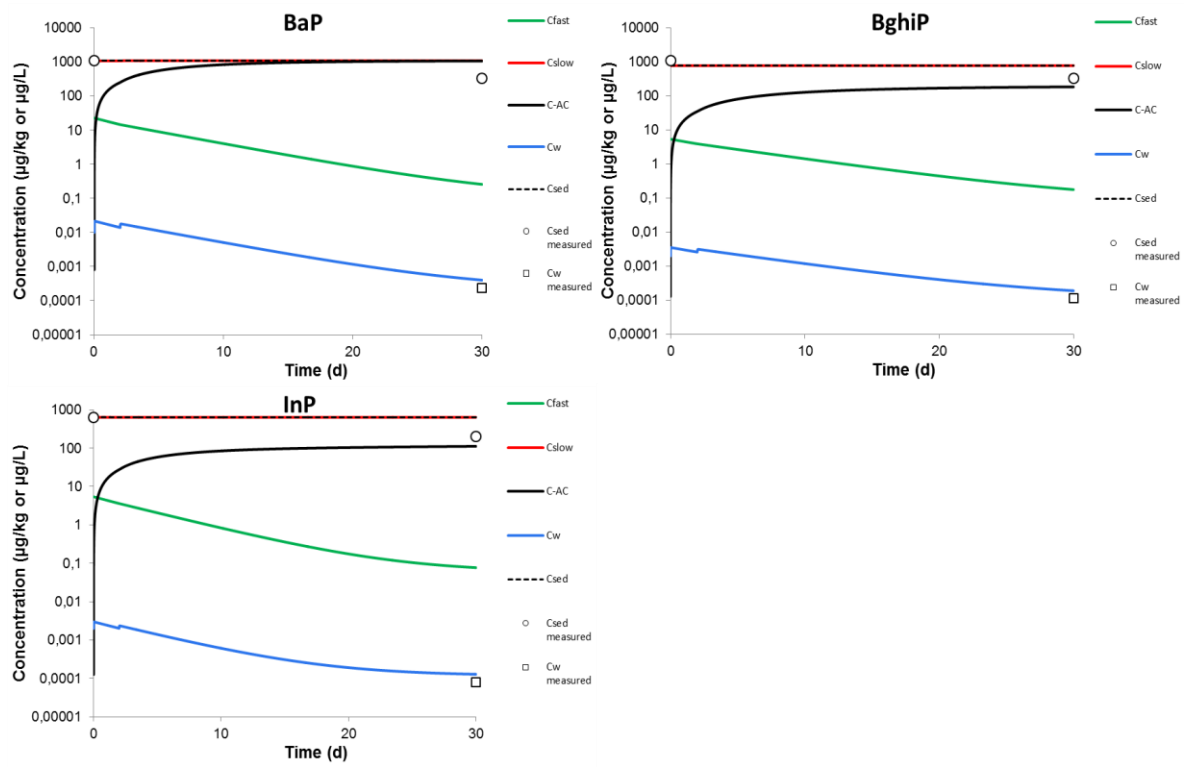


Figure S5. Concentrations of PAH in Biesbosch sediment and GAC (4%) as a function of time. Dashed lines represent modelled values by using Eq. S1-S4. ($n_F = 1$), whereas markers represent measured data. The dashed C_{sed} line is calculated as the sum of the modelled C_{fast} and C_{slow} curves.

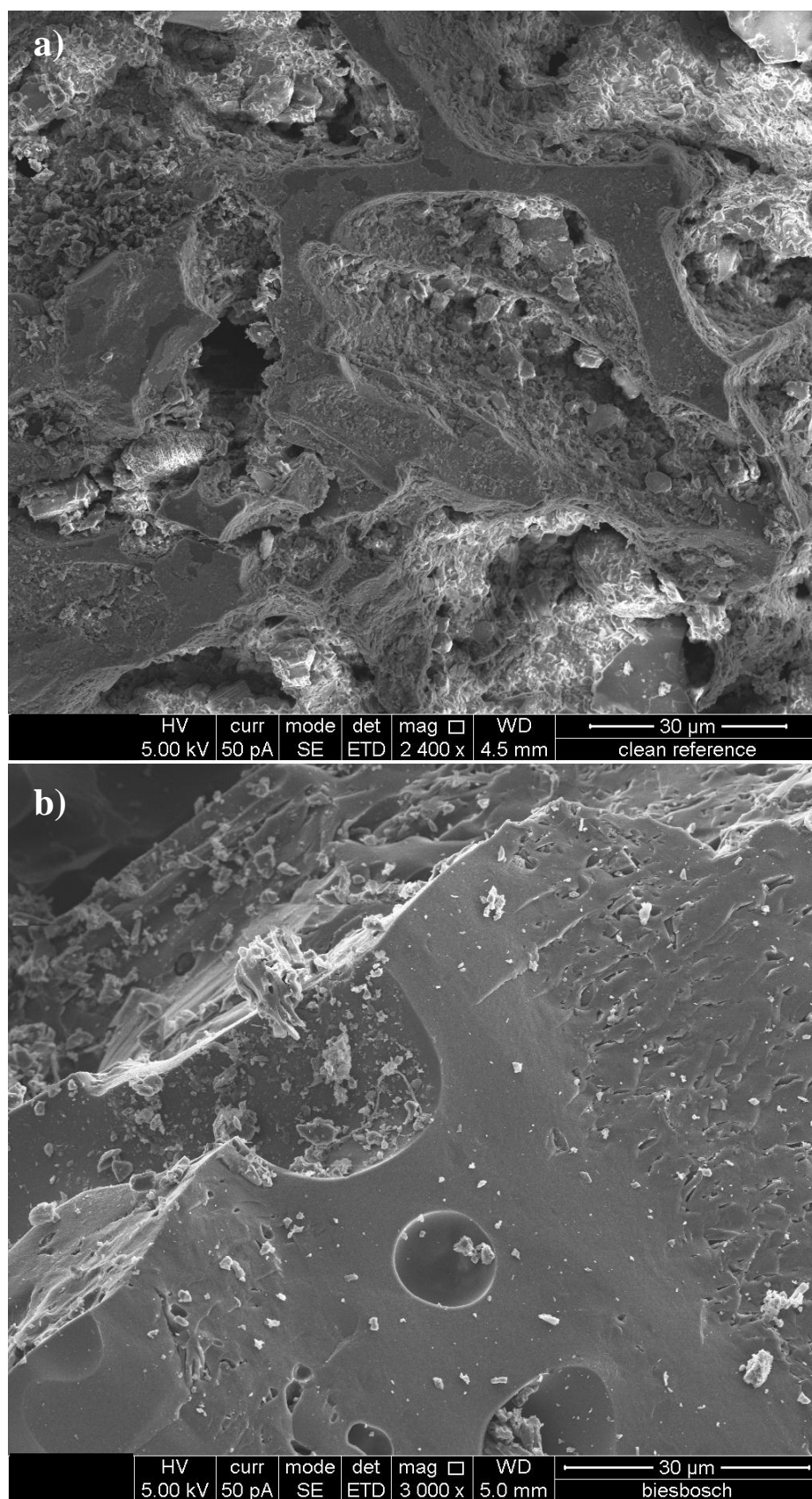


Figure S6. Scanning Electron Microscopy images of a) virgin GAC and b) after sediment stripping.

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CHAPTER 7

In situ treatment with activated carbon reduces bioaccumulation in aquatic food chains

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ABSTRACT

In situ activated carbon (AC) amendment is a new direction in contaminated sediment management, yet its effectiveness and safety have never been tested on the level of entire food chains including fish. Here we tested the effects of three different AC treatments on hydrophobic organic chemical (HOC) concentrations in pore water, benthic invertebrates, zooplankton and fish (*Leuciscus idus melanotus*). AC treatments were: mixing with powdered AC (PAC), mixing with granular AC (GAC), and addition-removal of GAC (sediment stripping). The AC treatments resulted in a significant decrease in HOC concentrations in pore water, benthic invertebrates, zooplankton, macrophytes and fish. In 6 months, PAC treatment caused a reduction of accumulation of polychlorobiphenyls (PCB) in fish by a factor of 20 bringing pollutant levels below toxic thresholds. All AC treatments supported growth of fish, but growth was inhibited in the PAC treatment, which was likely explained from reduced nutrient concentrations, resulting in lower zooplankton (i.e., food) densities for the fish. PAC treatment may be advised for sites where immediate ecosystem protection is required. GAC treatment may be equally effective in the longer term and may be adequate for vulnerable ecosystems where longer term protection suffices.

INTRODUCTION

Aquatic sediments are recognized to be a sink for many hydrophobic organic chemicals (HOCs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) [1]. In Europe, the Water Framework Directive requires surface waters to be chemically and ecologically healthy and safe [2]. In many cases contaminated sediments pose a threat to this desired state, such that remediation is needed. Traditional methods for sediment remediation include natural attenuation or sediment removal by dredging or *in situ* capping [3]. However, these methods do not always sufficiently reduce contaminant transport and bioavailability. Moreover, the latter approaches are energy-intensive, expensive and disruptive [3].

Sediment amendment with carbonaceous materials like activated carbon has received increasing attention over the past decade [4, 5]. Early laboratory experiments showed that activated carbon strongly binds HOCs present in the sediment and thus reduces available concentration of the contaminants [6-9]. So far, the effectiveness of *in situ* AC amendments mainly has been shown for reduction of HOC pore water concentrations and concentrations in benthic invertebrates. We are aware of only one pioneering study addressing AC effects on accumulation by fish [9]. Three decades ago, Shea et al. [9] tested the effects of AC on PCB accumulation in short term (5 d) laboratory exposures using goldfish and found a 70.9 to 99.9% reduction in PCB fish concentrations. It is not clear however, whether such reductions are feasible in outdoor field scale aquatic systems, where complex processes and factors such as varying food web composition and food ingestion are highly intertwined [10-12]. Furthermore, AC amendments should not only be efficient in reducing exposure to HOCs but

also be ecologically safe. So far, biological side effects of AC amendments have been studied mainly for benthic invertebrates [5, 13-17]. We are not aware of any studies that address biological effects on fish or that consider the entire food chain. Consequently, there is a need for ecosystem scale studies evaluating the effectiveness of AC that also address side effects on higher trophic levels such as zooplankton and fish. Because different AC types, i.e. granular and powdered activated carbons, may differ in effectiveness and ecological side effects [18-20], alternative AC treatments need to be evaluated.

The primary aim of the present study was to assess the effectiveness of AC in reducing HOC concentrations in pore water, in invertebrates, zooplankton, and in fish, taken from natural aquatic food chains, for three AC treatments: mixing sediment with powdered AC, mixing sediment with granular AC, and mixing sediment with granular AC with subsequent removal of granules, i.e. sediment stripping [21]. A Second aim was to assess biological side effects of AC amendments for these scenarios, by evaluating functional groups abundances, lipid contents and condition factors of the biota.

To accomplish these aims, natively contaminated sediment was dredged, transported to a test site, homogenized and inserted in control (untreated) or AC treated systems. The resulting outdoor ecosystems were designed to mimic full scale natural ditches in The Netherlands. Concentrations of PCBs and PAHs were monitored in sediment and pore water, as well as PCBs present in macrophytes, zooplankton, benthic macroinvertebrates, and fish over time. Pore water concentrations were measured using polyoxymethylene (POM) passive samplers, inserted in sediment samples agitated in the laboratory, thus measuring concentrations forced towards 28 d (pseudo-) equilibrium. Additionally, *in situ* pore water concentrations were measured using stationary SPME fibers, inserted in undisturbed cores for 30 d, thus sensing the true *in situ* concentration. By combining the two approaches, the state of equilibrium in the AC-sediment-water systems can be evaluated.

MATERIALS AND METHODS

Chemicals and materials

Virgin powdered coal-based activated carbon SAE Super (particle size 1-150 μm) and granular activated carbon GAC 1240W (0.425 - 1.70 mm) were a kind gift from Norit Activated Carbon, Amersfoort, The Netherlands. Details on other chemicals, materials, and pretreatment of materials are provided as Supporting Information.

Study area and remediation scenarios

The field experiment was conducted from December 2011 to September 2012. In December 2011 forty four metric tons of sediment (d.w. 53%, bulk density 1.7 t/m^3) were dredged from The Biesbosch National Park and transported to the experimental facility at the Sinderhoeve, Renkum, The Netherlands, where four identical ditches (15 m length, 1.5-2 m width, 1 m depth) were prepared prior to the experiment. The sediment was sieved on a 20 mm sieve, diluted with groundwater to 20% d.w., homogenized for 4 h, after which 25% of the sediment

was pumped into ditch 1 (untreated sediment) and 25% of the sediment into ditch 2. Powdered activated carbon (170 kg) was added to the sediment in ditch 2 to obtain 4% d.w. in the total volume of the sediment (PAC-sediment). Granular activated carbon (340 kg) was added to the remaining 50% of the sediment and homogenized for 3 h. Then, half of this mixture (25% of the original sediment quantity) was pumped into ditch 3 (GAC treatment). The other half of this mixture was homogenized for 48 h, after which the GAC was sieved out with a 1 mm sieve. The resulting stripped sediment was pumped into ditch 4 (stripped sediment). Because of the large quantities of sediment, industrial sieves (1.6x1.0 m, mesh size 1 mm) and two electric submersible pumps, i.e. Tsurumi Pump KTV2-80 (400V, 50Hz, 3-phase 80 mm hose coupling), were used on site.

After three months of acclimatization, in March 2012 every ditch was divided into three compartments by inserting non-permeable EPDM rubber curtains. In order to establish an invertebrate community, the test systems were seeded with a mix of invertebrates, mainly comprising macrocrustaceans (i.e., Asselidae and Gammaridae), microcrustaceans (cladocerans, copepods, and rotifers), snails (primarily *Lymnaea stagnalis*), dipterans (e.g., Chironomidae) and worms (*Lumbriculus variegatus*). All animals but worms, originated from uncontaminated ditches located at the Sinderhoeve test site. *Lumbriculus variegatus* was cultivated in house (for details see ref [19]). Golden Orfe (*Leuciscus idus melanotus*) was purchased from KoiDream, Veenendaal, The Netherlands. The fish comprised 1 year old animals, reared in outdoor ponds. Five days after introduction of the invertebrates, the fish were transported in plastic bags (containing rearing pond water) to the experimental test site. After acclimatization for 20 minutes they were released into their test compartment (10 individuals per compartment). The ditches were covered with metal fences to prevent predation by piscivorous birds. Macroinvertebrates and fish were analyzed for background levels of PCBs. The concentrations of individual congeners were very close to levels of quantification (Figure 1c,d).

Sampling

Samples were taken at six times (Figure S1). To determine total sediment concentrations as well as equilibrium (POM-SPE) PAH and PCB pore water concentrations, representative mixed sediment samples were taken from each ditch with a Jenkins core sampler (ø 4 cm). Sediment samples for *in situ* equilibrium (SPME) pore water concentrations were taken from each compartment with a Jenkins core sampler (ø 6 cm).

Fish was sampled by means of electrofishing equipment (Deka-Gertebau, Germany) and then sacrificed using metacaine (MS-222). Fish length and weight were measured on the same day, after which the fish samples were stored at -20°C until analysis. All fish operations were carried out by certified animal experts. Macroinvertebrates were sampled with a standard dipnet (mesh size 500 µm), sieved on a 1 mm sieve, sorted on site and then stored at -20°C until analysis. Macroinvertebrate samples taken after 1 month from the ditch with stripped sediment were lost during chemical analysis. To take zooplankton samples, 120 L of overlying water was filtered over a plankton net (mesh size 55 µm, Hydrobios, Kiel,

Germany). The same day, zooplankton samples were brought to the laboratory and filtered through glass microfibre filters (GF/C, Whatman, Maidstone, Kent, UK). Zooplankton was operationally defined by the specified sampling and filtration procedures (i.e. water column solids > 55 µm), and therefore may also contain some algae, suspended solids and detritus. Consequently, zooplankton samples were analysed for total organic carbon (TOC) rather than for lipids. The samples for TOC determination in zooplankton were analysed immediately. Samples for PCB analysis were stored at -20°C until analysis.

Sediment samples were analysed for total organic carbon, metals, PCB and PAH concentrations and PCB and PAH pore water concentrations. Fish, invertebrate and macrophyte samples were analysed for PCBs and lipid contents. Zooplankton samples were analysed for PCBs and TOC content.

Analytical procedures

Total contaminant concentrations in the sediment. Metals, mineral oil, PAH and PCB were analysed by the certified laboratory OMEGAM (Amsterdam, the Netherlands).

PAH and PCB concentrations in pore water. Details on the chemical and instrumental analyses are provided as Supporting Information. In short, PAH and PCB concentrations in sediment pore water were determined *ex situ* using the POM-SPE method [22] and *in situ* using a solid phase micro extraction (SPME) method [23]. The 76 µm POM strips were extracted using an Accelerated Solvent Extractor (ASE) and analysed for PCBs using GC and for PAHs using HPLC.

Biota analyses. PCBs in invertebrate, zooplankton, and fish samples were ASE extracted and analysed with GC. Method and quality assurance details are provided as Supporting Information.

Data analysis

To assess the health of fish from the test systems, Fulton's condition factor [24] and the Von Bertalanffy growth parameter [25] were used.

Fish condition factors (K) were calculated from fish weight (W ; g), and length (L ; cm) using Fulton's Condition Factor formula [24]:

$$K = 100 \frac{W}{L^3} \quad (1)$$

The growth rate of the fish was estimated with the Von Bertalanffy growth function [25]:

$$L_t = L_\infty \left(1 - e^{-K(t-t_0)}\right) \quad (2)$$

where L_t is the length at age t , L_∞ is the asymptotic length, K is a time constant (d^{-1}), and t_0 is the theoretical age of the fish at length zero (for details see Supporting Information).

Bioaccumulation factors (BAF, L/kg lipids) were calculated as [26]:

$$BAF = \frac{C_{biota,lipid}}{C_w} \quad (3)$$

where $C_{biota,lipid}$ is the lipid normalized (or in case of zooplankton, TOC normalized) PCB concentration in biota (ng/kg lipids), and C_w is the aqueous PCB concentration (ng/L). Biomagnification factors were calculated as [26]:

$$BMF = \frac{C_{fish,lipid}}{C_{prey,lipid}} \quad (4)$$

where $C_{fish,lipid}$ is the lipid normalized PCB concentration in fish (ng/kg lipids) and $C_{prey,lipid}$ is the lipid normalized PCB concentration in prey (ng/kg lipids).

Statistical tests (one-way ANOVA followed by Tukey's post-hoc test, $p = 0.05$) were performed using IBM SPSS Statistics 20 (SPSS, Chicago, IL, USA). Linear regression analyses were performed in Microsoft Excel 2010 (Microsoft Corporation, Redmond, WA, USA). The null hypothesis (no difference between treatments) was rejected when $p < 0.05$. Results were reported as a trend if $0.05 < p < 0.10$.

RESULTS AND DISCUSSION

Effects of activated carbon on total and bioavailable concentrations of contaminants

PAH and PCB concentrations in sediment. Σ_{10} PAH and Σ_{11} PCB in the Biesbosch sediment were 11 mg/kg and 700 μ g/kg, respectively (Table S1). Furthermore, concentrations of PAH, PCB and metals were a factor of 10, 32 and 40, above threshold effect levels, respectively (Table S1) [27, 28]. For the untreated sediment, total concentrations of PAH and PCB did not change significantly over time (Figure S2), which means that no substantial chemical or biological degradation occurred for these compounds.

Pore water concentrations. POM-SPE based pore water concentrations of PAHs and PCBs were determined *ex situ* after equilibrating sediment for 28 d. After 9 months, sediment treated with PAC, GAC, and GAC sediment stripping resulted in Σ_{13} PAH reductions by ~100, 93, and 97% (Figure S3a). Σ_{18} PCB concentration in PAC, GAC, and stripped sediment decreased by 100, 70 and 83% in a month, respectively, and even further to ~100, 83, and 91% after 4 and 9 months (Figure S3b). Treatment effectiveness was higher for PAH than for PCB (Figure S3, Figure S4 and S5), which is explained by the higher affinity and thus higher sorption of PAH to AC due to the higher planarity and molecular surface area of PAHs compared to PCBs [29, 30]. At roughly equal dosages, i.e. 4% d.w., PAC reduced the aqueous concentrations faster than GAC, probably due to the larger external surface area of the PAC particles and the short intra- and interparticle diffusive path lengths [18]. Thus, sequestration

by GAC will require a significantly longer contact time of months to years before the maximum reduction of pore water concentration is reached. The efficiency of AC treatments after 9 months decreased with increasing $\text{Log}K_{OW}$ of the compounds. Compounds with higher $\text{Log}K_{OW}$ have lower effective diffusion coefficients and thus are sequestered more slowly by AC. Consequently, their bioavailability is less affected by the added sorbent, and they require longer time to achieve bioavailability reductions similar to those with lower $\text{Log}K_{OW}$.

Pore water concentrations of PAHs were also measured *in situ* with SPME fibers. For PCBs, all concentrations were below detection limits. Sediment treatments with PAC, GAC, and sediment stripping with GAC resulted in *in situ* $\Sigma_{13}\text{PAH}$ reductions of on average ~100, 50, and 90% (Figure S3c, Figure S6). After 1 month, PAH pore water concentrations in the untreated sediment were two times higher than at the later time points. This could be attributed to the fact that the first sampling was performed immediately after sediment pretreatment (homogenization and dilution). Sediment agitation could have led to mobilization of PAH resulting in initially higher pore water concentrations. SPME-based *in situ* pore water concentrations were observed to decrease in time in all treatments, indicating non-equilibrium conditions (Figure S3c). Generally, *in situ* pore water concentrations measured with SPME were lower than those measured with POM-SPE (Figure S7), even considering the uncertainty in the data, (i.e. SD of $5.1 \pm 4.1\%$ for POM-SPE and $12 \pm 7.8\%$ for SPME). The difference was within one order of magnitude for less hydrophobic PAHs and 2 to 2.5 orders of magnitude for more hydrophobic PAHs. There are two possible explanations for the difference. First, there could be actual disequilibrium between sediment and pore water: that is, the *in situ* SPME pore water concentrations could have been lower than the equilibrium value, and detected as such by SPME. This would imply that PAHs are desorbing from the (treated) sediment rather than being transported to the sediment. Agitation for a month as is done with the POM-SPE method then would accelerate desorption, thus explaining the higher pore water concentrations measured in POM strips. Alternatively, it could be possible that sediment and pore water were in equilibrium, but that 1 month static exposure to the SPME fiber was insufficient for the PAH to reach equilibrium with the fiber. This would explain the lower concentrations inferred from SPME, as well as the larger difference for hydrophobic PAHs, as the uptake rates by SPME fibers are lower for chemicals that are more hydrophobic. We argue that this second explanation is more plausible for the following reasons. In the first place, lower than equilibrium pore water concentrations are not plausible for the natively contaminated untreated Biesbosch sediment. For the treated sediments, addition of AC results in transport to the solid phase, which implies that if non-equilibrium would exist, *in situ* pore water concentrations would be higher than equilibrium values rather than lower. The second explanation assumes non-equilibrium between the fiber and the pore water, which is plausible because polyacrylate coated SPME fibers were used, which have a higher partition coefficient and a lower surface area than PDMS coated fibers deployed previously [31]. Polyacrylate was required to be able to detect the low PCB concentrations in the pore water. However, this also requires much longer equilibration times in order to fully load the samplers under stationary conditions. In some sediments, it has been

shown that equilibrium may not be completed even after 7 weeks [31]. Because of the uncertainties with respect to the SPME data the subsequent interpretation of bioaccumulation use the POM-SPE data, which can be assumed to reflect the equilibrium pore water concentration especially for the later time points.

Effect of activated carbon on biota

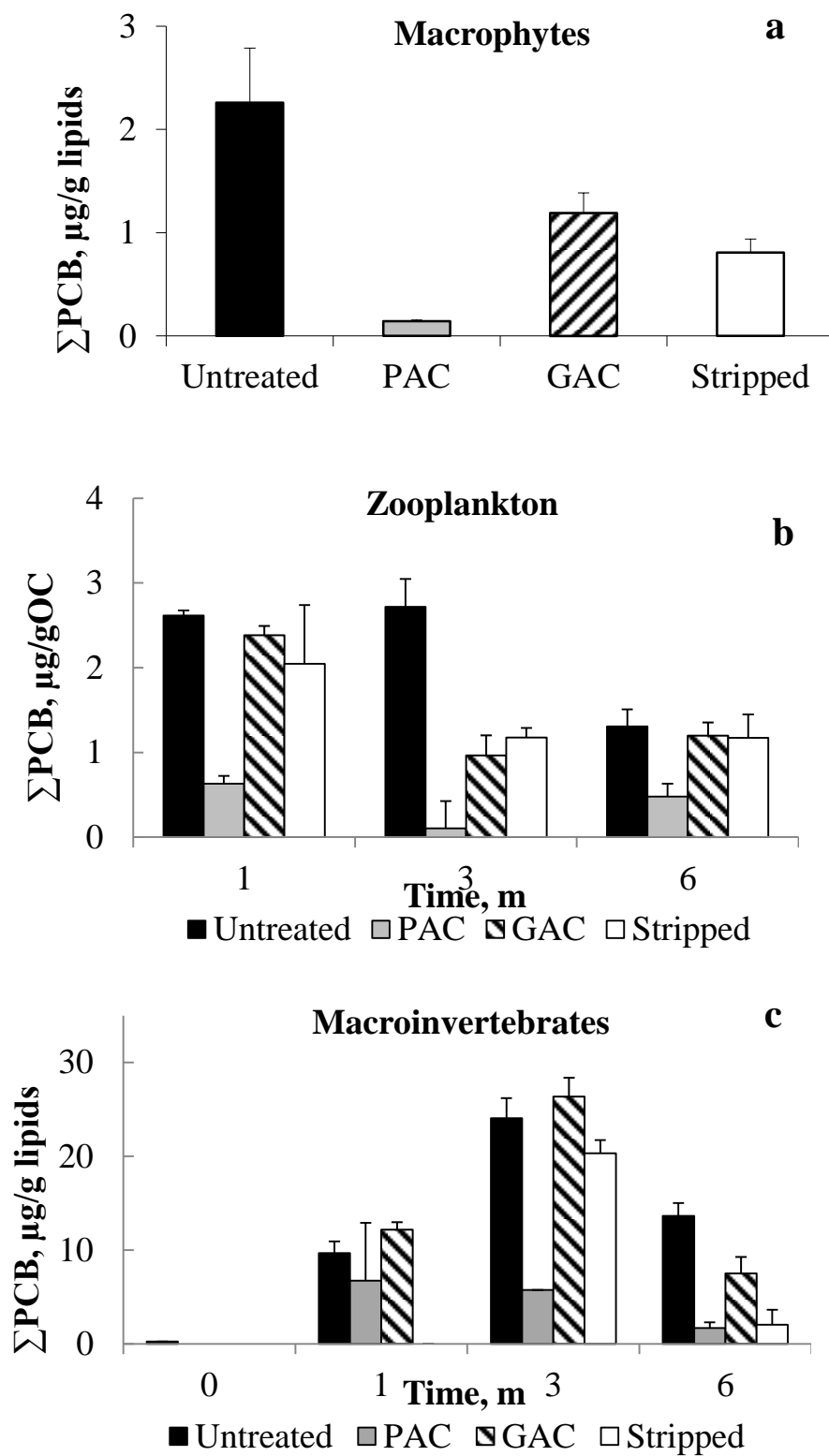
Macrophytes. In the ditch with untreated sediment, *Elodea nuttallii*, *Myriophyllum spicatum* and filamentous algae were observed, whereas the PAC ditch was dominated by pond weed (*Potamogeton sp.*). The GAC and stripped sediment ditches were dominated by algae. Total biomass of macrophytes was significantly different between treatments (Figure S8a, one-way ANOVA, $F(3,8)=4.367$, $p=0.042$). This may be explained by treatment-dependent decreases in nutrient availability. No effect of AC treatment was found on lipid content of the macrophytes (Figure S8b, $F(3,8)=0.501$, $p=0.692$).

Lipid normalized $\sum_{31}\text{PCB}$ concentrations in macrophytes followed the order untreated>GAC>stripped>PAC-sediment (Figure 1a) and correlated positively with PCB pore water and sediment concentrations ($p=0.001$ for both variables). To our knowledge, these are the first reported data on effects of AC amended sediments on HOC uptake, growth and lipid content of macrophytes.

The LogBAF values calculated for macrophytes ranged from 4.8 to 6.9 and showed a linear increase with $\text{Log}K_{ow}$: $\text{LogBAF}=(1.05\pm0.11)\text{Log}K_{ow}-(1.13\pm0.75)$, $R^2=0.686$, $p=1.3\cdot10^{-11}$ (Figure S11a-c), implying that uptake by macrophytes proceeded through a simple linear partitioning mechanism [32]. Consequently, no clear treatment effect on bioaccumulation factors was observed.

Zooplankton. Zooplankton was dominated by cyclopoid copepods and the cladoceran *Chydorus sphaericus*. Zooplankton biomass showed a slight increase in time, which probably reflects natural seasonal variability (Figure S9a). Zooplankton biomass was higher in GAC-treated sediment. However this was statistically significant only for the data after 3 months (one-way ANOVA, $F(3,7)=16.28$, $p=0.002$). It can be hypothesized that zooplankton density is positively related to nutrient availability (Figure S10). After all, the availability of the phytoplankton the zooplankton feed on depends on these nutrients. A positive trend was indeed found between zooplankton biomass and PO_4 concentration in the overlying water (linear regression, $p=0.058$).

TOC normalized concentration of $\sum_{19}\text{PCBs}$ in zooplankton in different treatments followed the order untreated>GAC>stripped>PAC sediment after 1 month, and untreated>GAC/stripped>PAC sediment after 3 and 6 months (Figure 1b), and significantly correlated with PCB pore water concentration ($p=0.009$). These are the first reported data on the effectiveness of AC treatments in reducing PCB bioavailability for zooplankton.



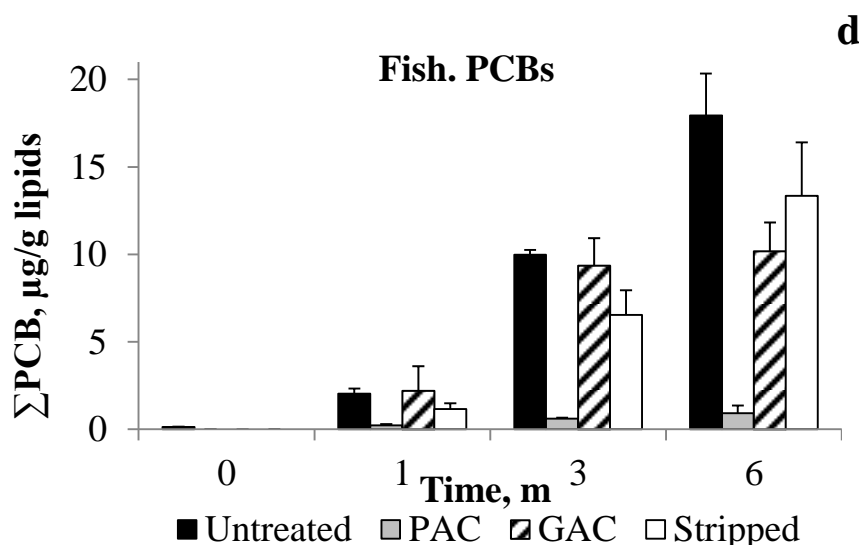


Figure 1. TOC-normalized Σ PCB concentrations in zooplankton and lipid-normalized Σ PCB concentrations in macrophytes, macroinvertebrates, and fish from the ditches with untreated, PAC-, GAC-, and stripped sediment, after 0, 1, 3, and 6 months of exposure (i.e. 3, 4, 6, and 9 months post treatment). Error bars relate to SD ($n=3$).

To study the net accumulation of PCBs by zooplankton through all exposure pathways, bioaccumulation factors (BAF) were calculated according to eq 3. LogBAFs increase linearly with $\text{Log}K_{OW}$ till $\text{Log}K_{OW}$ is approaching 7, after which the curves level off or even decline (Figure S11d-f). The relationship between LogBAF and $\text{Log}K_{OW}$ was significant with a linear model ($\text{LogBAF}=(1.48\pm0.08)\text{Log}K_{OW}-(3.77\pm0.52)$, $p=1.6\cdot10^{-42}$; $R^2=0.708$). The leveling off is sometimes explained from binding of PCBs to DOC, which increases the apparent aqueous phase concentration [33, 34]. This artifact however, plays no role because the POM strips only detected the truly dissolved PCBs. The leveling off could also be explained by slow uptake by the biota, i.e. non-equilibrium, which however is not likely given the long natural equilibration times and the small size of the zooplankton species. We therefore hypothesize that the leveling off and downward curvature may be explained by limited availability, i.e. rate-limited release from the sediment [19, 35]. After 1, 3 and 6 months, the BAF values are similar (Figure S11d-f) whereas the exposure concentrations vary considerably among treatments (Figure S3). This shows that the treatments affect exposure, but probably not the mechanisms underlying the accumulation, i.e. algae or particle ingestion rates or kinetics of zooplankton-water partitioning. The differences among treatments are limited although an order of magnitude random scatter is observed. This may be explained by variation in zooplankton composition among ditches due to macrophytes development or random error due to sampling and analysis. Again it is unlikely that this is explained by slow bioconcentration into zooplankton. On the short term, i.e. in the first weeks post treatment, zooplankton equilibrates with PCBs in the overlying water, whereas in the pore water, concentrations rapidly drop due to binding to PAC and GAC. This implies that the measured

sediment pore water concentrations do not accurately resemble the higher overlying water concentrations to which the zooplankton is exposed. Consequently, the 1 month calculated BAF values may be too high. This mechanism would imply that the difference is the least for untreated sediment, which indeed is true (Figure S11d-f).

Another explanation may relate to the inadequacy of the POM-SPE method to detect *in situ* pore water concentrations if pore water is not in equilibrium with the sediment particles. It is plausible that after 3 and 6 months of exposure (i.e. 6 and 9 months post treatment) the sediment pore water is closer to sorption equilibrium than after 1 month (i.e. 4 months post treatment). This means that after 3 and 6 months the data measured with POM more closely reflect the true pore water concentration. However, 1 month agitation with POM would still stimulate sorption to (treated) sediment, leading to an underestimation of the actual *in situ* pore water concentration and an overestimation of BAF. If indeed the 1 month BAF data would be one order of magnitude lower, they would more or less coincide with the 3 month BAF data.

Macroinvertebrates. After 1 month, macroinvertebrates were mainly represented by Chironomidae and some snails (*Lymnaea stagnalis*). The lipid contents of invertebrates were different between treatments (untreated>PAC>GAC>stripped, one-way ANOVA, $F(3,8)=7.267$, $p=0.011$) (Figure S12). This clear treatment effect could partly be explained by treatment effects on species fitness, by treatment induced community shifts, or both. After 3 months, only Chironomidae were found, which did not show big variations in lipid content. A factor 2 lower lipid content was detected in the samples from PAC-sediment only (one-way ANOVA, $F(3,8)=7.648$, $p=0.010$). It has been argued before that sediment amendment with PAC may change the dietary condition of deposit feeders by reducing the nutritional value of the sediment [16, 36]. In order to avoid starvation, deposit feeders may start to live on their own lipids [8, 37]. After 6 months of exposure, diversity and abundance of the benthic communities were higher than after 1 and 3 months, suggesting that time is the most important factor for community recovery in sediment treated with AC, as was recently reported [16]. Regardless of the treatment, observed taxa were Anisoptera, Notonectidae, Chironomidae, Lumbricidae, Asellidae, Lemnidae, and Hirudinea. The lipid contents of invertebrates did not differ among treatments (one-way ANOVA, $F(3,8)=3.086$, $p=0.090$).

PCB analysis revealed that the most abundant congeners in the macroinvertebrate samples were CB-101, 138, 149, and 153 (Figure S13e). In general a good agreement between PCB profiles in sediment and invertebrates was observed, which suggests that sediment was a primary source of PCBs to invertebrates. Correlations between PCB concentration in invertebrates and sediment or pore water were positive and highly significant ($p=4.2\cdot10^{-5}$ and 0.002, respectively), which is in line with earlier findings [38, 39]. The concentration of the Σ_{19} PCBs in macroinvertebrates after 1 month of exposure was 9.5 $\mu\text{g/g}$ lipids (ranging from 4.6 to 14.7 $\mu\text{g/g}$ lipids) and, again remarkably, did not differ between treatments (one-way ANOVA, $F(3,6)=1.167$, $p=0.373$) (Figure 1c). So, although POM-SPE based pore water concentrations were reduced, especially in the PAC treatment (Figure S3b), exposure to the

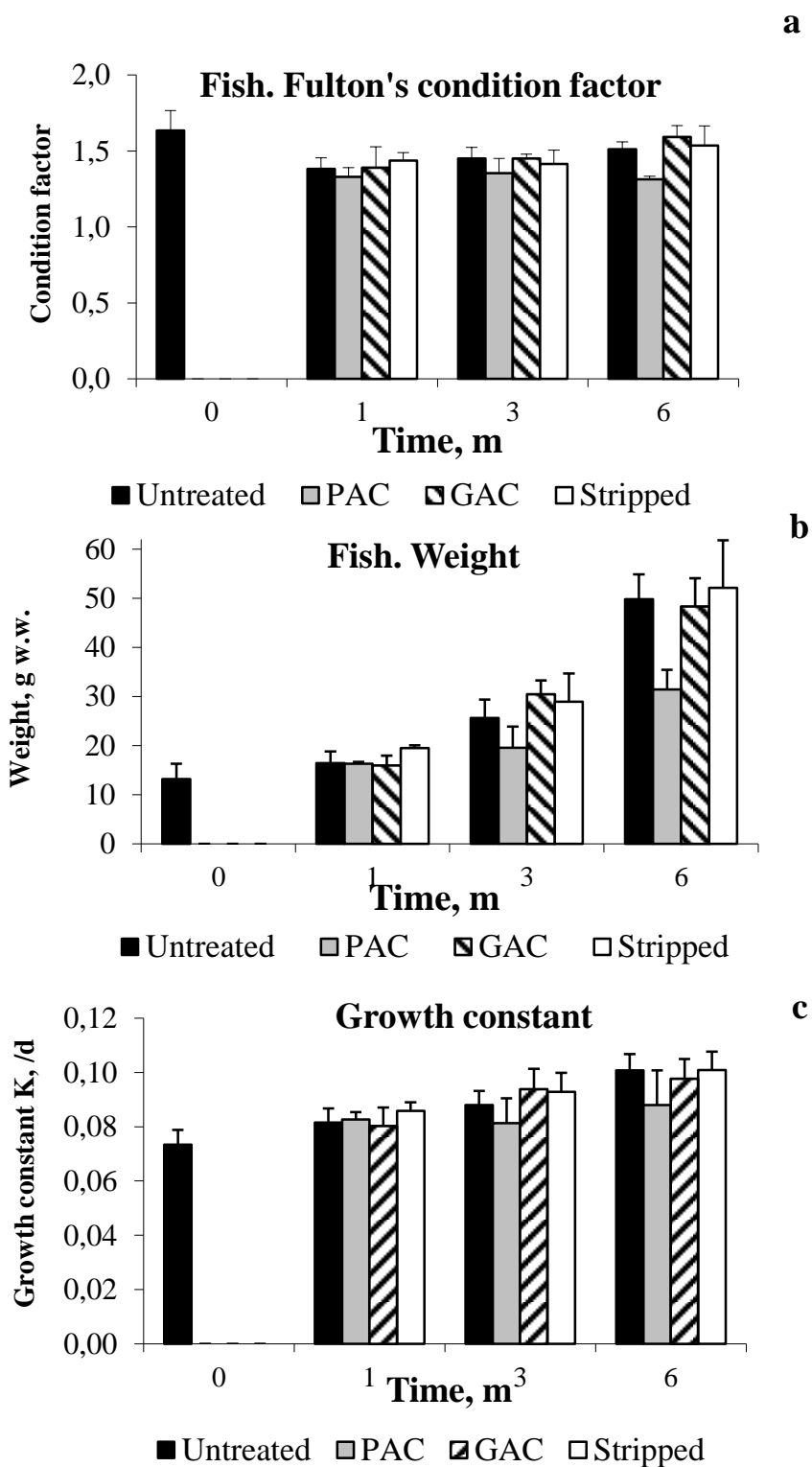
invertebrates was not. We hypothesize that POM based equilibrium concentrations for this time point may have underestimated the actual bioavailable *in situ* pore water concentrations, due to sediment-pore water non-equilibrium as was mentioned above. Treatment effects were visible for PAC after 3 months (one-way ANOVA, $F(3,8)=13.36$, $p=0.002$), and for all treatments after 6 months of exposure ($F(3,8)=19.70$, $p=4.7 \cdot 10^{-4}$) (Figure 1c). The observed decrease in the $\sum_{19}\text{PCBs}$ might be due to a biodilution mechanism, i.e. increase in lipid content as a result of changes in benthic community composition as discussed above.

LogBAF values calculated for macroinvertebrates ranged from 4.4 to 8.3 and showed a linear increase with $\text{Log}K_{ow}$: $\text{LogBAF}=(1.90 \pm 0.10)\text{Log}K_{ow}-(5.70 \pm 0.69)$, $R^2=0.708$, $p=1.35 \cdot 10^{-22}$ (Figure S11g-i). No clear treatment effect on bioaccumulation was observed, which is in line with the lack of difference in $\sum\text{PCBs}$ observed in macroinvertebrates from untreated, GAC, and stripped sediment after 1, 3, and 6 months of exposure. Note that PAC treatment effects on BAF could not be assessed because the pore water concentrations required for calculating BAF values were below detection limits in this treatment.

Fish. Upon introduction to the ditches, one-year-old Golden Orfe had a condition index of 1.64 ± 0.13 (Figure 2a). After 1 and 3 months of exposure to the treated sediments, the condition index was approximately 1.40 ± 0.11 , which is considered a good condition for fish according to standards for salmon and trout. The slightly lower value compared to the fish as received was significant only for the PAC treatment. The differences in fish condition among treatments were significant after 6 months of exposure ($F(3,8)=6.854$, $p=0.013$), yet small. Fish weight increased in time (Figure 2b), with fish in the PAC treatment having a lower body weight compared to other treatments after 6 months ($F(3,8)=6.421$, $p=0.016$). The Von Bertalanffy growth parameter K was calculated for all treatments (for details see Supporting Information) [25]. The results show that K values were $0.10 (\pm 0.01)$ for untreated, GAC and stripped sediment and $0.09 (\pm 0.01)$ for PAC sediment (Figure 2c) which is very close to the Von Bertalanffy growth parameter $K = 0.11$ estimated for mature individuals of *Leuciscus idus melanotus*, i.e. >2 years old [40]. The difference in K between PAC and other treatments was significant ($F(3,35)=4.725$, $p=0.007$), but small. Zooplankton abundance was shown to be lower in the PAC-treatment after 3 months of exposure (Figure S9), which may contribute to the slightly lower value. These results show that sediment treatment with GAC had no effect on the condition and weight of fish, whereas the PAC treatment resulted in a small inhibition of growth. To our knowledge, these are the first reported effects of AC sediment treatment on fish. Fish lipid contents decreased in time due to growth (Figure 2d). Treatment effects on lipid content were not significant ($F(3,8)=3.147$, $p=0.087$, respectively).

PCB analysis in fish showed that the most abundant PCB congeners were 52, 49, 153, 101, and 149. The PCB profile in fish partly resembles that of pore water (presence of lower chlorinated congeners, e.g. 49 and 52) and that of sediment (higher chlorinated congeners, e.g. 149 and 153) (Figure S13). It has been argued that direct uptake from water via the gills is predominant in small fish individuals e.g., early life stages and for low $\text{Log}K_{ow}$ PCB congeners, whereas uptake from food dominates in adult fish and for higher chlorinated PCBs

[23, 41, 42]. One-year-old Golden Orfe feeds mainly on zooplankton, both in pelagic and benthic habitats and thus is subjected to PCB uptake from both food and water.



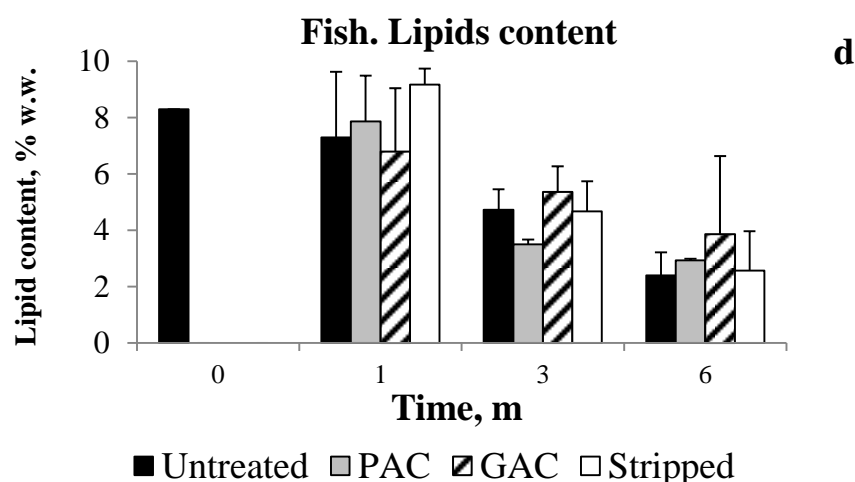


Figure 2. Fulton's condition factor (a), weight (b), Von Bertalanffy growth parameter (c), and lipid content (d) of fish from the ditches with untreated, PAC-, GAC-, and stripped sediment before and after 1, 3, and 6 months of exposure (i.e. 4, 6, and 9 months post-treatment).

The \sum_{31} PCB concentrations in fish from 1 to 6 months of exposure increased from 2 to 18 $\mu\text{g/g}$ lipids in untreated sediment, from 0.2 to 0.9 in PAC sediment, from 2.2 to 10 in GAC sediment, and from 1.2 to 13 in stripped sediment, with levels in the PAC-treatment being statistically lower than those in the other treatments (one-way ANOVA, $F(3,8)=34.59$, $p=6.3 \cdot 10^{-5}$) (Figure 1d). The concentration of individual PCB congeners also increased in time. However, concentration of congeners with low $\text{Log}K_{OW}$ (i.e. CB-28, 31, 47, 49) were observed to level off after 3 months (Figure S14) suggesting equilibrium conditions. The fact that bioaccumulation in fish was lower in the PAC treatment (Figure 1d) does not automatically imply that this is due to PCB binding to AC. After all, the macrophyte biomass increased considerably in the ditches (Figure S8a), and macrophytes may thus have reduced the PCB mass available for uptake by fish, a process referred to as biodilution [10, 11]. We argue that this process was not important for two reasons. First, macrophytes developed only after 3 months, so could have competed for bioaccumulation with other matrices only for 3 months. For macrophytes, the time to reach 95% of steady state ranges from ~ 33 d for tetra-CB and ~ 150 d for hexa-CB, to > 1000 d for higher chlorinated PCBs [32]. Consequently, given the long kinetic time scales for bioaccumulation in macrophytes, 3 months is too short, especially for the higher chlorinated PCBs. Second, the macrophytes had limited binding and storage capacity (i.e. lipid mass) compared to fish. Fish dominated the mass distribution among biological compartments, followed by macrophytes and zooplankton in untreated, GAC, and stripped sediment, and by zooplankton and macrophytes in PAC sediment (Figure S15). This is supported by a mass balance equilibrium partitioning calculation (detailed in the Supporting Information) showing that the reduction in uptake in fish due to presence of macrophytes was negligible ($< 0.3\%$). The sediment compartment was omitted from these calculations because it contained an almost constant 99.8% of total PCB mass in the system.

The PCB concentrations can be compared to lethal body burden (LBB) [43] concentrations in order to evaluate the effects of the treatments on the reduction of risk for this fish species. For the untreated and GAC treated sediment, molar PCB concentrations in fish were similar to the LBB, which would imply that the fish were exposed to near-lethal levels, also because \sum PCB in fish underestimates total HOC exposure, because PAH exposure was not accounted for. \sum PCB body burdens in the systems with GAC stripped sediment were lower than the LBB, but this was not significant given the analytical error in \sum PCB. In the PAC treatments however, \sum PCB molar concentrations were reduced substantially by a factor of 20 compared to LBB for baseline toxicity as present in the untreated sediment systems. These data for the first time show that PAC treatment reduces PCB bioaccumulation in fish (Figure 1d), and reduces originally lethal exposure levels to levels much lower than lethal concentrations that would occur under field conditions. The data also show that after 6 months, bioaccumulation is not reduced by the GAC treatment or by sediment stripping with GAC. To identify the variables that explain the PCB body burden in fish in the four ditches, the lipid normalized PCB concentrations in fish were correlated with the concentration in sediment, pore water, zooplankton, and invertebrates. It appeared that all these variables, except for PCB concentration in sediment, correlate positively with PCB concentrations in fish (i.e. $p=0.002$, 0.029 , and $3.9 \cdot 10^{-12}$ for pore water, zooplankton, and invertebrates, respectively), indicating the importance of these compartments in the exposure of fish to PCBs. This means that the observed differences in accumulation among chemicals and treatments can be explained from the treatment specific differences in uptake by the organisms lower in the food chain. A detailed mechanistic model analysis was beyond the scope of this study but will be addressed in a follow up paper.

The LogBAF values calculated according to eq 3, varied between 5.3 and 7.5 (Figure S11j-l) and again increased linearly with $\text{Log}K_{OW}$: $\text{LogBAF}=(1.00 \pm 0.09)\text{Log}K_{OW}-(0.03 \pm 0.62)$ ($R^2=0.428$, $p=4.8 \cdot 10^{-21}$). This trend was observed for all treatments at all time points. No treatment effect on fish LogBAF was observed. This implies that the differences in PCB bioaccumulation were determined only by the differences in PCB concentration in water, invertebrates and zooplankton, which in turn were caused by the different AC treatments. These treatments, however did not visibly affect the feeding mechanisms of the fish, i.e. the relative importance of PCB uptake from water versus uptake through food ingestion or major differences in fish diet as these would have affected BAF.

Initial LogBMFs ranged from -2 to 0 and increased to a range of 1 to 2.4 after 6 months, thus indicating biomagnification (Figure S16). These patterns are consistent with earlier reports showing slow PCB uptake, especially for the more hydrophobic congeners [41, 44]. Furthermore, growth dilution may result in lower than equilibrium steady state concentrations, especially for PCBs with higher $\text{Log}K_{OW}$ [41, 45].

IMPLICATIONS

Sediment treatment with AC resulted in a significant decrease of HOC pore water concentrations, with PAC addition being the most efficient, followed by sediment stripping and GAC addition. After 6 months, sediment treatment with PAC effectively reduced PCB bioaccumulation in all levels of the aquatic food chain. PCB concentrations in fish were reduced to concentrations far below thresholds for baseline toxicity, which proves the capacity of AC treatment to rapidly eliminate HOC associated risks for fish. Furthermore, fish grew in all systems, which implies that habitat quality was sufficient to support this species irrespective of treatment. However, in the PAC treatment fish growth rates were lower, which may relate to changes in food availability. Although we do not have conclusive evidence that nutrient limitation is relevant, nutrient co-amendments may be advised as a precautionary measure. On the time scale studied, sediment stripping as well as sediment treatment with GAC turned out to be slower in reducing PCB bioaccumulation in biota, but the treatments were not harmful to any of the biota either. Therefore, *in situ* PAC treatment may be advised for sites where HOC concentrations are high and immediate ecosystem protection is required, whereas GAC *in situ* treatment may be adequate for vulnerable ecosystems where longer term protection may suffice. Furthermore, factors such as costs, ease of application/implementation and long term ecological viability obviously should be taken into account when selecting and designing *in situ* remedial actions.

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Supporting Information for Chapter 7

Methods details

Chemicals and materials. Polyoxymethylene sheets (POM; thickness 76 μm) were purchased from CS Hyde Company, Lake Villa, IL, USA. Before use, coupons of desired weight (approximately 30-100 mg) were cut, washed with hexane, acetonitrile, and methanol, and air-dried. Disposable SPME fiber (glass fiber core diameter 110 μm , polydimethylsiloxane (PDMS) coating thickness 28.5 μm) was from Poly Micro Industries, Phoenix, AZ. It was cut into pieces of 3 cm length, which were shaken three times with methanol and three times with Millipore water for PAH experiments. The PCBs standards IUPAC numbers 18, 20, 28, 29, 31, 44, 52, 66, 72, 77, 101, 103, 105, 118, 126, 138, 143 (internal standard), 149, 153, 155, 156, 169, 170, 180, 187, 194, 204 and 209 for invertebrate and zooplankton analysis were obtained from Promochem (Wesel, Germany). PCB (>99%) congeners for fish analysis were purchased from Sigma-Aldrich (Zwijndrecht, The Netherlands) and CN Schmidt (Amsterdam, The Netherlands). Internal standard was CB-112. Florisil, pentane (picograde), dichloromethane (picograde) and isooctane (picograde) were purchased from LGC standards (Wesel, Germany). Sulphuric acid and sodium sulphate were obtained from Merck (Darmstadt, Germany). Anthracene (ANT), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[e]pyrene (BeP), benzo[ghi]perylene (BghiP), benzo[k]fluoranthene (BkF), chrysene (CHR), dibenzo[a,h]anthracene (DBA), fluoranthene (FLU), indeno[1,2,3-cd]pyrene (InP), naphthalene (NAP), phenanthrene (PHE), and pyrene (PYR) were obtained from Sigma-Aldrich or Acros Organics, The Netherlands, all with a purity of >98%. Internal standard 2-methylchrysene (99.2% pure) was supplied by the Community Bureau of Reference (BCR), Geel, Belgium. Other chemicals used were hexane and acetone (Promochem; picograde), methanol (Mallinckrodt Baker, Deventer, The Netherlands; HPLC gradient grade), acetonitrile (Lab-Scan, Dublin, Ireland; HPLC grade), 2,2,4-trimethylpentane (Mallinckrodt Baker, Deventer, The Netherlands), Barnstead Nanopure water (Sybron-Barnstead, Dubuque, IA, USA), calcium chloride (Merck; p.a), aluminum oxide-Super I (ICN Biomedicals, Eschwege, Germany), and silica gel 60 (Merck; 70-230 mesh). Prior to use, silica gel was activated at 180 °C for 16 h, and aluminum oxide was deactivated with 10% (w/w) Nanopure water. Contaminated freshwater sediment was dredged from Biesbosch National Park, The Netherlands, in the second half of 2011.

PAH and PCB concentrations in pore water. PAH and PCB concentrations in sediment pore water were determined *ex situ* using the POM-SPE method [1]. An amount of wet sediment corresponding to about 10 g of dry weight was brought into a full glass 50 mL bottle, which was filled with an aqueous solution of sodium azide (50 mg/L) and calcium

chloride (0.01 M) in Nanopure water. After the addition of a POM coupon with a known weight, the bottles were shaken on a shaker table at 20 °C and 150 rpm for 28 d, which is sufficient to obtain equilibrium of the HOCs with the POM sampler [1-3]. Then, the pieces of POM were recovered, cleaned with wet tissue, and extracted with acetonitrile. Finally, internal standards (CB-209 and 2-methylchrysene) were added. PAH and PCB aqueous concentrations were calculated from equilibrium concentrations measured in POM (C_{POM}) using previously published POM-water partitioning coefficients (K_{POM}) [2, 3]. Because the sediments were shaken for 28 d, this method would yield *in situ* pore water concentrations only if the sediments were already at equilibrium at the moment of sampling, like for instance in the control systems. In case HOCs were still being transported to AC, however, 1 month agitation yields the systems to be closer to the equilibrium state than the actual systems were at the moment of sampling. Additionally, PAH concentrations in pore water were determined *in situ* using solid phase micro extraction (SPME) fibers [4], containing a 30 µm thick coating of polyacrylate. These fibers were exposed statically in sediment cores that had been taken by a Jenkins core sampler (ø 6 cm). Cores were carefully transported to the lab in order not to disturb the core integrity. In the lab, 7 SPME fibers with a length of 3 cm each were added to stainless steel envelopes [4, 5], which were then inserted into the upper 4.5 cm layer of the sediment cores. The envelopes were left in the cores in a fully undisturbed fashion for 30 days at 20 °C. Prior to insertion, the fibers had been washed 3 x 30 min with 1:1 methanol:Millipore water and 3 x 30 min with Millipore water, respectively. Upon finishing the exposures, the envelopes were withdrawn from the cores one by one and the fibers were recovered, cleaned with wet tissues, and put in autosampler vials, fit with an insert containing acetonitrile. All fibers from one envelope were pooled in one vial. 2-Metylchrysene was finally added as internal standard. Numerous experimental and analytical blanks were used. All data were corrected for blanks. To minimize losses of compounds by photolysis, only amber-colored or aluminum foil-covered glassware was used for PAH analysis. For further QA details on the POM-SPE method, we refer to [1, 2].

Biota analysis. Invertebrate and zooplankton samples were extracted with 70 ml hexane/acetone (3:1 w/w) using an Accelerated Solvent Extractor (ASE 350, Dionex, USA). Extracts were concentrated to 1 mL, exchanged to hexane, and cleaned over Al₂O₃/silica gel columns. Eluates were concentrated to 1 mL, desulpherized using Cu powder in the ultrasonic bath, and exchanged to iso-octane. Finally, all eluates were reduced to 0.2 mL and an internal standard (CB-143) was added. Clean-up blanks (three per every 12 samples) and recoveries (three per every 12 samples) were determined. All data were corrected for blanks. Recoveries ranged 86-108%. Fish analysis used mixed samples of three golden orfe individuals per treatment, homogenized with a Waring blender. Fish samples were ASE extracted with pentane/dichloromethane, supplied with 1 ml iso-octane and concentrated again to 1 ml. Quality control included control samples of cod and eel, and numerous blanks.

Lipids in macroinvertebrates and fish were extracted with chloroform/methanol/water following Bligh and Dyer [6] and were quantified gravimetrically. TOC in zooplankton samples was measured as a loss on ignition after combustion at 520°C until constant weight.

Instrumental analysis. PCBs in zooplankton and invertebrate samples were measured by splitless injection of 1 µL of sample in an upgraded HP5890 series II gas chromatograph equipped with an HP 7673A autosampler system, two fused silica capillary columns, CP Sil-8 CB and CP Sil-5 CB (both 50 m; d.i. 0.15 mm; d.f. 0.20 µm), and two ⁶³Ni electron capture detectors. The injector and detector temperatures were 250 and 325°C, respectively. Carrier gas was N₂ (1 mL/min). PCBs in fish were detected by GC-MS using a Shimadzu 2010 Plus GC coupled to a Shimadzu GCMS-QP2010 Ultra quadrupole MS detector (Den Bosch, The Netherlands) equipped with a 30 m x 0.25 mm i.d. HT8 column with a film thickness of 0.25 µm. A 1 µL sample was injected using split/splitless mode with an injection temperature of 290°C. Transfer line and source temperatures were 290 and 230°C, respectively. The oven program was as follows: 90°C, hold for 3 min, then 30°C/min to 170, 1.5°C/min to 270, 30°C/min to 300°C hold for 3 min. Ionization was performed using electron impact ionization (EI) mode. PCBs 31 and 28 were quantified on m/z 256 with 258 as qualifier ion, CBs 52, 49, 47, 44, 74, 66 and 56 were quantified on m/z 292 using 290 as qualifier ion, CBs 101, 99, 97, 87, 85, 110, 112, 118 and 105 were quantified on m/z 326 using 324 as qualifier ion, PCBs 151, 149, 153, 141, 137, 138, 128, 143 and 156 were quantified on m/z 360 using 362 as qualifier ion, PCBs 187, 180, 207 and 170 were quantified on m/z 394 using 396 as qualifier ion, PCBs 202 and 194 were quantified on m/z 430 using 432 as qualifier ion and PCB 206 was quantified on m/z 462 using 464 as qualifier ion.

PCB concentrations in POM were determined on a TRACE GC Ultra, equipped with a Triplus autosampler and an electron capture detector (all Thermo Scientific, Waltham, MA, USA). Samples were injected on-column on a deactivated fused silica pre-column (2 m), connected to a Zebron ZB-5Msi analytical column (30 m, d.f. 25 µm, d.i. 0.25 µm) Phenomenex, Torrance, CA, USA). PAHs concentrations in POM were analyzed by HPLC as described in ref [7].

Estimating the Von Bertalanffy growth parameter

The growth rate of the fish was estimated with the Von Bertalanffy growth function [8]:

$$L_t = L_{\infty} \left(1 - e^{-K(t-t_0)}\right) \quad (1)$$

where L_t is the length at age t , L_{∞} is the asymptotic length, K is a time constant (d^{-1}), and t_0 is the theoretical age of the fish at length zero. Rearrangement of eq 1 gives:

$$K = -\frac{1}{t-t_0} \ln \left(1 - \frac{L_t}{L_{\infty}}\right) \quad (2)$$

L_t and t were known from experimental conditions. The t_0 parameter was estimated using the methods described by Froese and Binohlan [9]. An empirical relationship was used to estimate asymptotic length (L_{∞}) from maximum length (L_{max}) [9]:

$$\text{Log}L_{\infty} = 0.044 + 0.984 \text{Log}L_{max} \quad (3)$$

The maximum length of *Leuciscus idus melanotus* was taken from Froese and Binohlan [9].

Estimating the effect of macrophytes on PCB uptake by fish

If the biota and abiotic compartment mass fractions in the system are known, as well as the PCB partition coefficients for all biota and compartments, the effect of adding macrophyte mass on the steady state concentration in other biota such as fish, can be calculated.

Assuming equilibrium or steady state, the mass balance for any of the ditches after 9 months of exposure, can be calculated as:

$$Q_{tot} = C_W(V_W + m_{sed}K_d + m_{DOC}K_{DOC} + m_mK_m + m_zK_z + m_iK_i + m_fK_f) \quad (4)$$

where Q_{tot} is the total amount of PCB in the system (μg), V_W is water volume in the ditch (L), m_{sed} , m_{DOC} , m_m , m_z , m_i , and m_f are the masses of sediment, dissolved organic carbon (DOC), macrophytes, zooplankton, invertebrates, and fish (kg), K_{sed} , K_{DOC} , K_m , K_z , K_i , and K_f are partitioning coefficients between sediment, dissolved organic carbon (DOC), macrophytes, zooplankton, invertebrates, fish and the water phase (L/kg), respectively, defined as:

$$K_j = \frac{C_j}{C_W} \quad (5)$$

where C_j is the PCB concentration in compartment j ($\mu\text{g/kg}$) and C_W is the PCB concentration in the overlying water ($\mu\text{g/L}$).

When macrophytes are not present in the system PCB mass balance will be:

$$Q_{tot} = C_W^* (V_W + m_{sed}K_d + m_{DOC}K_{DOC} + m_zK_z + m_iK_i + m_fK_f) \quad (6)$$

where C_W^* is concentration in the overlying water in the absence of macrophytes.

Because the concentration in fish is proportional to the concentration in water ($C_f = K_f C_W$), the factor decrease in PCB concentration due to presence of macrophytes for fish is the same as the factor decrease in PCB concentration in the overlying water:

$$\frac{C_f}{C_f^*} = \frac{C_W}{C_W^*} = \frac{V_W + m_{sed}K_{sed} + m_{DOC}K_{DOC} + m_zK_z + m_iK_i + m_fK_f}{V_W + m_{sed}K_{sed} + m_{DOC}K_{DOC} + m_mK_m + m_zK_z + m_iK_i + m_fK_f} \quad (7)$$

Because all parameters in eq 7 are known, the factor change due to presence of macrophytes can be calculated. The parameters m_{DOC} and K_{DOC} were measured in the context of an earlier study [10]. Parameters m_m , m_z , m_i , and m_f and C_m , C_z , C_i , and C_f were determined during the experiment. For m_{sed} the mass of the sediment present in the top 3 cm was taken, assuming that this mixed sediment top layer is involved in the redistribution of PCBs over time [11]. For C_{sed} the fast-desorbing concentration of PCB was used [12].

Using eq 7, the factor decrease in the concentration of PCBs in fish was calculated to be 0.9989-0.9997 for untreated sediment, 1 for PAC, 0.9975-0.9998 for GAC, and 0.9972-1.0000 for stripped sediment.

Table S1. Total concentrations of PCBs, PAHs, metals, mineral oil and DDT in Biesbosch sediment.

PAHs	C, mg/kg	Threshold effect level ^a , mg/kg	PCBs	C, µg/kg	Threshold effect level ^a , µg/kg
Naphthalene	0.51	0.03	CB-18	14 (0.7)	
Phenanthrene	1.1	0.09	CB-20	10 (0.3)	
Anthracene	0.87	0.05	CB-28	74 (1.9)	
Fluoranthene	2.2	0.11	CB-29	1.0 (0.01)	
Benzo[<i>a</i>]anthracene	1.2	0.07	CB-31	43 (1.2)	
Chrysene	1.4	0.11	CB-44	14 (0.7)	
Benzo[<i>k</i>]fluoranthene	1.0	0.06	CB-52	82 (1.2)	
Benzo[<i>a</i>]pyrene	1.1	0.09	CB-101	75 (4.1)	
Benzo[<i>ghi</i>]perylene	0.78		CB-105	17 (0.8)	
Indeno[1,2,3- <i>cd</i>]pyrene	0.64		CB-118	29 (0.7)	
ΣPAHs	11	0.87	CB-138	69 (3.2)	
Metals			CB-149	80 (2.3)	
As	50	7.2	CB-153	95 (2.9)	
Cd	6.5	0.68	CB-155	3.0 (0.1)	
Cr	190	52	CB-170	19 (0.7)	
Cu	120	19	CB-180	40 (1.2)	
Hg	5.1	0.13	CB-194	7 (0.3)	
Pb	170	30	CB-204	4 (0.1)	
Ni	26	16	CB-209	22 (1.0)	
Zn	920	124	ΣPCBs	700 (28)	22
Mineral oil	700		TOC, %	5.86 (0.51)	-
ΣDDT/DDE/DDD	0.22	0.0045	BC, %	1.15 (0.19)	-

^aref [13]

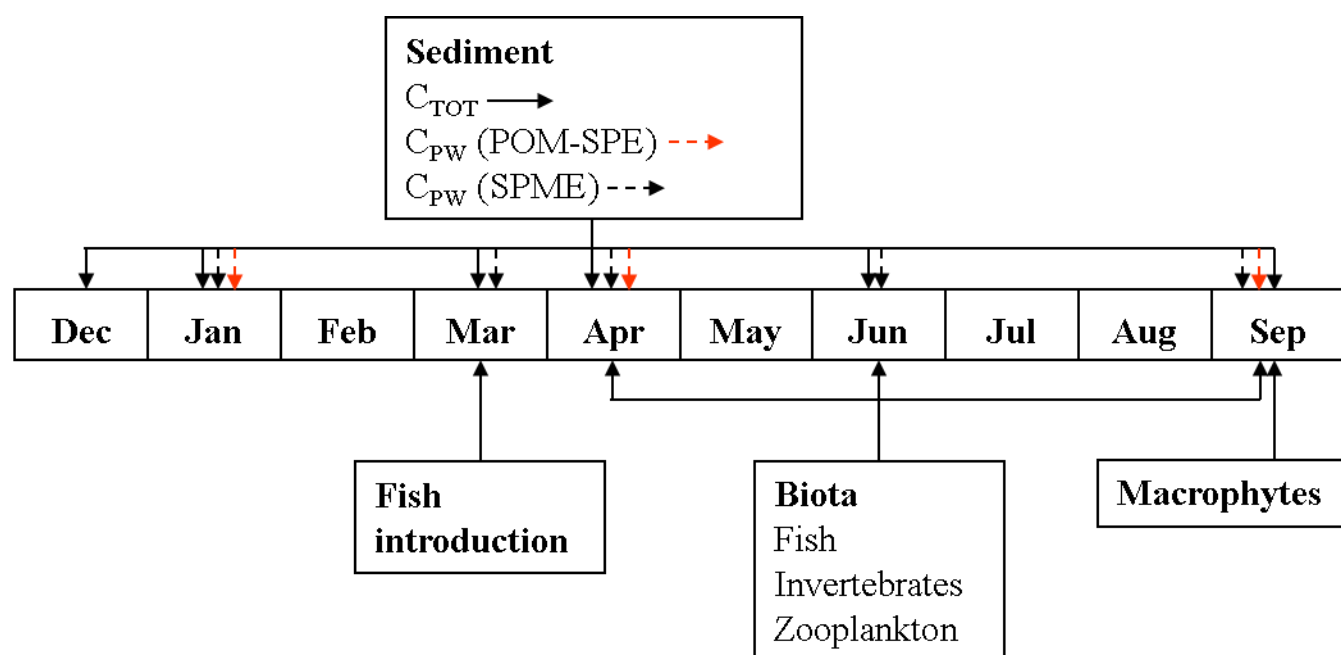


Figure S1. Monitoring scheme, showing which abiotic and biotic compartments were sampled over time.

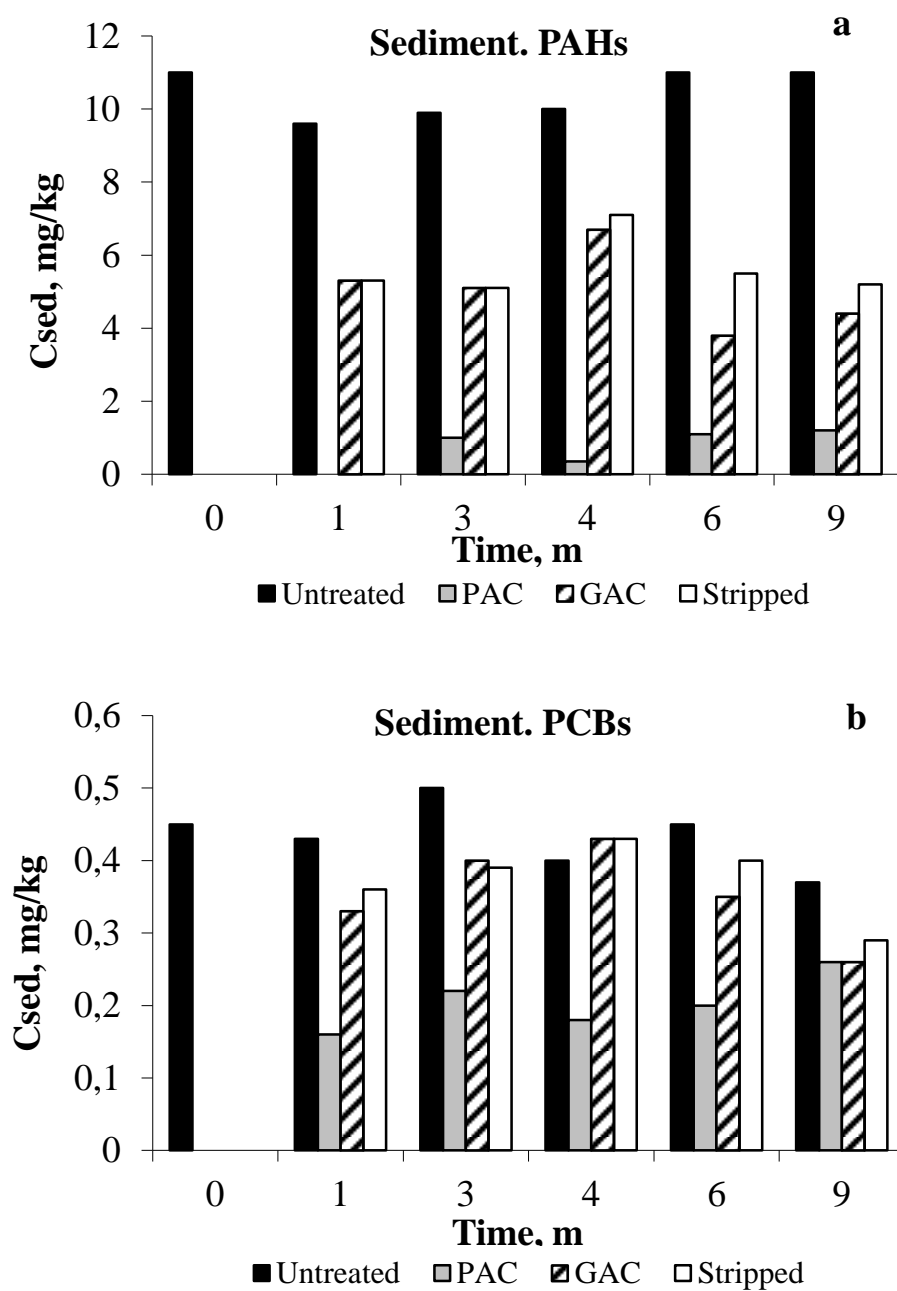


Figure S2. Σ_{13} PAH (a) and Σ_7 PCB (b) concentration in untreated, PAC, GAC, and stripped sediment.

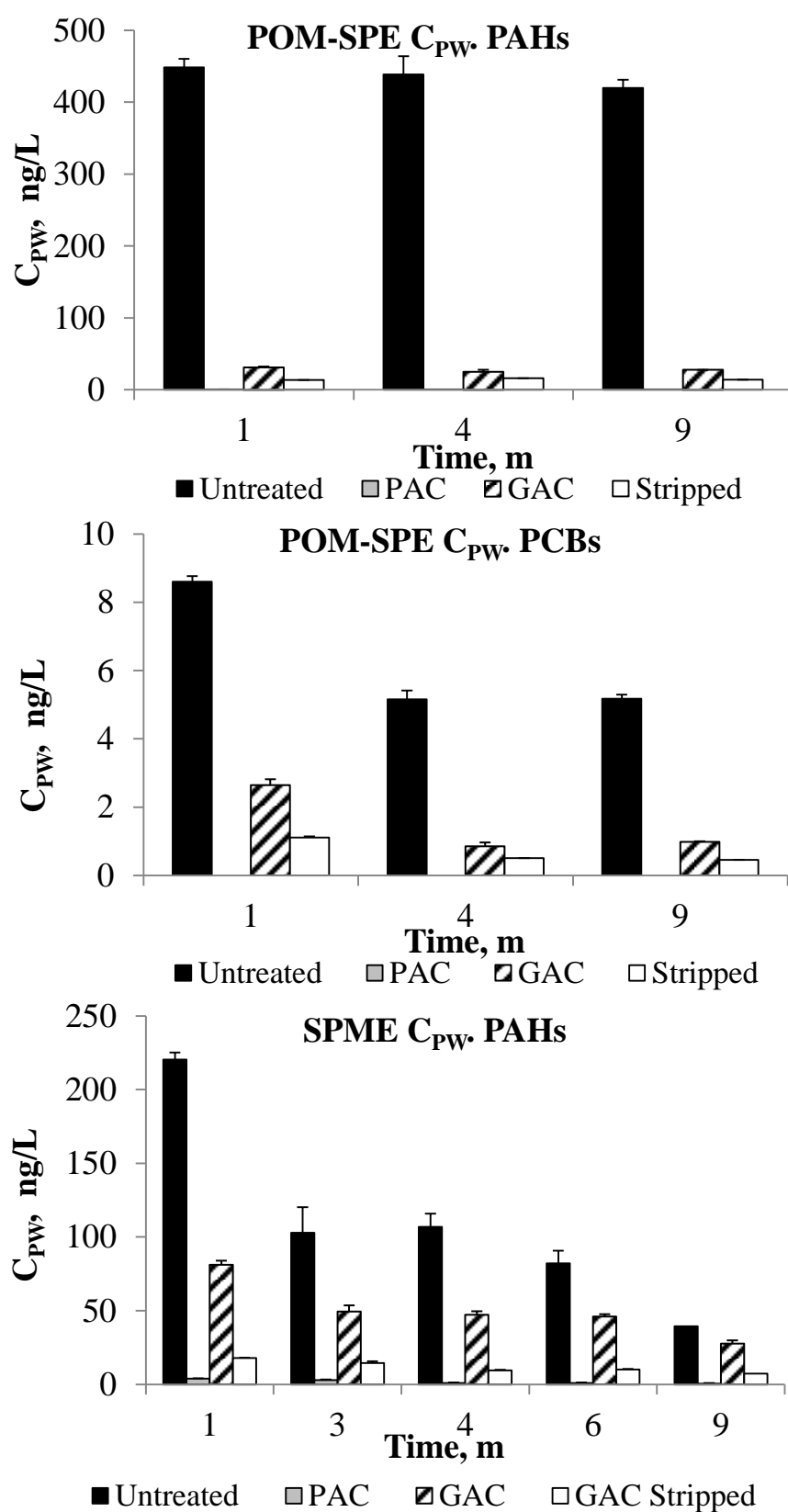


Figure S3. Σ_{13} PAH and Σ_{18} PCB equilibrium pore water concentrations measured with POM (a and b) and SPME (c) passive samplers. PCB concentrations in the PAC treatment (a and b) were below LOD, so C_{pw} for PAC was close to zero. Error bars relate to SD (n=3).

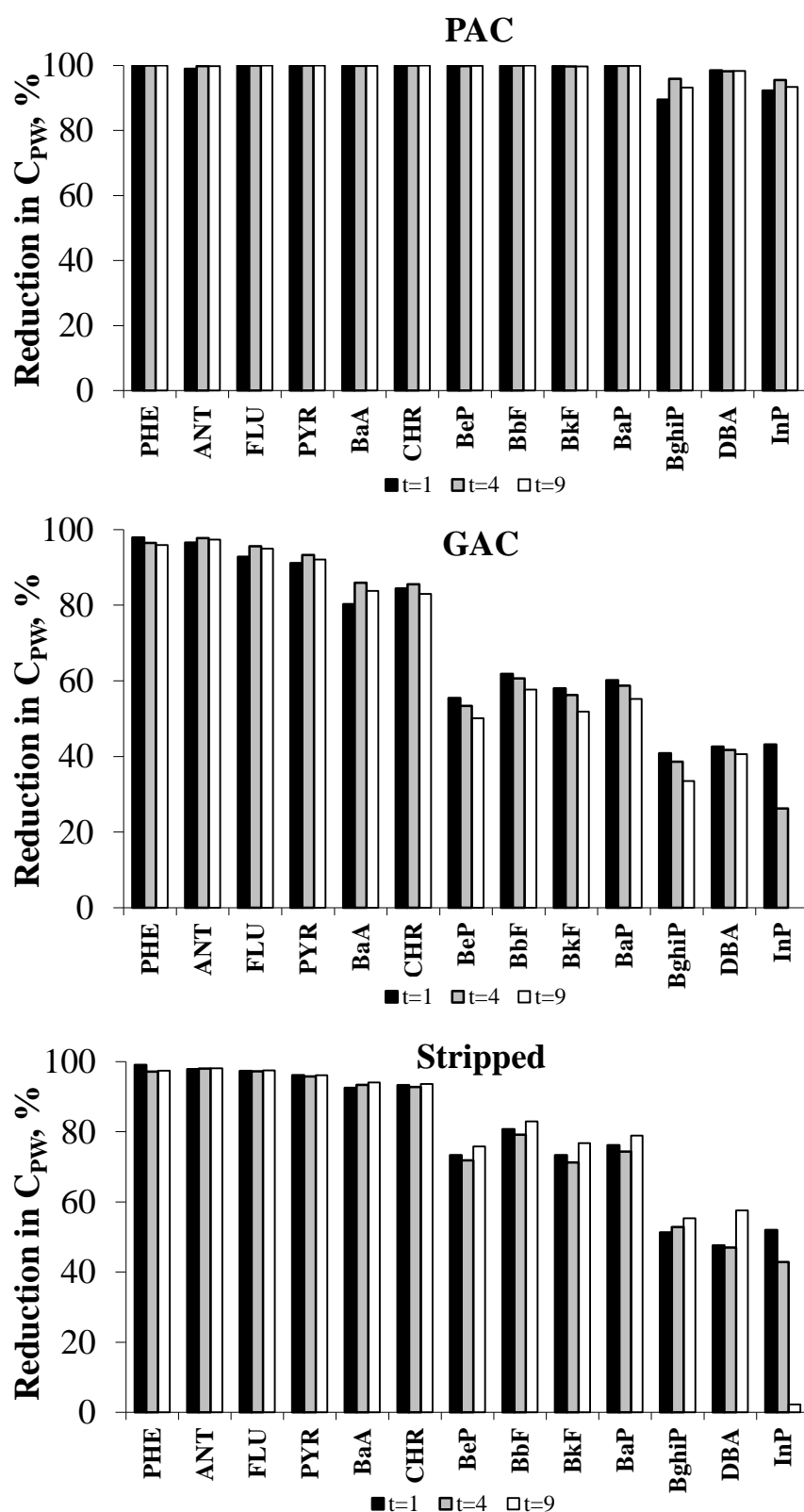


Figure S4. Reduction in PAH pore water concentrations due to AC treatments (PAC, GAC, stripping) as a function of time (m), as measured with POM-SPE passive samplers.

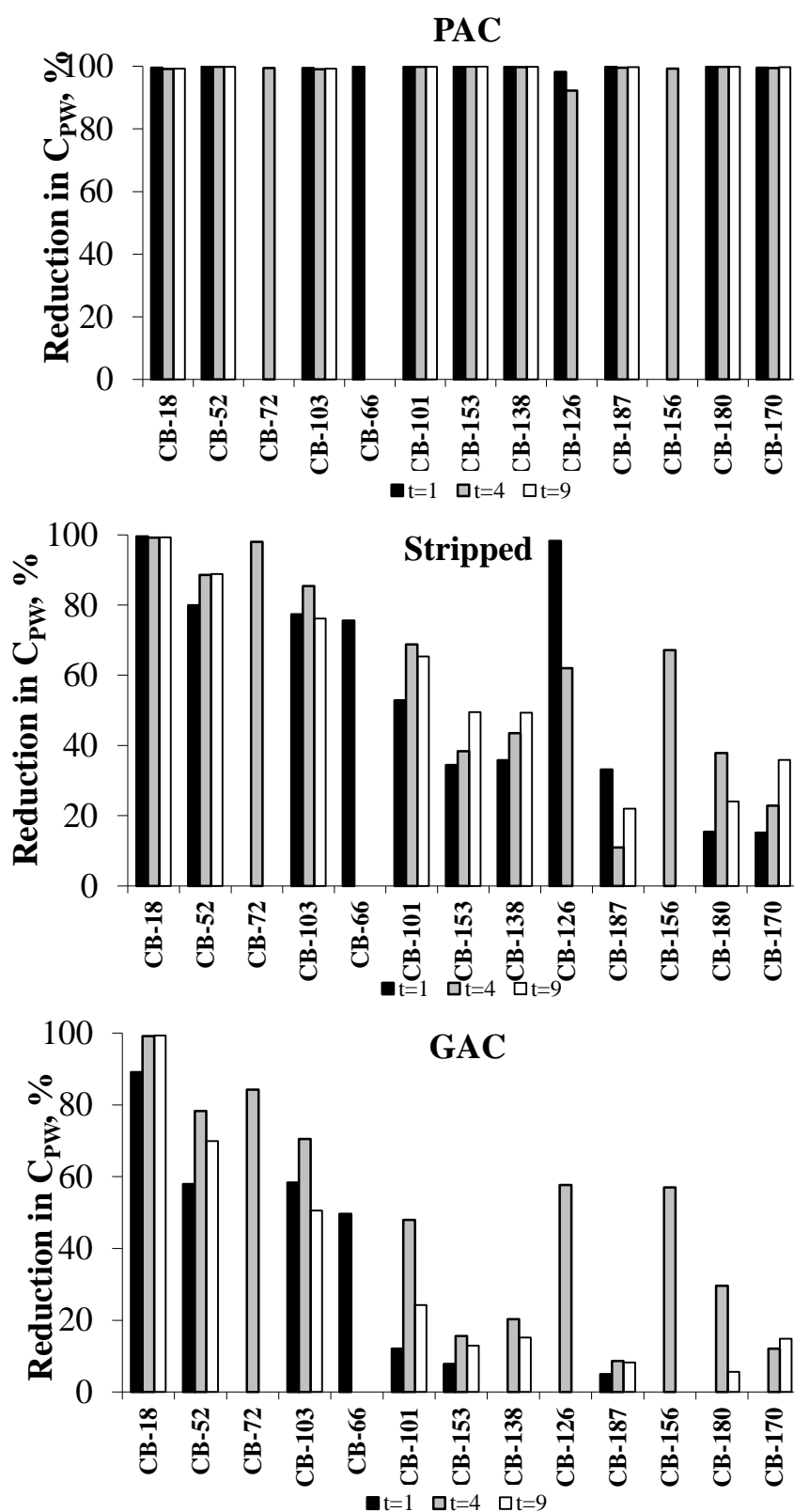


Figure S5. Reduction in PCB pore water concentrations due to AC treatments (PAC, GAC, stripping) as a function of time (m), as measured with POM-SPE passive samplers.

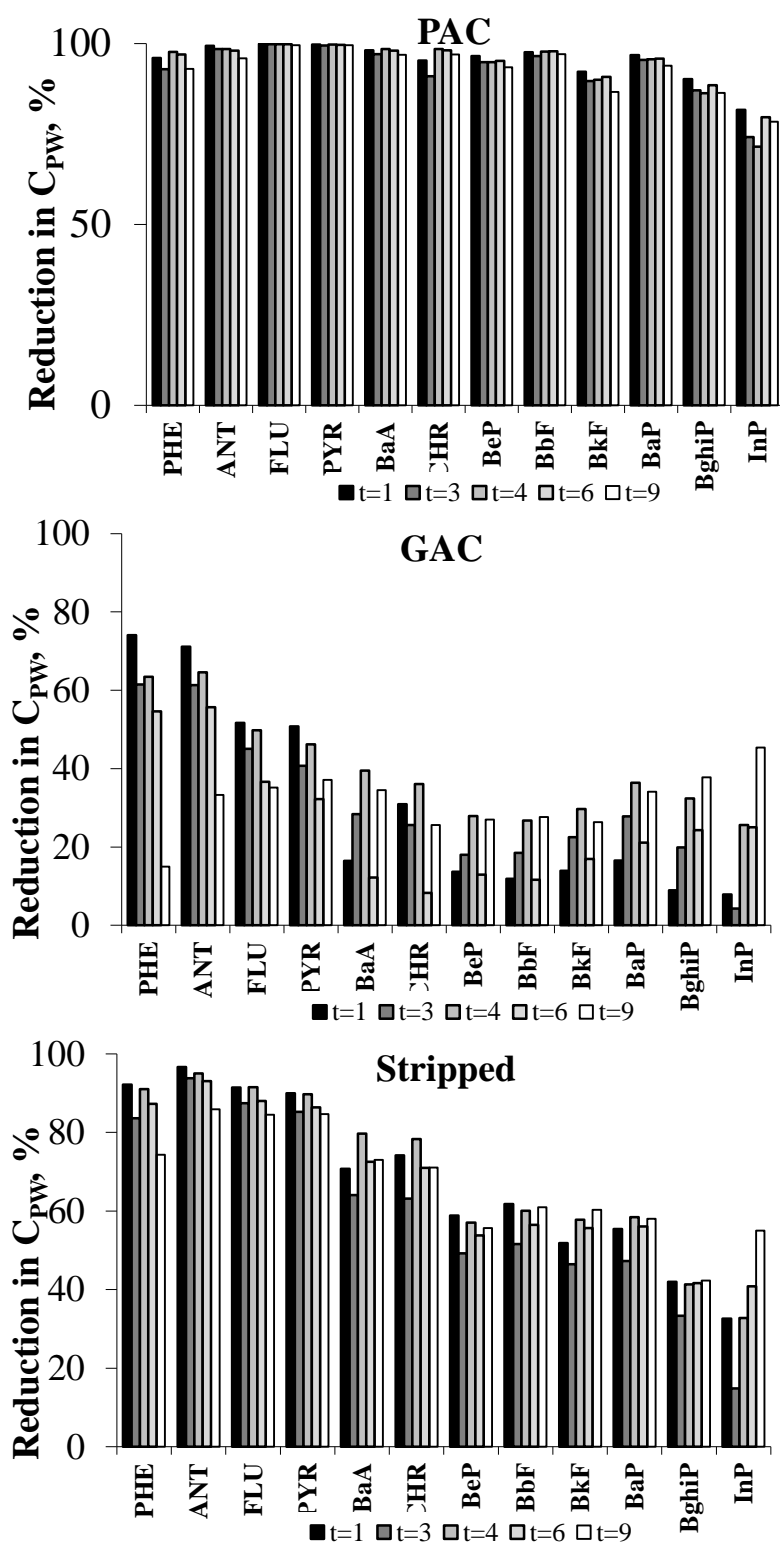


Figure S6. Reduction in PAH pore water concentrations due to AC treatments (PAC, GAC, and stripping) as a function of time (m), as measured with SPME passive samplers.

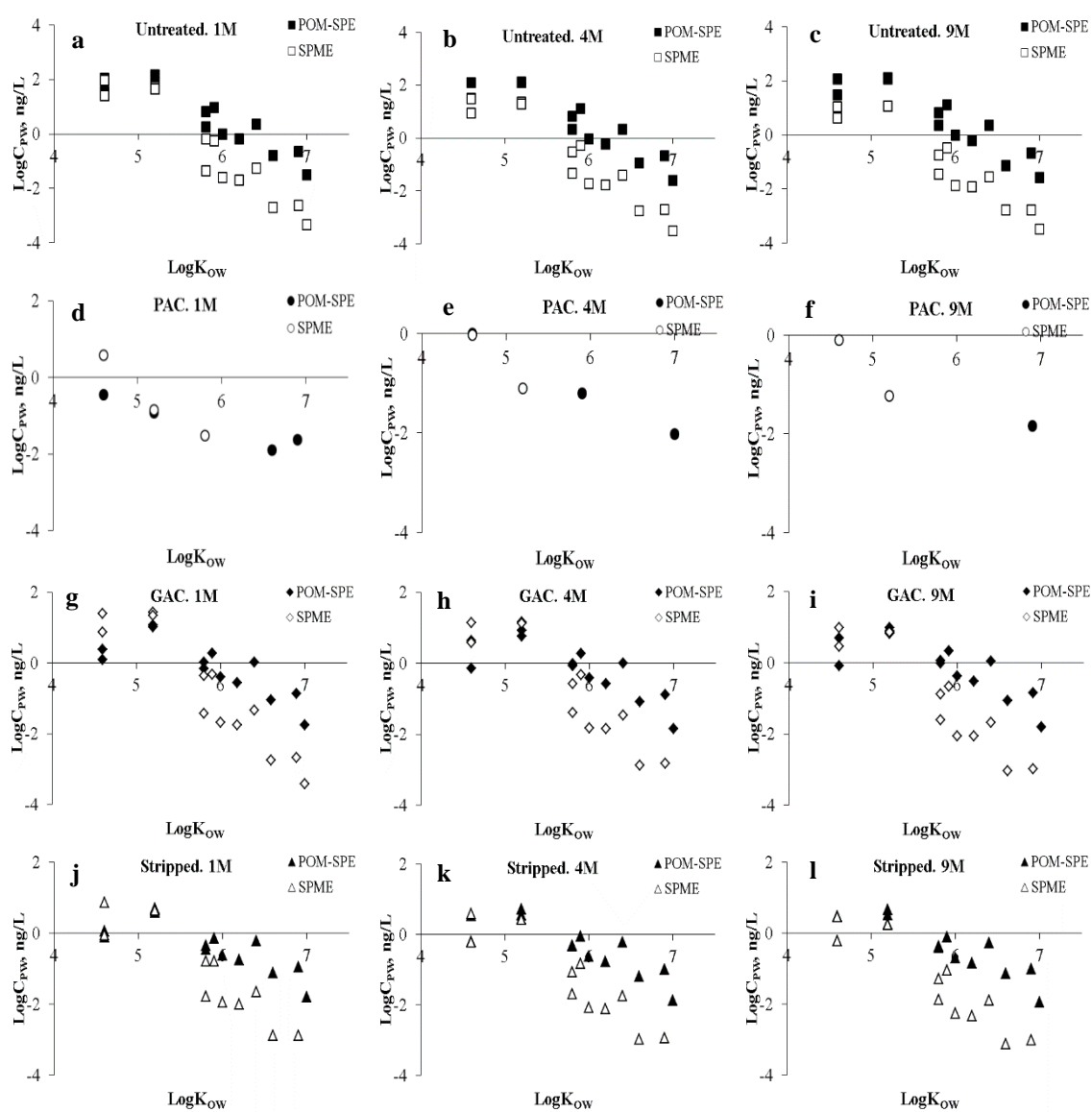


Figure S7. PAH $\text{Log}C_{pw}$ measured *ex situ* with POM-SPE and *in situ* with SPME passive samplers as a function of $\text{Log}K_{ow}$ in untreated (a-c), PAC-treated (d-f), GAC-treated (g-i), and stripped (j-l) sediment at 1, 4, and 9 months post-treatment.

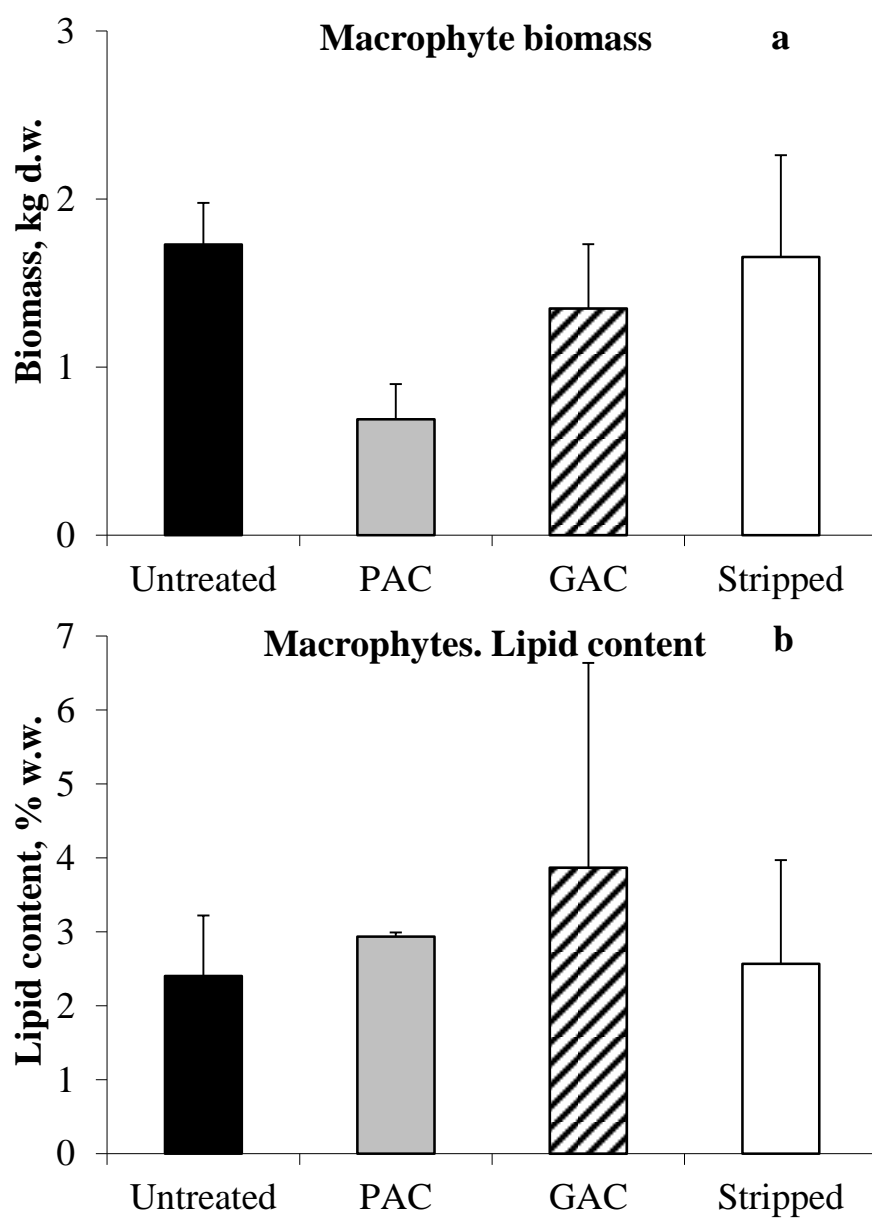


Figure S8. Biomass (a) and lipid content (b) in macrophytes/algae from the ditches with untreated, PAC, GAC, and stripped sediment after 6 months of exposure (i.e. 9 months post-treatment).

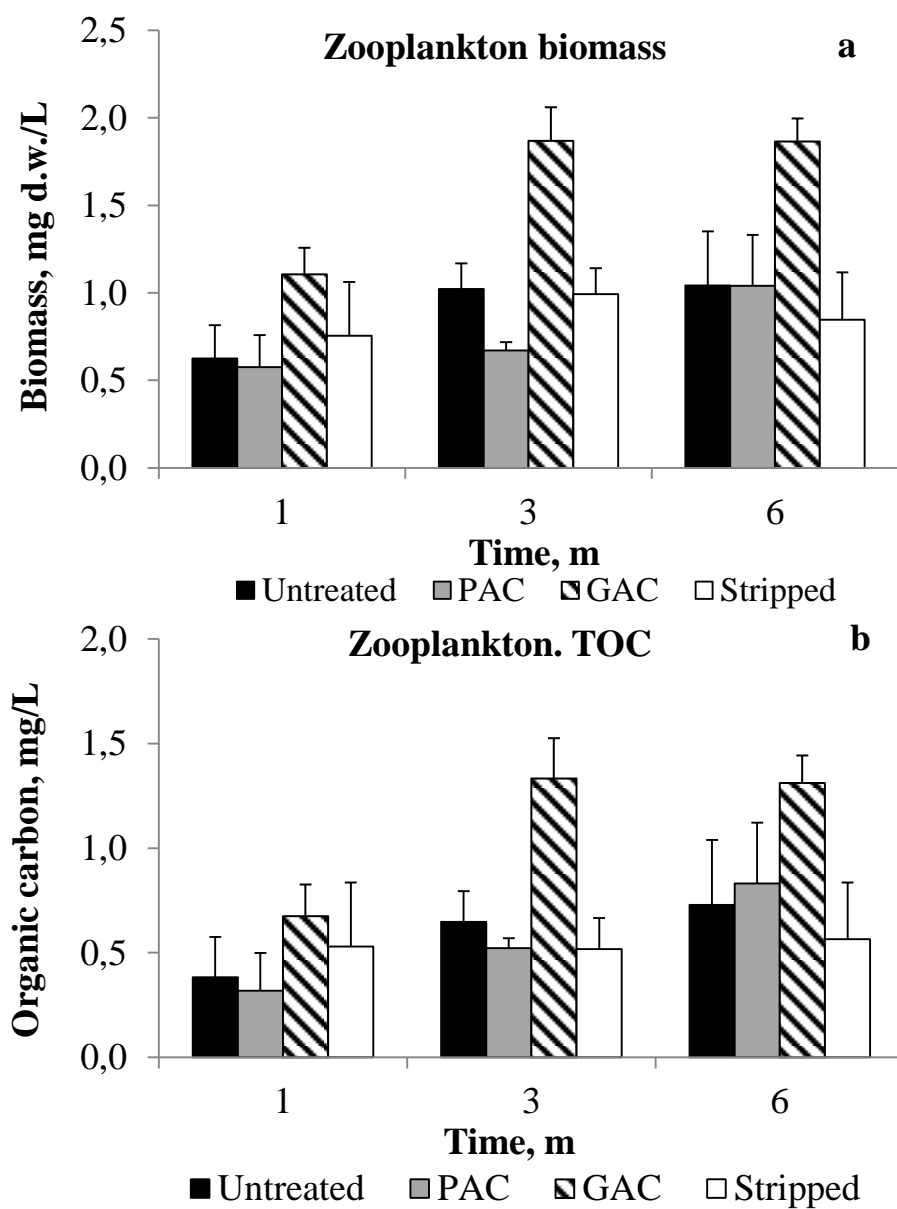


Figure S9. Biomass (a) and total organic carbon (b) in zooplankton from the ditches with untreated, PAC-, GAC-, and stripped sediment after 1, 3, and 6 months of exposure (i.e. 4, 6, and 9 months post-treatment).

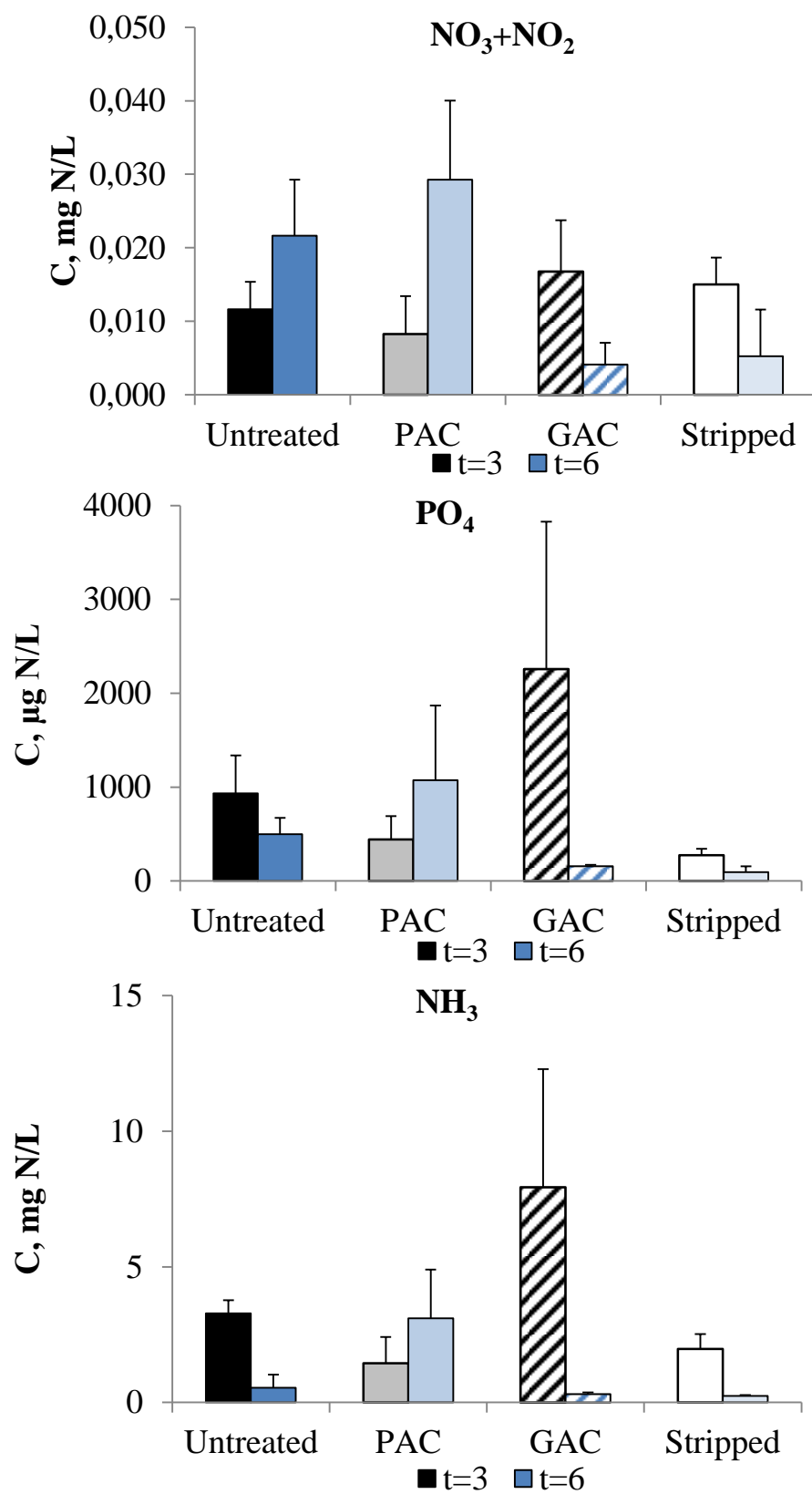


Figure S10. Concentration of nutrients (nitrate, phosphate, and ammonium) in the ditches with untreated, PAC-, GAC-, and stripped sediment.

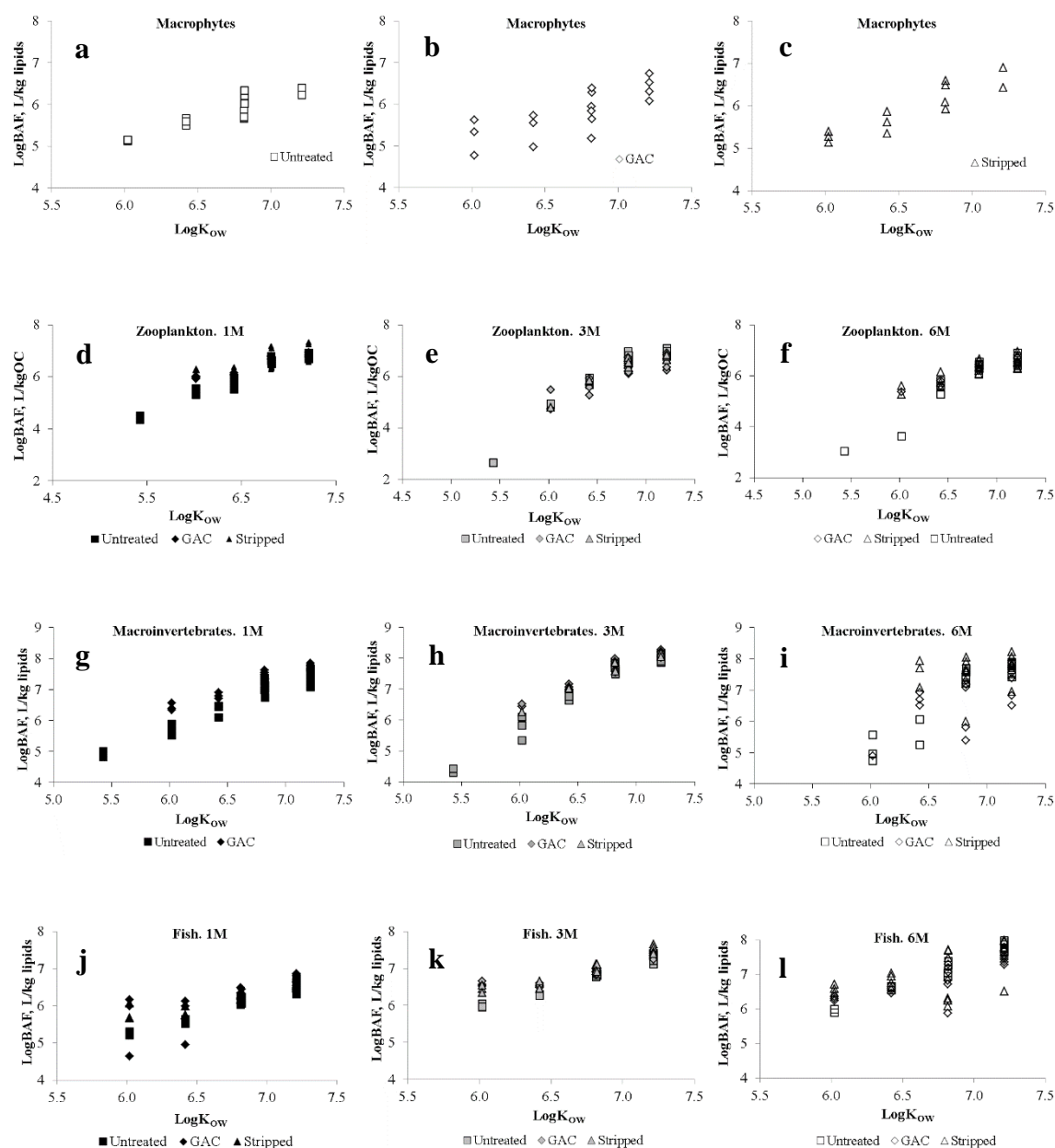


Figure S11. PCB LogBAF for macrophytes (a-c) zooplankton (d-f), macroinvertebrates (g-i), and fish (j-l) based on pore water concentrations determined with the POM-SPE method. The black, grey, and open symbols relate to the measurements done after 1 (d, g, j), 3 (e, h, k), and 9 (a-c, f, i, l) months of exposure (i.e. 4, 6, and 9 months post-treatment), respectively.

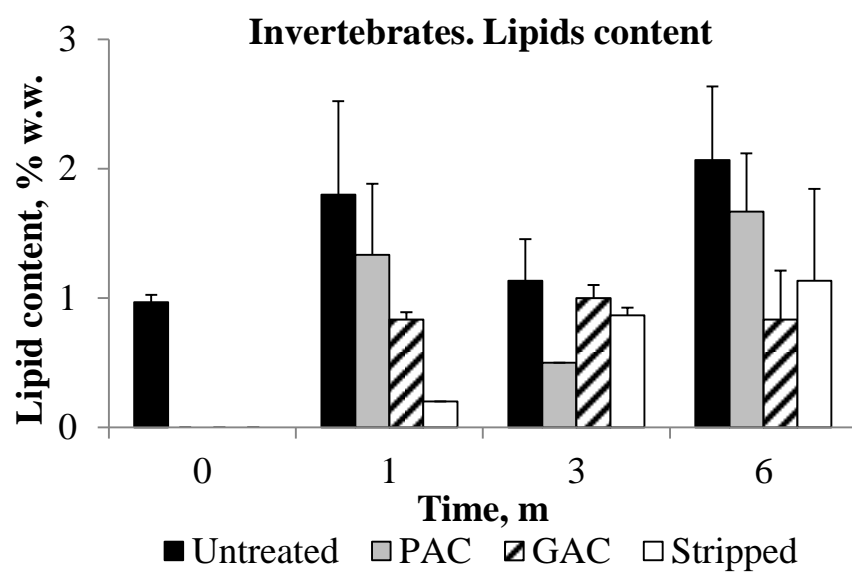


Figure S12. Lipid content of benthic invertebrates from the ditches with untreated, PAC, GAC, and stripped sediment before and after 1, 3, and 6 months of exposure (i.e. 4 and 6 months post-treatment).

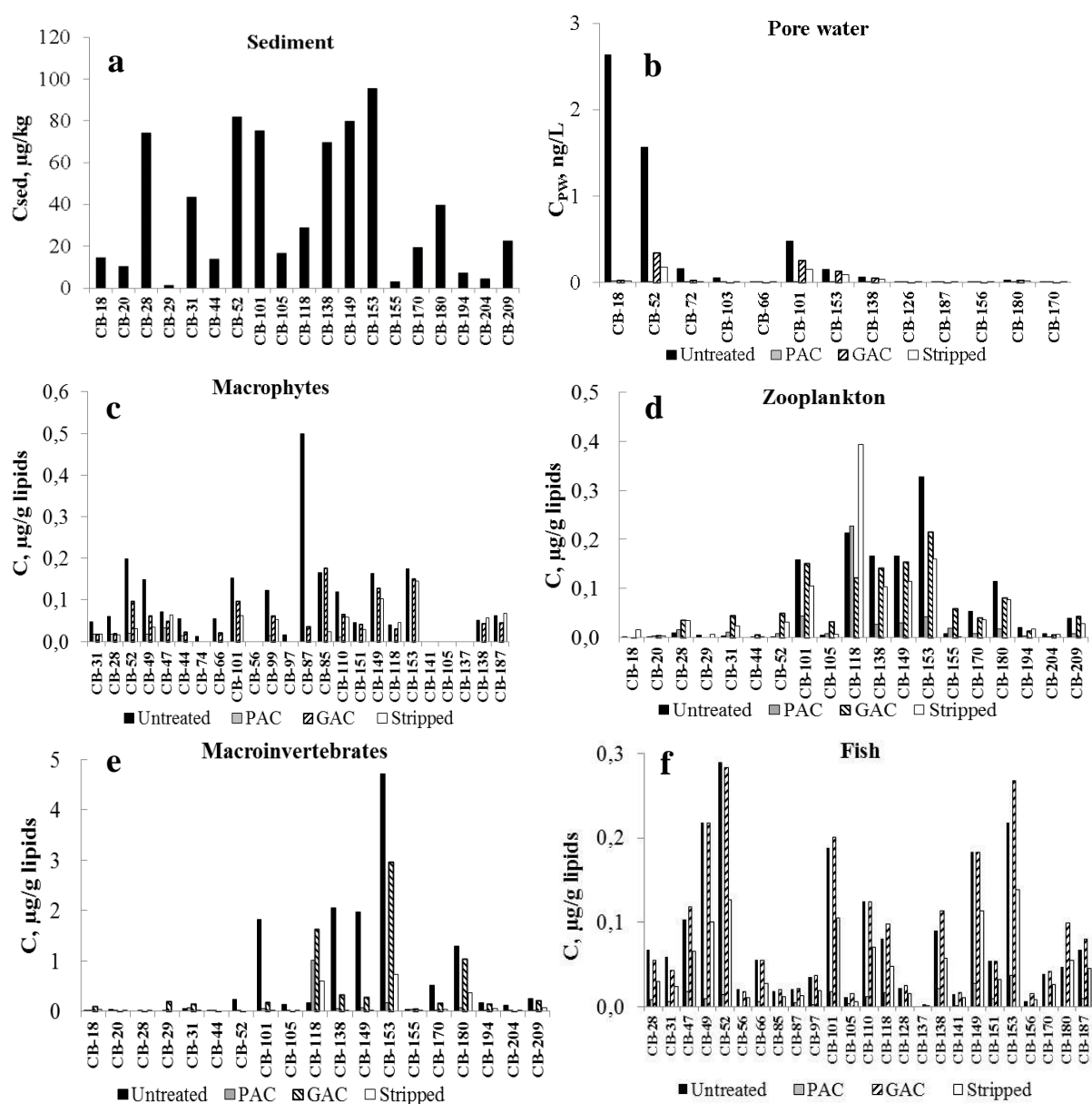


Figure S13. PCB profiles in sediment (a), pore water (b), macrophytes (c), zooplankton (d), invertebrates (e) and fish (f).

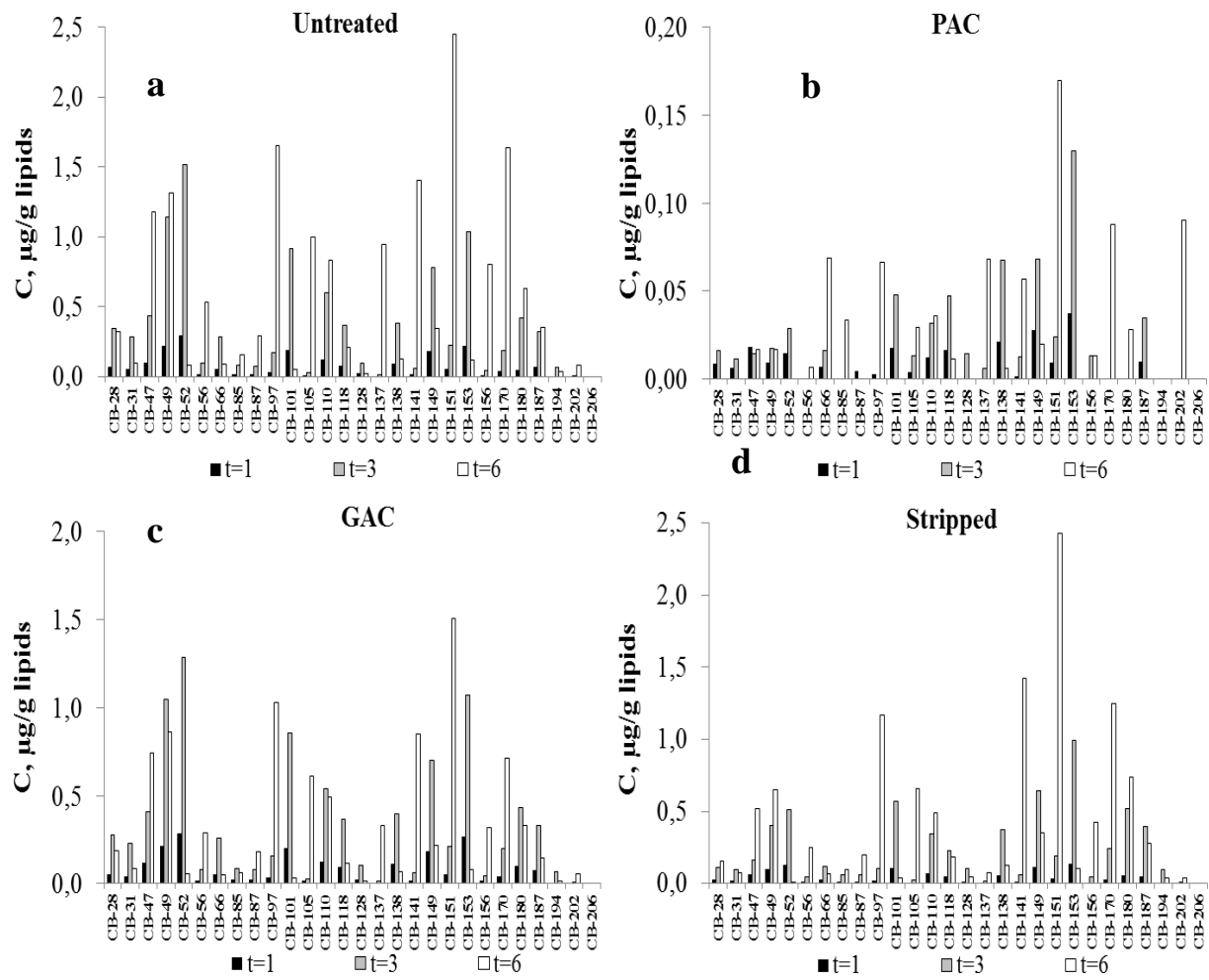


Figure S14. Concentration of individual PCB congeners in fish in untreated (a), PAC (b), GAC (c), and stripped (d) sediment after 1, 3, and 6 months of exposure (i.e. 4, 6, and 9 months post-treatment).

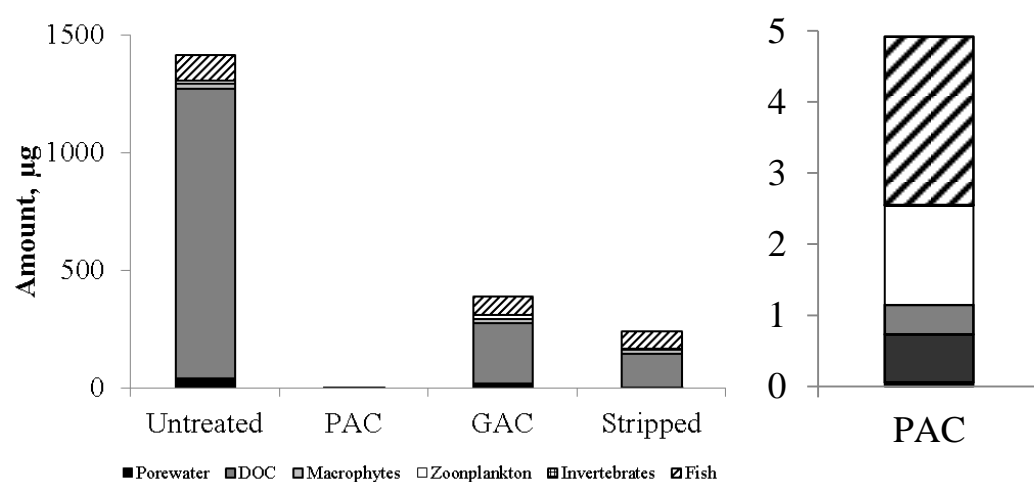


Figure S15. Total amount of Σ_5 PCBs per compartment after 9 months.

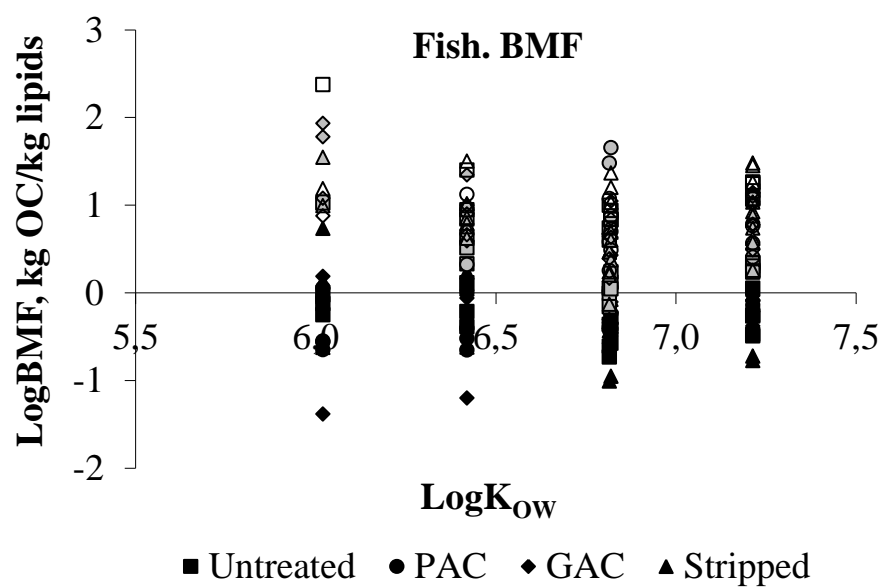


Figure S16. PCB LogBMF for *Leuciscus idus melanotus* estimated using eq 4. The black, grey and open symbols relate to the measurements performed after 1, 3, and 6 months of exposure (i.e. 4, 6, and 9 post treatment), respectively.

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CHAPTER 8

General discussion

Extraction of hydrophobic organic compounds from sediments by GAC: towards a new remediation technology

Due to the large scale anthropogenic activities and increasing use of chemicals by growing human population, surface water, groundwater, sediments, soils and biota are contaminated with hydrophobic organic compounds (HOCs). This group of compounds includes polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organohalogen chemicals including brominated flame retardants, perfluorooctane sulfonate (PFOS) and pesticides like DDT and lindane. During the 20th century, environmental contamination with HOCs has been primarily caused by incomplete combustion of organic matter and fossil fuels as well as by other industrial processes such as coal gasification and wastewater discharges [1]. Sediments accumulate HOCs and thus may pose serious risks to ecosystems and human health [2].

The focus in this thesis is on developing a new remediation option for sediments contaminated with HOCs, with PAHs and PCBs as model compounds, because these are most frequently found as the main organic pollutants in sediments (**Chapters 1 and 2**).

Contaminated sediments and soils amendment with commercial sorbents such as activated carbon (AC) has received considerable attention in the past years for the possibility of *in situ* site remediation (**Chapter 2**). Significant reductions of HOC concentrations and bioaccumulation have been achieved by AC application *in situ*. However, *ex situ* treatments are required since large parts of harbor and waterway sediments have to be dredged to maintain the water depth for shipping and naval purposes. In The Netherlands, approximately 30 million m³ of sediment is dredged annually (**Figure 1**). Dredged sediments are disposed at sea, confined in disposal facilities, or directly used or processed towards a valuable material. However, about 30% of fresh-water sediment is contaminated (class 3-4, i.e. with pollutant levels above Dutch standard and intervention values [3]) and cannot be relocated to river, sea or used on land. Therefore, 24 % is located in final end depots and 10% is stored temporally, which is currently the most common management alternative. From the fresh-water sediment a part is distributed on land (35%) whereas the remainder (31%), consisting mainly of sand fractions is used directly especially in civil engineering applications (**Figure 1**).

Potentially valuable dredged materials are disposed by open water dumping or confinement each year. On the other hand, the primary concerns with open water disposal relate to risks for contaminant leaching, and adverse ecotoxicological effects on benthic organisms and fish. Although *ex situ* remediation approaches seem to be environmentally functional and cost effective, they are not accepted by the public. Thus, disposal in confined facilities and the low acceptance of products coming from processed sediment makes it a less attractive remedial option [5]. For example, in The Netherlands there was a temporal ban on the use of former sand pits for storing sediment due to public concern for leaching of pollutants to groundwater in the vicinity of the sand pits [6].

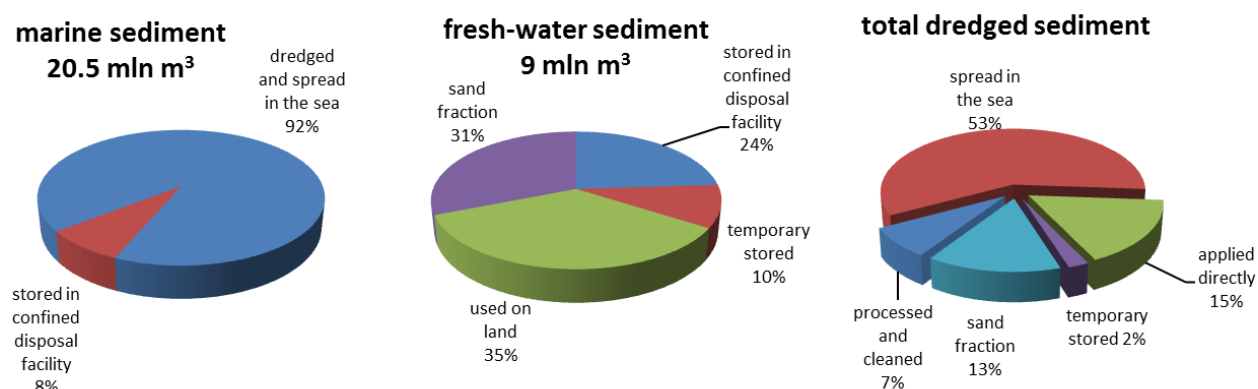


Figure 1. Quantities of dredged sediment in The Netherlands [3, 4]

The primary aim of this thesis was to explore *ex situ* extraction of sediment by granular AC (GAC) as a novel approach in comparison to AC sediment remediation technologies using amendments of powdered AC (PAC) or GAC *in situ*. The results of this research are expected to facilitate the use of GAC in the context of *ex situ* remediation and increase its feasibility for full scale application. The findings of the present work can be used in developing alternatives to existing remediation techniques, including addition of GAC to dredged sediment followed by storage in a depot, isolation of dredged materials by GAC layers, and cleaning dredged sediments with subsequent deposition on land or beneficial reuse of treated material.

Activated carbon amendment strategies reduce the exposure of organisms to sediment-associated organic chemicals. The current state of the art in AC sorbent amendment technology as a method for sediment remediation was reviewed in **Chapter 2**. This review was based on literature and datasets from laboratory as well as field studies with AC amendments. The chapter reviewed the main factors such as AC type, particle size, dosage, sediment and sorbate characteristics affecting the efficiency of AC amendment to sequester HOCs in aquatic sediments. Furthermore, the effectiveness of AC in reducing HOC bioaccumulation and toxicity to benthic species was discussed. The literature suggested that the maximum efficiency of *in situ* AC application, i.e. reduction of freely dissolved HOC concentrations and HOC bioaccumulation in aquatic organisms, can be achieved by applying AC with a small particle size at a high enough concentration and given sufficient contact time. Thus, the dose and particle size dependency can be explained by kinetic processes for sequestration. The kinetics of these processes depends on the homogeneity of the amended material and the presence of competing sorbates. AC amendments to contaminated sediment have a beneficial effect on the survival of aquatic organisms. However, reduced growth and lipid content were the dominant secondary effects of AC amendments. This implies that the overall effect of AC application in contaminated sediments will be beneficial and will lead to a substantial improvement of habitat quality for biota, especially in highly contaminated areas where the beneficial toxicity reduction overshadow any negative ecotoxicological side effects.

In AC amendment technology the ideal sorbent should fulfill multiple criteria: high specific surface area, high surface area to pore volume ratio and sufficiently small particles that should be added in a dose to effectively sequester organic pollutants. A prerequisite for application of active *ex situ* remediation with AC i.e. addition of GAC to a contaminated sediment slurry or stream is effective reduction of pollutant concentrations. The treatment includes the following steps: extraction of HOCs from sediment by GAC, separation of contaminated GAC from the cleaned sediment slurry, and regeneration of GAC. After these steps cleaned sediment can be and re-used in the construction of for instance dikes, roads or highways. However, to enable separation of AC from treated sediment using conventional techniques, such as sieving, additional requirements are mandatory for the AC particles that must be sufficiently large and resistant to erosion. In pioneering studies on AC amendments the particle size was suggested to be the decisive parameter explaining differences in sorption effectiveness of different ACs.

Similar observations were made in **Chapter 3**, in which different types of GAC and extruded sorbents were compared. The effectiveness of four GACs in extracting polycyclic aromatic hydrocarbon (PAH) from heavily contaminated ‘hot spot’ sediment in the presence of associated organic matter was explored by comparing 24-h single-step GAC extraction efficiency vs. traditional 24-h Tenax extraction as reference. Generally, the efficiency of different types of GAC in extracting PAHs from heavily polluted sediment decreased with increasing GAC particle size. GAC with the smaller particles was less prone to sorption attenuation by amorphous organic carbon or oil present in the sediment. At equal AC-to-sediment ratio smaller particles have larger external surface areas and, therefore a higher capacity to bind organic pollutants. The best performing GAC was selected for further testing in the context of *ex situ* sediment remediation. Despite the considerable fouling of GAC by organic matter and/or oil, 50 to 90% of the most available PAH was extracted by 4% GAC within 28-days, which also is a commonly used dose in field-scale applications. GACs were shown to preferentially adsorb low molecular weight PAHs. Low molecular weight PAHs contribute more to the free aqueous concentrations than high molecular weight PAHs and they are more easily transported in the aqueous phase. Moreover, in the studied sediment the fraction of low molecular weight PAHs was much larger than the fraction of high molecular weight PAH. The removal by GAC strongly reduced the risk of the most mobile PAHs in sediment. Although this behavior was primarily demonstrated for PAHs, it will most likely apply also to other small compounds having a similar structure.

The efficiency of the remediation method using GAC largely depends on the rate by which contaminants are transferred from the sediment to the surface of GAC. However, in sediment-GAC mixtures with relatively low GAC dose, i.e. 4%, GAC may not always act as an infinite sink, indicating that backward transport from GAC to the ambient water has to be taken into account. In **Chapter 4**, GAC uptake kinetic parameters for binding of PAHs to GAC in mixed sediment-GAC systems were determined using a tiered first-order model approach. PAH uptake rate constants (k_{GAC}) by GAC ranged from 0.44 to 0.0005 d⁻¹ and GAC sorption coefficients (K_{GAC}) ranged from 10^{5.57} to 10^{8.57} L kg⁻¹. The resulting kinetic data

again showed that 4% GAC would effectively reduce pore water concentration of PAH with lower K_{OW} (i.e. FL, PHE, ANT and FLU) within days, which is sufficiently fast given the characteristic *ex situ* remediation mixing times of days. This is partly because desorption of PAHs out of the sediment matrix to GAC is retarded by strong sorption of PAHs to sediment pore walls and the latter sorption can be stronger for more hydrophobic, higher molecular weight PAHs. A first order multi-compartment model with a non-linear sorption term for GAC used in this chapter has proven to be a promising tool in designing remediation mixing times or GAC doses. Using the data from **Chapters 3** and **4** the effect of GAC dose on the efficiency of the remediation can be assessed over time. This assessment shows that enhancement of GAC remediation efficiency can be easily obtained by increasing the GAC dose (**Figure 2**).

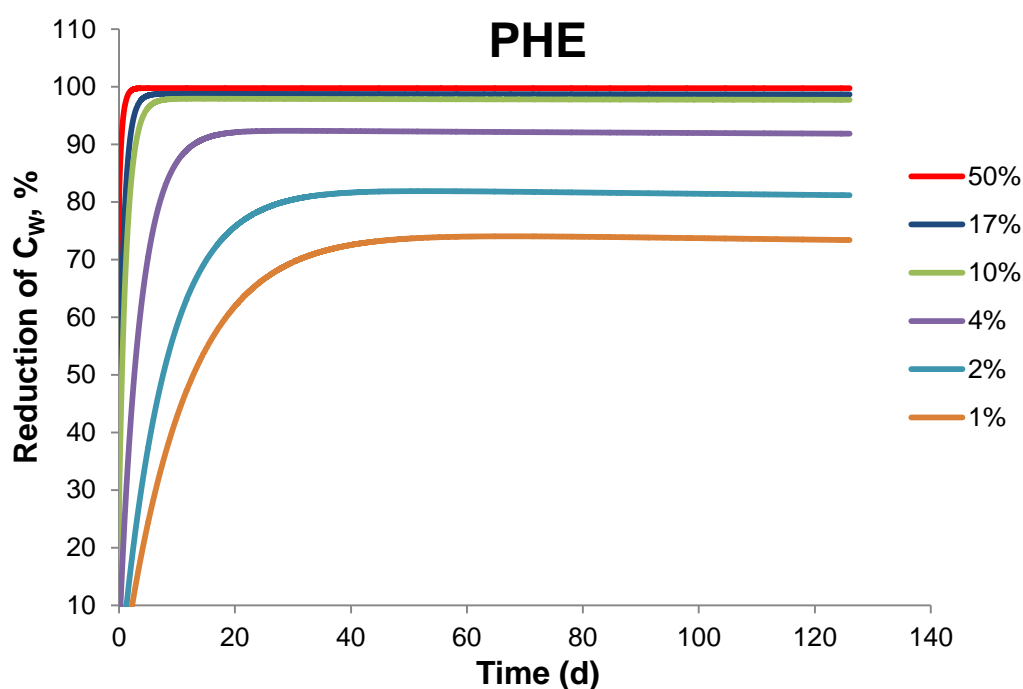


Figure 2. Percentage reduction of aqueous phase concentration ($\mu\text{g/L}$) of phenanthrene as a function of time at variable GAC doses (GAC addition varies from 1 to 50% GAC/sediment (d.w.).

Sediment stripping with GAC, one of the remediation methods using activated carbon, is a promising remediation technique. The efficiency of this method is highly dependent on the rate of contaminant extraction from the sediment by the GAC. Since mixing affects the desorption rates in **Chapter 5**, the effect of mixing intensity on desorption of PAHs from contaminated sediment was investigated. This was done by monitoring uptake in Tenax using a completely mixed batch reactor with adjustable mixing intensity. In order to be able to interpret desorption data in terms of particle size; they were interpreted using a radial diffusion model. It has been estimated that desorption rate constants D_e/r^2 with D_e the

effective diffusion coefficient and r the particle radius, range from 3.7×10^{-3} to $1.1 \times 10^{-1} \text{ d}^{-1}$ (PHE) and 6×10^{-6} to $1.9 \times 10^{-4} \text{ d}^{-1}$ (CHR), and increase with the intensity of mixing. The D_e/r^2 values correspond to D_e value ranges of 1.8×10^{-14} – $1.2 \times 10^{-16} \text{ m}^2 \times \text{d}^{-1}$ and 1.8×10^{-12} – $3.7 \times 10^{-15} \text{ m}^2 \times \text{d}^{-1}$, assuming fast desorption from the measured smallest particle size classes at 200 and 600 rpm, respectively. Desorption of PAHs was substantially accelerated by a reduction of particle aggregate size caused by turbulence. This was explained from mobilization of DOC and colloids from the sediment, which therefore may have caused a higher condensed carbon fraction in the remaining small particles and caused higher affinity for the PAH.

So far, the remediation effectiveness and ecological side effects of AC application have been studied in the short term, and mainly in laboratory studies. However, it is still not clear to what extent these reduced pore water concentrations change over time and how they differ for chemicals and for different AC remediation scenarios under field conditions. In **Chapter 6**, apparent equilibrium and kinetic parameters for *in situ* sorption of a series of PAHs and PCBs to powdered and granular activated carbons were determined during three different sediment treatments: mixing sediment with powdered AC (PAC), mixing with granular AC (GAC), and addition of GAC followed by 2 d mixing and subsequent removal ('sediment stripping'). Remediation efficiency was assessed using the measured fluxes towards SPME passive samplers inserted in the sediment top layer. The results showed that the treatment efficiency decreased in the order of PAC > GAC stripping > GAC addition. PAC demonstrated the strongest sorption of HOCs, with log K_{AC} values up to 10.5. Log K_{AC} values for GAC ranged from 6.3 to 7.1 and from 4.8 to 6.2 for PAHs and PCBs, respectively. Log K_{AC} values for GAC in the stripped sediment were 7.4 - 8.6 and 5.8 - 7.7 for PAH and PCB. Apparent adsorption rate constants for GAC (k_{GAC}) in the stripping scenario, calculated with a first-order kinetic model, ranged from 0.016 (PHE) to 0.000017 d^{-1} (InP). It was shown that sorption affinity parameters did not change within 9 months, confirming the longer term effectiveness of AC in field applications for PAC and GAC.

To date, the negative ecological effects of AC application in sediment remediation have been studied for the benthic compartment only. It is not clear, however, whether efficiency and ecological side effects can be observed on the level of an entire aquatic food chain, including fish. In **Chapter 7**, the effects of the same three AC treatments as mentioned in the previous chapter, viz. mixing sediment with powdered AC, mixing with granular AC, and mixing with granular AC with subsequent removal of granules, i.e. sediment stripping, on bioaccumulation of PCBs by benthic invertebrates, zooplankton and fish (*Leuciscus idus melanotus*) were investigated. Furthermore, biological side effects of AC amendments for the aforementioned scenarios were studied by evaluating functional groups abundances, lipid contents, and condition factors of the biota. The AC treatments resulted in a significant decrease in HOC concentrations in pore water, benthic invertebrates, zooplankton, macrophytes, and fish. In 6 months, PAC treatment caused a significant reduction of accumulation of PCB in fish, bringing pollutant levels below toxic thresholds. The GAC treatment required more time to achieve maximum sorption efficiency. The overall distance from the contaminated sediment particles to AC, is smaller in the PAC than the GAC

treatment resulting in a faster decline of aqueous phase concentrations and thus a faster reduction in the availability of the pollutants for bioaccumulation. All AC treatments supported growth of fish, but growth was slightly (i.e. 15%) inhibited in the PAC treatment, which was explained by reduced nutrient concentrations, resulting in lower zooplankton (i.e., food) densities for the fish. GAC treatments were again shown to preferentially reduce aqueous concentrations of low molecular weight PAHs and low chlorinated PCBs. The results of the research described in **Chapter 3, 4, 6 and 7** demonstrate that GAC is an effective sorbent for specific contaminants.

Altogether, the above findings show that a higher treatment efficiency of larger GAC particles can be obtained by 1) increasing sorbent dose, 2) mixing intensity, or 3) applying longer contact times or by combinations of these measures. Conversely, the reduction of particles size may be effectively balanced by lower GAC dose. However, the extent of this enhancement will depend on several factors such type of chemical, the presence of other sorbing, competing molecules and particles. The modeling approach described can be used to tailor any GAC amendment strategy. Hydrodynamic conditions should be chosen such that external resistances to mass-transfer are minimal.

Advantages and disadvantages of remediation with GAC

In situ amendment studies involving AC have demonstrated effective immobilization of PAHs and organochlorine compounds i.e. PCBs and DDTs by aqueous phase concentration reductions exceeding 90% and by a reduced availability for bioaccumulation in aquatic organisms (**Chapter 6 and 7**) [7-16]. PAC is most effective and less prone to organic matter fouling and ongoing natural processes in the field, whereas the GAC surface may suffer more from sorption competition or pore blocking by DOM fouling.

Although PAC has been shown a superior sorbent in reducing HOC pore water concentrations and bioaccumulation compared to GAC, adverse ecological effects of AC were observed in some studies including changes in growth, lipid content, behavior, and survival [17, 18]. Majority of these negative effects on individual species and benthic communities appear to depend on the sediment characteristics and AC dose and particle size and disappear in time [19, 20]. However, limited negative effects on benthic communities have been observed in GAC amendment strategies and no negative effects on higher organisms in the food chain i.e. fish (**Chapter 7** [21]). Fine AC particles i.e. $< 75 \mu\text{m}$ affected lipid content and growth more strongly than coarser AC (**Chapter 2**). A quantitative assessment model has been developed however, which enables to calculate the trade-off between positive HOC toxicity reduction and the negative effects of PAC addition on benthic populations such that PAC is only applied to contaminated sediments in an ecologically safe window [22]. Most probably, this window is larger for *in situ* GAC application than for PAC application, at the cost of a lower efficiency.

Previous literature examples showed significant weight loss of earthworms and reduced plant growth in PAC amended soil, whereas GAC stimulated the growth rate of

plants [23, 24]. It is possible that in the short term PAC reduces bioavailability of essential substances to a larger extent as compared to GAC, leading to a shortage of nutrient supply for biota as well as for plants. In contaminated sediments, however, these negative effects are likely to be counterbalanced by effective sequestration of HOCs [22].

The results of the research described in this thesis showed favorable sorption of low molecular weight PAHs and PCBs by GAC. Data reported by other researchers confirm that the reduction in free aqueous concentration and biota uptake is highest for smaller PAHs [15, 25, 26]. Although the exposure via pore and overlying water can be significantly reduced, considerable fractions of more hydrophobic chemicals can be associated with sediment particles and thus pose risks to sediment ingesting organisms. Consequently, active treatment with GAC appears to be limited to more soluble and mobile compounds in short term. GAC application *in situ* may not be relevant for highly contaminated sites where urgent remedial actions are required.

GAC removal from treated sediment is feasible using conventional separation techniques. Consequently, sediment treatment with GAC is more suitable and flexible *ex situ* and offers further possibilities for sediment reuse. Therefore, direct exposure of higher organisms to GAC treated sediment will likely be limited. Furthermore, from an ecological point of view, there is lower probability of leaching of sorbed contaminants from coarse GAC particles (long diffusion path lengths) and unwanted spreading of GAC in the environment compared to PAC [27].

Addition of PAC and GAC in the field reduce the risks of HOCs in moderately contaminated sediments (**Chapter 6** and **7**) [7, 9]. Furthermore, in laboratory studies with a ‘hot spot’ contaminated sediment effective reduction of the most available PAH was obtained even in the presence of high TPH concentrations (**Chapter 3** and **4**). The effectiveness of active stripping with GAC is expected to be higher for sediments with highly bioavailable fractions of HOCs. Treatment of sediments with low availability for bio-uptake will probably be useless.

Sorption to GAC is affected by soil and sediment type, composition of the aqueous phase, organic matter content, and presence of DOC and oil in the environment under study. Organic matter and oil might attenuate sorption to AC by pore blockage or sorption competition by co-adsorbing HOCs, OM molecules and oil.

Overall, the results presented in this thesis seem promising and broaden the perspectives for AC amendment approaches. However, sediment stripping with GAC is operationally demanding and the capital-intensive slurry treatment processes are in general less attractive.

Prospects of *ex situ* GAC remediation technology

The preferred order of destination for dredged sediment is relocation, direct reuse, and treatment for beneficial use and at the end disposal [5, 28]. However, most of the contaminated dredged material is disposed of in sub-aquatic confined disposal sites and only about 7% is treated for beneficial use (**Figure 1**). Since risk assessment procedures are often

based on total contaminant concentrations, implementation of *ex situ* remediation approaches with GAC may not be warranted.

The results of the research described in this thesis demonstrated the potential of the GAC remediation approach. Owing to the high complexity of sediment stripping with GAC, however, perspectives for up-scaling and application as an independent stand-alone technique in daily remediation practices may be rather limited.

As shown in **Figure 1** there is high potential for reuse of confined sediment. Therefore, sediment treatment with GAC could be coupled with any management approach mentioned above or with other technologies either sequentially or simultaneously i.e. treatment chains to bring dredged sediment to a more sustainable material. An extensive range of treatment combinations of GAC with simple technologies such as sand separation, land farming, ripening and stabilization could be made. Since these techniques already operate with specific equipment and transfer of sediment, the overall treatment costs would probably not increase substantially. However, these techniques can process only a limited quantity of dredged sediment into usable products. Therefore, application of GAC in more advanced technologies, such as soil washing, and treatment of residues from sand separation could increase the quantity of potentially reusable material (including recyclable water) and reduce overload in sediment depots. Earlier literature examples showed the potential of AC to stimulate bacterial degradation of HOCs [29-31]. A recent study demonstrated a community shift to putative organohalide respiring phylotypes in the presence of GAC that coincided with more extensive dechlorination, involving especially *ortho* and unflanked chlorine atoms in various PCB congeners [32]. The shift in activity by GAC was shown to have the potential to enhance degradation *in situ* by promoting accumulation of less chlorinated compounds that are more liable to complete mineralization by aerobic PCB degrading bacteria. Therefore, GAC could be combined with biological treatments or applied in cases where one technique is not sufficient to remediate sites. Thus more research may be needed to explore the large variety of treatment combinations, interactions and their effects. Further research is needed at pilot scales to optimize their application and select the enhancement that can be made. The handling of the sediment is more complex compared to just addition of PAC and subsequent immobilization of HOCs. However, as policy is still focusing on total concentrations rather than on risk reduction, the sediment stripping with GAC in combination with necessary dredging activities remains an attractive alternative to stimulate reuse of sediment.

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SUMMARY

Over the last decades, industrial and urban development and emissions of many hazardous organic compounds have threatened the ecological quality of marine and freshwater sediments. Sediments accumulate hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and thus may pose serious risks to ecosystems and human health. Over the past years sediment treatment by sorbent addition such as activated carbon (AC) to achieve sequestration of HOCs *in situ* has been proposed as an alternative approach to traditional remediation technologies such as dredging and disposal. The present research was meant to explore *ex situ* extraction of sediment by granular AC (GAC) ('active stripping') as a novel approach in comparison to traditional *in situ* AC sediment remediation technologies using amendments of powdered AC (PAC) or GAC.

Chapter 2 discusses the current state of the art in AC amendment technology as a method for sediment remediation. In this chapter, major knowledge gaps are revealed on sediment-AC-HOC interactions controlling the effectiveness of HOC binding such as AC type, particle size, dosage, sediment and sorbate characteristics, and efficiency of AC to reduce bioaccumulation in benthic invertebrates. In addition, the review discusses potential negative effects of AC on aquatic life. Finally, we discuss whether the effects of AC addition can be predicted using fate and transport models.

Chapter 3 explores the potential of GAC in the context of *ex situ* sediment remediation technology. Since the added GAC would compete for the sorption of HOCs with natural sediment phases, its effectiveness would strongly depend on its dosage. Consequently, in this chapter we investigate the distribution coefficients for short-term sorption processes, and the optimal dosage level of GAC to be used in intensive sediment remediation. A suite of candidate GAC materials is screened for maximum efficiency in extracting PAHs from sediment with very high PAH and oil pollution levels within 24 h. The effectiveness of GAC is compared to a single-step solid phase extraction (SPE) with Tenax beads. Sorption data are interpreted in terms of aqueous phase concentration reduction ratios and distribution coefficients. Despite the considerable fouling of GAC by organic matter and oil, 50-90% of the most available PAH was extracted by the GAC during 28-d contact time, at a dose as low as 4%.

A prerequisite for the application of active stripping with GAC in contaminated sediment remediation is effective transport of pollutants from the sediment to the GAC during the relatively short mixing stage. Therefore, in **Chapter 4** kinetics of PAH transfer from sediment using GAC at a relatively low dose as a solid extraction phase kinetic parameters are obtained by modeling experimental sediment-GAC exchange kinetic data following a two-stage model calibration approach. Rate constants (k_{GAC}) for PAH uptake by GAC range from 0.44 to 0.0005 d⁻¹, whereas GAC sorption coefficients (K_{GAC}) range from 10^{5.57} to 10^{8.57} L kg⁻¹. These results show that *ex situ* extraction with GAC is sufficiently fast and effective to reduce the risks of the most available PAHs among those studied, such as fluorene, phenanthrene and anthracene.

It is unclear how the GAC/sediment mixing step affects desorption kinetics of HOCs for instance by changing the sediment particle size distributions, and whether these factors may influence the effectiveness of *ex situ* GAC extraction technology. **Chapter 5** presents the results of investigations on the effect of mixing intensity on the extraction rate of PAHs from contaminated sediment. Desorption data are interpreted using a radial diffusion model. Mixing caused the 161 μm particles originally present at a stirring rate of 200 rpm to decrease in size to 9 μm at a rate of 600 rpm. Desorption rate constants decreased with increasing PAH hydrophobicity but increased with the intensity of mixing. The results demonstrate that desorption of PAHs is significantly accelerated by a reduction of particle aggregate size caused by shear forces induced by mixing.

So far, the remediation effectiveness and ecological side effects of AC application have been studied in the short term, and mainly in laboratory studies. However, it is still not clear to what extent these reduced pore water concentrations change over longer times and how they differ for chemicals and for different AC remediation scenarios under field conditions. **Chapter 6** presents (pseudo-)equilibrium as well as kinetic parameters for *in situ* sorption of a series of PAHs and PCBs to powdered and granular activated carbons (AC) after three different sediment treatments: sediment mixed with powdered AC (PAC), sediment mixed with granular AC (GAC), and addition of GAC followed by 2 d mixing and subsequent removal ('sediment stripping') in the field. Remediation efficiency is assessed by quantifying fluxes towards SPME passive samplers inserted in the sediment top layer, which shows that efficiency decrease in the order of PAC > GAC stripping > GAC addition. Sorption was very strong to PAC, with $\log K_{AC}$ (L/kg) values up to 10.5. $\log K_{AC}$ values for GAC ranged from 6.3 - 7.1 and 4.8 - 6.2 for PAHs and PCBs, respectively. $\log K_{AC}$ values for GAC in the stripped sediment were 7.4 - 8.6 and 5.8 - 7.7 for PAH and PCB. Apparent first order adsorption rate constants for GAC (k_{GAC}) in the stripping scenario were calculated with a first-order kinetic model and ranged from 1.6×10^{-2} (PHE) to $1.7 \times 10^{-5} \text{ d}^{-1}$ (InP). This study showed that sediment treatment with PAC is most effective and less prone to organic matter fouling and ongoing natural processes in the field. The effectiveness of GAC is higher in the 48 h sediment stripping scenario than in the GAC amendment approach.

In **Chapter 7** the effects of three different AC treatments (see above) on HOC concentrations in pore water, benthic invertebrates, zooplankton and fish (*Leuciscus idus melanotus*) are tested. The AC treatments result in a significant decrease in HOC concentrations in pore water, benthic invertebrates, zooplankton, macrophytes and fish. In 6 months, PAC treatment caused a reduction of accumulation of PCBs in fish by a factor of 20 bringing pollutant levels below toxic thresholds. All AC treatments supported growth of fish, but growth was inhibited in the PAC treatment, which is likely to be explained from reduced nutrient concentrations, resulting in lower zooplankton (i.e., food) densities for the fish. During the course of the field study, sediment stripping as well as sediment treatment with GAC turned out to be slower in reducing PCB bioaccumulation in biota, but the treatments were not harmful to any of the biota either.

In the final chapter (**Chapter 8**), overarching answers to the main research questions (see above) are formulated and an outlook regarding the actual use of *ex situ* GAC is provided.

SAMENVATTING

De afgelopen tientallen jaren wordt de ecologische kwaliteit van zout- en zoetwater sedimenten bedreigd door industriële en stedelijke ontwikkeling en de uitstoot van vele schadelijke organische stoffen. Hydrofobische organische componenten (HOCs), zoals polycyclische aromatische koolwaterstoffen (PAKs) en polychloor bifenylen (PCBs), hopen zich op in sediment en kunnen daardoor een risico vormen voor het ecosysteem en de menselijke gezondheid. Als een alternatief op traditionele sanerings technologie zoals baggeren en afvoeren is er de afgelopen jaren aandacht voor het vastleggen van HOCs in situ door het toedienen van adsorberende stoffen zoals actieve kool (AC). Het voorliggend onderzoek heeft tot doel om *ex situ* extractie van granulair AC (GAC) te verkennen als een nieuwe benadering in vergelijking met traditionele *in situ* AC sediment sanerings technologie, waarbij AC wordt toegediend in poedervorm (PAC) of als GAC.

Hoofdstuk 2 bespreekt de huidige gang van zaken bij AC toevoeging als sediment saneringstechnologie. In dit hoofdstuk worden de voornaamste kennishiaten benoemd wat betreft sediment-AC-HOC interacties die de effectiviteit van de binding met HOC bepalen, zoals AC type, deeltjes grootte, dosis, sediment en sorptie eigenschappen en de efficiëntie waarmee AC bioaccumulatie in bentische ongewervelden verlaagd kan worden. Daarnaast worden potentieel negatieve effecten van AC op aquatische levensvormen besproken. Tot slot bespreken we of de effecten van AC toediening kunnen worden voorspeld met transport modellen.

Hoofdstuk 3 verkent de mogelijkheden van GAC in de context van *ex situ* sediment sanerings technologie. De HOC verontreiniging kan adsorberen aan de toegevoegde GAC, maar ook aan natuurlijk sediment, en hierdoor wordt de effectiviteit van de toegevoegde GAC sterk bepaald door de gebruikte dosis. Daarom onderzoeken we in dit hoofdstuk de distributie coëfficiënten voor korte-termijn sorptie processen, en de optimale dosis GAC die gebruikt moet worden bij intensieve sediment sanering. Verschillende mogelijke GACs worden vergeleken op basis van de maximale efficiëntie waarmee ze PAKs van sediment kunnen verwijderen voor een sediment met een hoge concentratie PAK en olievervuiling in een periode van 24 uur. De effectiviteit van GAC is vergeleken met een enkelvoudige vaste fase extractie (SPE) met Tenax korrels. Sorptiedata worden geïnterpreteerd op basis van de verlaging van concentraties in de waterfase en distributie coëfficiënten. Ondanks de aanzienlijke aanslag van organisch materiaal en olie op het GAC, was 50-90% van de beschikbare PAK geadsorbeerd door de GAC gedurende een blootstelling van 28 dagen, bij een dosis van 4%.

Een voorwaarde voor het toepassen van actieve sanering ('active stripping'), waarbij GAC wordt toegevoegd aan verontreinigd sediment gedurende een relatief korte tijd, waarna de GAC met verontreinigingen wordt verwijderd, is dat de contaminanten effectief van het sediment naar de GAC getransporteerd worden. Daarom worden in **hoofdstuk 4** kinetische parameters bepaald waarmee PAK worden overgedragen van het sediment naar de GAC bij relatief lage dosering door het modeleren van experimentele sediment-GAC uitwisselingsdata met een 2-staps model kalibratie. Reactiesnelheden (KGAC) voor opname van PAK door GAC variëren tussen de 0.44 en 0.0005 d⁻¹, terwijl GAC-sorptiecoëfficiënten (KGAC)

variëren tussen de 105.57 en 108.57 L kg⁻¹. Deze resultaten tonen aan dat *ex situ* extractie met GAC voldoende snel en effectief is om risico's van de meest voorkomende PAHs die bestudeerd zijn te reduceren, zoals fluoreen, phenanthreen en antracene.

Het is onduidelijk hoe menging van GAC/sediment de desorptie kinetiek van HOCs beïnvloedt, bijvoorbeeld voor variërende grootte-verdeling van sedimentdeeltjes, en of deze factoren de effectiviteit van *ex situ* GAC extractie beïnvloeden. **Hoofdstuk 5** presenteert de resultaten van onderzoek naar het effect van meng intensiteit op de extractie snelheid van PAKs van verontreinigd sediment. Desorptie data worden geïnterpreteerd met een radiaal diffusie model. Het mengen veroorzaakte een afname van de deeltjesgrootte van 161 µm bij een roersnelheid van 200 rpm naar 9 µm bij 600 rpm. Desorptie snelheids constanten namen af bij toenemende PAK hydrofobiciteit maar namen toe met de meng intensiteit. De resultaten laten zien dat desorptie van PAKs significant sneller gaat wanneer de deeltjes grootte afneemt door schuifkrachten die veroorzaakt worden door het mengen.

In voorgaande studies zijn de sanerings effectiviteit en ecologische bij-effecten van AC behandeling op de korte termijn voornamelijk bestudeerd in het laboratorium. Het is echter nog niet duidelijk hoe de lagere porie-water concentraties zich ontwikkelen over langere tijdschalen en hoe dit verschilt tussen de verschillende chemische stoffen en voor verschillende scenarios voor AC sanering onder veld condities. **Hoofdstuk 6** bespreekt we (pseudo-)evenwichts en kinetische parameters voor *in situ* sorptie van een serie PAKs and PCBs voor actief koolstof in poeder- en korrelvorm na drie verschillende sediment behandelingen: sediment gemengd met AC in poedervorm (PAC), sediment gemixed met AC in korrelvorm (GAC toediening), en toediening van GAC gevolgd door 2 dagen mengen en verwijdering (*GAC stripping*) in het veld. De efficiëntie van de sanering wordt gegeven door de flux te bepalen naar de SPME *passive samplers* die in de toplaag van het sediment zijn geplaatst. Dit laat zien dat de efficiëntie afneemt volgens PAC > *GAC stripping* > GAC toediening. Sorptie met PAC was erg sterk, met een maximale log K_{AC} (L/kg) waarde van 10.5. Log K_{AC} waarden voor GAC varieerden van 6.3 – 7.1 en 4.8 – 6.2 voor PAKs en PCBs, respectievelijk. Log K_{AC} waarden voor GAC in het gestripte sediment waren 7.4 – 8.6 en 5.8 – 7.7 voor PAH en PCB. Schijnbare eerste orde adsorptieconstanten voor GAC (k_{GAC}) in het gestripte scenario zijn berekend met een eerste orde kinetisch model en varieerden van 1.6x10⁻² (PHE) tot 1.7x10⁻⁵ (InP). Deze studie laat zien dat sediment behandeling met PAC het meest effectief is en minder vatbaar voor vervuiling met organisch materiaal en voortgaande natuurlijke processen in het veld. De effectiviteit van GAC is hoger in het 48-uurs experiment waar het sediment gestript werd dan in het scenario waarin GAC is toegediend.

In **hoofdstuk 7** worden de effecten getest van drie verschillende AC behandelingen (zie hierboven) op HOC concentraties in porie water, bentische ongewervelden, zoöplankton en vissen (*Leuciscus idus melanotus*). De AC behandeling resulteerde in een significante daling van HOC concentraties in porie water, bentische ongewervelden, zoöplankton, macrofyten en vissen. Na 6 maanden behandeling met PAC was een verlaging veroorzaakt van PCBs in vissen met een factor 20, waardoor contaminant- niveaus onder de toxische grenswaarden

kwamen. Groei van de vispopulatie was mogelijk in alle AC behandelingen, maar deze groei was minder in het PAC experiment. Waarschijnlijk komt dit door verlaagde nutriënt concentraties die leiden tot lagere zoöplankton (voedsel) dichtheid voor vissen. Gedurende het veldexperiment bleek dat de verlaging van PCB ophoping in organismen langzamer was bij het gestripte sediment en sediment behandeling met GAC, maar beide behandelingen waren niet schadelijk voor de organismen.

In het laatste hoofdstuk (**hoofdstuk 8**) wordt antwoord gegeven op de onderzoeksvragen (zie hierboven) en implicaties voor *ex situ* toepassing van GAC in de praktijk.

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Curriculum vitae

Magdalena Iwona Rakowska was born on November 21, 1983 in Plock, Poland. In 2007 she received an MSc degree in General and Applied Chemistry at Maria Curie-Sklodowska University in Lublin. During her studies she specialized in Analytical Chemistry and worked with laboratory procedures suitable for the isolation and measurement of trace levels of inorganic compounds in water and biological samples. In her MSc thesis she focused on preconcentration of arsenic on activated carbon before their further determination by Graphite Furnace Atomic Absorption Spectrometry. Magdalena was an exchange visitor at the Department of Biotechnology, Chemistry and Environmental Engineering Aalborg University, Aalborg (Denmark) where she specialized in chemical processes and sorption of inorganic contaminants in incinerator bottom ash. After her graduation she worked at Polish Oil Refinery (PKN ORLEN S.A.) in Plock where she focused on implementing biofuels in fossil fuels. Since, sorption processes were of particular interest to Magdalena she decided to start her PhD research at the Sub-department of Environmental Technology of Wageningen University. Aim of the research was to explore the potential of activated carbon addition for the remediation of PAH- and PCB- contaminated sediments.

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SENSE PhD Courses

- o Environmental risk assessment of micropollutants (2010)
- o Biological processes in environmental technology (2010)
- o Environmental Research in Context (2010)
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- o Teaching and supervising thesis students Course (2010)
- o Co-organisation of Workshop 'Innovations in sediment remediation technology' (2012)

Oral Presentations

- o *Ex Situ Remediation of PAH- and PCB-contaminated Sediment with Granular Activated Carbon. A Pilot Field Study.* 12th International UFZ-Deltares Conference on Groundwater-Soil-Systems and Water Resource Management, 16-19 April 2013, Barcelona, Spain
- o *Ex Situ Remediation of PAH-Contaminated Sediments with Granular Activated Carbon.* Battelle Seventh International Conference on Remediation of Contaminated Sediments, 4-7 February 2013, Dallas, USA
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