ACTIVATED CARBON IN SEDIMENT REMEDIATION. BENEFITS, RISKS AND PERSPECTIVES

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To my mother
“who told me songs were for the birds,
then taught me all the tunes I know
and a good deal of the words.”
Ken Kesey

Contents

CHAPTER 1

GENERAL INTRODUCTION

Over the past decades, numerous trace contaminants have been produced and released into the environment as a result of anthropogenic activities like industry, agriculture and transport. Hydrophobic organic compounds (HOCs) such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides, dioxins and furans, brominated flame retardants (BFR), polyfluorinated compounds (PFCs) are of particular concern since they are very persistent, poorly degradable, bioaccumulative, can be transported over long distances and stay in the environment for a very long time *(1)*. Either as a result of direct discharges or hydrologic and atmospheric transport processes, the aquatic environment becomes an important sink for many of these contaminants. In water these contaminants bind to organic particles which eventually settle in depositional areas *(2, 3)*. Aquatic organisms may get exposed to these compounds, either directly through their diet or through uptake from the water column (dermal adsorption) or indirectly through HOC release after resuspension or bioturbation and subsequent transfer of contaminants to biota *(4-8)*. To reduce the risks associated with these persistent, bioaccumulative, and toxic (PBT) pollutants and to restore ecosystem quality and beneficial uses like fisheries and recreation, the sediments are often subjected to restoration (remediation) activities *(9)*. Remediation often costs tremendous amount of efforts, resources and money, and mainly relies on monitored natural recovery and more invasive capping and dredging.

Monitored natural recovery or natural attenuation is the least disruptive and least expensive restoration approach and is usually applied to sensitive and unique environments *(9)*. The deposition of clean particles and fresh organic matter are believed to be key processes in natural recovery. Newly formed clean layers cover the sediment surface and bury the contaminants, eventually disconnecting them from the bed surface layer, the overlying water, and aquatic organisms. In addition, processes like biological and chemical degradation, sequestration and bed consolidation contribute to a decreased contaminant exposure in time and facilitate natural recovery *(10)*. However, in aquatic systems with unfavourable water flow conditions or physical and biological disturbances causing release of sediment-associated contaminants, natural recovery might be not the optimal remediation strategy *(11-13)*. Furthermore, natural attenuation may take years or even decades.

In situ capping aims at reducing exposure by creating a 30-100 cm protective barrier made of clean material such as silt or sand on the bed source material, which isolates contaminated sediments *(9)*. However, capping does not always sufficiently reduce contaminant transport due to permeability of capping materials or wave pumping *(14, 15)*. In addition, capping may not be efficient in sensitive ecosystems and in systems with a dynamic topography *(9)*.

Dredging involves excavation of large quantities of the contaminated material from the aquatic environment. It is a highly site-specific technique and is usually applied to sediments liable to erosion and to variations in hydrologic conditions. Dredging, however, leads to sediment disturbances and resuspension of underlying deep sediment particles, temporarily increasing pore water concentrations of contaminants. Dredging is very disruptive to the ecosystem. Moreover, inefficient removal of contaminated sediment during dredging may result in residual concentrations of contaminants in sediment and pore water still exceeding safe levels *(9)*. The dredged material is usually subjected to two cleaning techniques, viz. bioremediation and/or physical separation. Since the total volume of dredged material is exceeding the capacity of the cleaning facilities and both techniques are quite expensive, dredged materials typically are disposed in confined or hazardous disposal facilities. Even though sediment dumping is cheaper than cleaning, the costs of sediment disposal at sediment depots are high and the number of facilities is limited *(16, 17)*. Hence, the need for depot capacity is widely acknowledged, but social acceptance of the construction of new depots is low. Public fear for leaching of contaminants from depot is an important factor causing delays or prevention in the realization of new depots *(18)*.

It should be noted that remediation activities should not only reduce human health risks and toxicological risks on the single species level, but should also reduce the impact of sediment contamination on benthic communities. Dredging and capping remove chemical risk but at the same time partially or completely destroys benthic habitats and benthic communities. Recovery of benthic communities following a major physical disturbance like sediment dredging or capping, has been shown to be a very complex and site specific process. Community recovery depends on a number of factors such as ecosystem resilience, community composition, sediment characteristics, hydrological conditions, duration and scale of the disturbance and may last from 6 months to 10 years *(19-21)*. Thus, traditional approaches are complex, do not always achieve risk reduction goals for ecosystem and human health protection and can even be destructive for natural environments. Therefore, new remediation approaches are needed that either supplement or provide less laborious, less expensive, less disruptive alternatives to existing methods, and which are still able to reduce human and ecosystem exposure.

In the past decade, it has been shown that naturally occurring carbonaceous materials in sediment, such as soot and charcoal, often referred to as “black carbon” (BC) are able to bind organic pollutants very effectively, reducing exposure and risk by one order of magnitude or even more *(22, 23)*. This binding is similar to that of clean manufactured carbonaceous materials like activated carbons (AC), as used in water-cleaning technologies and as poison control for many years *(24-27)*. These findings have led to several studies investigating whether deliberately added AC to polluted sediment can reduce risks towards aquatic organisms as well as the risks of transport and leaching of contaminants *(28-30)*. Rather than excavation and relocation of contaminated material, AC sorbent amendments directly reduce chemical exposure on site, thus saving costs compared to traditional methods *(28, 30-32)*.

AC is a porous, manufactured material with a high surface area and affinity for adsorbing organic chemicals *(22, 23, 33, 34)*. AC reduces pore water concentrations by sequestration of the chemicals through partitioning or adsorption to the surface within its pore structure *(35-38)*. In addition, AC has a slow kinetics of contaminant desorption, which implies that fluxes of HOCs to the aqueous phase are low, which limits contaminant mobility in the aquatic environment *(12, 36)*. Early studies showed that the efficiency of AC depends on several factors: (i) AC characteristics, e.g. particle size and pore geometry *(11, 39-41)*, (ii) the steric properties of the sorbates, such as hydrophobicity, molar volume, and planarity of molecular conformation *(42-45)*, (iii) AC dose applied *(11, 41, 46)*, (iv) sorption competition among different HOC or organic matter (OM) adsorbates (OM "fouling") *(47)*, (v) homogeneity of the AC-sediment mixture *(48, 49)*. Furthermore, the redistribution of HOCs in AC-amended sediment can be rate-limited, which can have a negative effect on the remediation effectiveness *(46, 48, 50, 51)*.

Even though much progress has been made over the past years to better understand the mechanisms by which AC affects bioavailability and thus toxicity of HOCs, there are two main research gaps. First, it is unclear to what extent reductions of pore water concentrations and bioavailability as detected in laboratory studies apply to field applications of AC remediation technology. The effectiveness of AC treatments on the field scale may be different for different types of AC applied. Second, full scale applications of AC remediation technology are to be considered premature, because sediment treatment with AC might cause ecological and ecotoxicological side-effects that should be known first *(52-56)*. Although some studies on the ecological safety of AC amendments have been performed, they can be considered fragmentary and incomplete. For instance, more information is needed on behavioural effects on benthic species, impacts on benthic communities, and effects on the level of the entire aquatic ecosystem including HOC transfer along the aquatic food chain. Furthermore, an important question is how the trade-off between positive and negative effects of AC amendments to benthic populations may be addressed. At start of the present project, data on AC effects on single species were limited and contradictory. Data on higher levels of biological organization were not available.

The current research was meant to increase our mechanistic understanding of the effects of AC application on HOC exposure and toxicity reduction for benthic species and communities, and to bridge the gap between laboratory and field settings for AC remediation. This included the evaluation of alternative methods of AC deployment and application. The obtained knowledge may help in gaining regulatory acceptance of this emerging remediation technique and can be used to improve risk assessment and decision support with respect to contaminated sediments, reduce risks caused by polluted sediment sites, and take away public resistance against contaminated sediments and sediment remediation.

Sediment amendment with strong sorbents like carbonaceous materials is a rapidly developing management strategy. An overview of the state of the art for the use of carbonaceous materials as *in situ* method for sediment remediation, covering technological as well as ecotoxicological issues is presented in **Chapter 2**. This Chapter addresses the key factors (e.g. AC dose, type, particle size, sediment and sorbent characteristics) affecting AC efficiency to immobilize HOCs in aquatic sediments and also discusses the literature on biological responses to AC amendments.

Since sediments and AC types obviously differ in their characteristics, it is highly relevant to identify the affinity parameters for *in situ* sorption of HOCs to AC in order to be able to design and evaluate applications of AC in sediment remediation. In **Chapter 3**, datasets from single and multiple site AC amendment trials are analyzed (a) to identify the variation in effectiveness of AC and (b) to explore to what extent HOC binding to AC may be generalized for different AC types in different sediments in different field settings.

Activated carbon is known to bind sediment-bound HOCs strongly and to efficiently reduce their bioavailable fractions. However, effects of AC on HOC sediment-to-water fluxes have not been studied, whereas exposure to pelagic communities may depend on such fluxes. Moreover, it is not clear how the presence of AC and occurrence of bioturbation interact. In **Chapter 4**, combining experimental and modelling approaches, the efficiency of four treatments, viz. no AC addition, powdered AC addition, granular AC addition and addition and subsequent removal of GAC (sediment stripping), is investigated by evaluating polychlorobiphenyl (PCB) pore water concentrations, sediment-to-water fluxes, DOC-inclusive mass transfer coefficients, and survival of two benthic species. This is the first time that support for DOC facilitated transport in a field AC remediation setting is obtained and evaluated by model analysis.

Apart from the advantageous effects of sediment treatment with AC, AC itself may have negative effects on aquatic organisms, raising the question to what extent the addition of AC to sediments can be considered ecologically safe. Therefore, effects of AC addition on locomotion and ventilation, sediment avoidance, mortality and growth of two benthic species, *Gammarus pulex* and *Asellus aquaticus*, in clean versus polycyclic aromatic hydrocarbon (PAH) contaminated sediments are evaluated in a series of single species laboratory bioassays (**Chapter 5)**.

Although AC binds toxic compounds, it cannot be ruled out that there may be negative effects on the biological system. It is important that these possible side-effects are properly addressed before AC amendments can be implemented as a safe and accepted method for sediment remediation. In **Chapter 6**, a conceptual model to quantify the trade-off, in terms of biomass changes, between the advantageous PAH toxicity reduction and the negative effects of AC on populations of benthic species is developed and presented. The model describes population growth, incorporates concentration-effect relationships for PAHs in the pore water and for AC, and uses equilibrium sorption models to estimate PAH pore water concentrations as a function of AC concentration.

At the time of starting this research, AC effect studies were limited to single species laboratory tests. However, it can be hypothesized that actual community effects are less severe in field settings, where recolonization occurs and where dispersion of AC and fresh input of organic matter will continuously form new habitats on top of treated sediments. Therefore, in **Chapter 7**, the effects of sediment treatment with AC on the recovery of benthic communities over time are described. For the first time, the significance of AC effects is analysed using variance partitioning of the community data, quantifying the relative impacts of time and environmental variables on the recovery of the community.

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, yet its effectiveness and safety have never been tested on the level of entire food chains including fish. In **Chapter 8**, the effects of three different AC treatments, viz. mixing sediment with powdered AC, mixing with granular AC, and mixing with granular AC with subsequent removal of granules, i.e. sediment stripping, are assessed on polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyls (PCB concentrations in pore water, benthic invertebrates, zooplankton and fish. In addition, biological side effects of AC amendments for the aforementioned scenarios are assessed for fish, by evaluating functional group abundances, lipid contents and condition factors.

In the final chapter (**Chapter 9**), the results of the project are summarized and synthesised. Benefits and risks associated with AC application are considered and perspectives are defined.

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CHAPTER 2

IN SITU REMEDIATION OF CONTAMINATED SEDIMENTS USING CARBONACEOUS MATERIALS: A 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, 40, 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)*. 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.

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 in SPMD^{b} uptake, %	Adsorbate	LogK_{AC}^{c}	Reference
TOG®/TOG-NDS	virgin granulated	coal	935	0.074-0.297	3.2	2-3	31	67	-	DDT	-	*(13)*
Calgon Carbon				0.074-0.177				83	80		-	
(Pittsburgh, PA, USA)			938	0.075-0.3	3.4	3	28	74	83	PAHs	-	*(27)*
							180	84			-	
							28	87	77	PCBs	7.5	
							180	92			7.6	
							-	-	-		7.5^{d}	*(60)*
			938	0.075-0.3	0.34	3	28	70	68	PAHs	-	*(66)*
					1.7			81	84		-	
					3.4			84	87		-	
					0.34			44	17	PCBs	7.4	
					1.7			74	45		7.7	
					3.4			87	73		7.4	
				0.025-0.075	3.4	3	28	97	-	PCBs	-	*(84)*
			938	0.075-0.3	0.7	2-3	30	82	54	PCBs	-	*(63)*
					1.3			94	83		-	
					2.5			97	92		-	
			1032	0.020-0.25	-	-	-	-	-	PAH/PCB	-	*(86)*
			938	0.074-0.177	3.2	2	31	91	80	DDT	-	*(65)*
			938	0.075-0.3	3.4	3	28	87	-	PCBs		*(52)*
			938	0.075-0.3	0.4	3	28	69	-	PCBs	7.0	*(12)*
					1.6			77			7.2	
					1.9			77			7.3	
					2.6			97			7.1	
			938	0.075-0.350	2.6	-	28	77	-	PCBs	-	*(64)*
							180	82			-	
			938	0.075-0.350	2.0	2	28	96	78	PCBs	-	*(54)*
							180	98	91		-	
							540	99	97		-	
			-	0.075-0.3	2-3.2	rotovator	180	80,73^{e}		PCBs	8.1	*(23)*
						injector		-			-	
					3.4	2	14	80^{f}	-	PCBs	-	*(57)*
								37^{g}			-	
					3.4	4	28	99	-	PCBs	-	*(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				83	91		-	
				0.074-0.177	3.2	2	31	95	91	DDT	-	*(65)*
				0.595-2.38	3.2	2-3	28	-	8	DDT	-	*(13)*
					6.4			-	20		-	
					9.6			-	46		-	
				0.074-0.177	0.8		28	-	21		-	
							180	-	30		-	
							780	-	73		-	
					1.6		28	-	50		-	
							180	-	80		-	
							780	-	95		-	
					3.2		28	-	87		-	
							180	-	95		-	
							780	-	99		-	
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	50%<0.015; 3%>0.150	2	-	42	96[h];55[i]	-	PAH	-	*(71)*
					1	-	2	90	-	PAH	7.2	*(74)*
					3			99	-		7.9	
					6			>99	-		7.7	
					15			>99	-		7.8	
					30			>99	-		7.7	
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	-	*(56)*

[a] Specific surface area (SSA). [b] Semi-permeable membrane device (SPMD). [c] $\mathrm{Log}K_{AC}$ values from *(61)*. [d] Average $\mathrm{Log}K_{AC}$ 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 *(55)*. [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 *(56)*. [l] Capping with PAC-clay mixture *(56)*.

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, 23, 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* LogK_{AC} values, with associated standard deviations (SD) were 7.2 (0.3) for PCBs (LogK_{OW} 4.9–6.3) and 8.5 (0.5) for PAHs (LogK_{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 LogK_{AC} for PAHs and PCBs was found in a relatively narrow range. The LogK_{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* 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 LogK_{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, 77, 78)*. 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 *(79)*. 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)* performed laboratory experiments with intensively mixed (shaken end-over-end) systems, whereas Cornelissen et al. *(56)* 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, 56)*. 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% *(55)*. 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 *(56)*. 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 *(56)*. However, in contrast with earlier field trials *(23, 24)*, Cornelissen et al. *(56)* 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. *(55)* 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, 80, 81)*. 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, 82-84)*. 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, 85-90)*. 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, 85)*, 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 bioacumulation of PCBs decreases by 70 to 95% within 1 month *(12, 51, 52, 63, 64, 84)*. 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, 80, 81)*.

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, 81, 82)*. 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, 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 *(82)*, coal *(51)*, and charcoal *(51)*, respectively.

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	*N. arenaceodentata* *L. plumulosus*	AC: TOG (Calgon, Pittsburgh, PA, USA) 75–300 µm, 3.4%;	28 days	not significant	*(52)*
	M. eduli	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)*
	M. balthica	AC: TOG (Calgon, Pittsburgh, PA, USA) 75-300 µm, 2.5, 1.3, and 0.7%	28 days	25, 15%, <5%, respectively	*(63)*
	M. nasuta	AC: TOG (Calgon, Pittsburgh, PA, USA) 74-177 µm, 3.2%	28 days	not significant	*(24)*
	A. aquaticus *C. volutator*	AC: Organosorb 200-1 (Desotec Activated Carbon, Belgium), 90% < 74 µm, <25%	28 days	not significant	*(82)*
	G. pulex *A. aquaticus*	AC: SAE Super (Norit, Amesfoort, The Netherlands), D_{50}=15 µm, < 30%	28 days	LC_{50}=3.1% not significant	*(74)*
	N. arenaceodentata	AC: TOG-NDS (Calgon , Pittsburgh, PA, USA) 75-300 µm, 3.4%	14 days *in situ* 14 days *ex situ*	not significant	*(57)*
Growth/ condition index	*N. arenaceodentata* *L. plumulosus*	AC: TOG (Calgon, Pittsburgh, PA, USA) 75–300 µm, 3.4%	28 days	decrease by 50% w.w. non-significant decrease	*(52)*
	M. eduli	AC: TOG (Calgon, Pittsburgh, PA, USA) 75–300 µm, 3.4%	28 days	minor decrease in average condition index	*(65)*
	C. fluminea	AC: TOG (Calgon, Pittsburgh, PA, USA) 74-177 µm, 3.2%	28 days	non-significant decrease	*(63)*
	G. pulex *A. aquaticus*	AC: SAE Super (Norit, Amesfoort, The Netherlands), D_{50}=15 µm, < 30%	28 days	not significant (AC < 3%) EC_{50}=5.3%	*(74)*
	N. arenaceodentata	AC: TOG-NDS (Calgon , Pittsburgh, PA, USA) 75-300 µm, 3.4%	14 days *in situ* 14 days *ex situ*	non-significant difference	*(57)*

Lipid content	*Limnodrilus sp*	Coal, 1.48% Charcoal, 1.48%	28 days	decrease by 28% decrease by 38%	*(51)*
	L. variegatus	AC: Organosorb 200-1 (Desotec Activated Carbon, Belgium), 90% < 74 µm, < 25%	16 weeks	decrease by 75%	*(82)*
	H. reticulatus *N. diversicolor*	AC: 100–400 mesh (Sigma-Aldrich, Oslo, Norway), 37–149 µm, 2%	28 days	non-significant decrease	*(72)*
	N. arenaceodentata *L. plumulosus*	AC: TOG (Calgon, Pittsburgh, PA, USA) 75–300 µm, 3.4%	28 days	non-significant decrease	*(52)*
	N. arenaceodentata	AC: TOG-NDS (Calgon , Pittsburgh, PA, USA) 75-300 µm, 3.4%	14 days *in situ* 14 days *ex situ*	non-significant difference significant decrease	*(57)*
Avoidance/preference	*A. aquaticus* *C. volutator*	AC: Organosorb 200-1 (Desotec Activated Carbon, Belgium), 90% < 74 µm, 4, 7, 15, and 25%	3 days	non-significant avoidance significant avoidance	*(82)*
	G. pulex *A. aquaticus*	AC: SAE Super (Norit, Amesfoort, The Netherlands), D_{50}=15 µm, < 30%	3 days	non-significant avoidance	*(74)*
Locomotion/ventilation	*G. pulex* *A. aquaticus*	AC: SAE Super (Norit, Amesfoort, The Netherlands), D_{50}=15 µm, < 30%	1 day 5 days	non-significant change	*(74)*
Reproduction	*L. plumulosus*	AC: TOG (Calgon, Pittsburgh, PA, USA) 75–300 µm, 3.4%	28 days	non-significant decrease	*(52)*
Egestion rate	*L. variegatus*	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	*(82)*
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	*(56)*
	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	*(82)*

The reduced lipid content (74%) was caused by reduced feeding (92%) by these worms when exposed to sediment with 10% AC *(82)*. 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 *(82)* whereas egestion rates of worms exposed to 4% AC declined by 92% over 10 d *(82)*. 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. *(83)*. 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, 82)*. 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 Cornelissen et al. *(56)*. 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, 82)*. 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, 82)*, 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, 82)*, 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 *(82)*. 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 *(82)*. 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, 83, 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, 84, 96)*. Some studies combined HOC intraparticle diffusion models or desorption and adsorption by native or added particles with biodynamic modeling *(53, 97, 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, 98)*. 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 “Effects of CM dosage in sediment remediation” section. 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 *(55)*.Whereas these model studies emphasized the true diffusive transport mechanisms, Matilla and 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, 84, 87, 96, 97, 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, 84)* and Selck et al. *(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, 97, 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.

Because 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 *(56)*. 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

IN SITU SORPTION OF HYDROPHOBIC ORGANIC COMPOUNDS TO SEDIMENT AMENDED WITH ACTIVATED CARBON

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Abstract

Contaminated sediments can be remediated by adding carbonaceous materials (CM), e.g. activated carbons (AC). Here, we analyze published datasets from AC amendment trials to identify variation in the effectiveness of AC in reducing pore water concentrations of hydrophobic organic contaminants (HOCs). The analysis uses a model that separates the contribution of HOC sorption to AC by parameterzing the sorption contributions by amorphous organic matter and black carbon (BC). It appears that sorption to BC increased with LogK_{OW}, whereas sorption to AC showed a relatively narrow range of affinity properties with a median Freundlich Log$K_{F,AC}$ value of 7.2 (μg/kg$_{AC}$)/(μg/L)^n (IQR=7.0-7.5) for polychlorinated biphenyls (PCBs) and 8.6 (IQR=8.3-8.8) for polycyclic aromatic hydrocarbons (PAHs). Estimated Freundlich exponents were $n_{F,AC}$=0.74 for PCBs and 0.82 for PAH. Sorption to AC was stronger than to BC for chemicals below LogK_{OW}=6.3–6.6. For HOC risk reduction this is favorable, because chemicals with low K_{OW} show generally higher bioavailable concentrations.

Introduction

Aquatic sediments form an ultimate sink for legacy contaminants such as persistent organic compounds *(1)*, thereby posing a source of exposure to aquatic ecosystems. Sediment-bound contaminants may become available to organisms through desorption from sediment or particle ingestion *(2)*. In the past few years several studies demonstrated the ability of carbonaceous materials (CM), like soot and charcoal, often referred to as “black carbon” (BC), to bind sediment-bound hydrophobic organic chemicals (HOCs) very efficiently *(3-5)*. This limits the mobile and bioavailable concentrations of contaminants, which has been hypothesized to have beneficial effects on ecological risks of HOCs as well as the risks of their transport and leaching. The sequestration of HOCs can be significantly enhanced by addition of manufactured carbon materials such as activated carbons. Therefore, over the past years the potential of adding CM such as commercial activated carbons (AC) to polluted sediment as a means to reduce pore water HOC concentrations has been explored *(6, 7)*. Several studies demonstrated that addition of 3-4% of AC results in dramatic reduction of pore water concentration of HOCs *(8-12)*. The results of these studies suggest that AC addition may be used in sediment remediation as an efficient and safe engineering approach, which is less disruptive compared to dredging.

Since sediments and AC types obviously differ in their characteristics, it is highly relevant to identify the affinity parameters for *in situ* sorption of HOCs to AC in order to be able to design and evaluate applications of AC in sediment remediation. For instance, sediments with high natural CM or oil contents already may sequester HOCs very effectively *(13, 14)*, thus limiting the added value of AC amendments. Furthermore, sediments contain considerable quantities of particulate and dissolved organic matter known to attenuate sorption to CMs, including activated carbons *(14-16)*. Particle sizes and compositions may differ among sediments, thus affecting the rate at which HOCs equilibrate between dissolved and sorbed states, including the state of HOCs bound to AC after intentional AC amendment in a remediation context *(17)*. In turn, AC differs among brands and types in particle size, porosity, surface area and composition, which may also affect the intended enhanced sequestration of native HOCs. Despite the above, there are other arguments supporting limited variation in reported HOC sequestration among AC-sediment combinations. Organic matter fouling may overrule differences in AC sorption properties by pore blocking or competitive sorption mechanisms. Differences in AC sorption capacity or HOC - AC sorption isotherms may become irrelevant at the targeted low concentration levels after AC amendment *(18, 19)*. Third, studies that aimed at exploring the efficiency of AC from a remediation perspective have used similar criteria for AC characteristics (e.g., small particles with a high porosity). This may limit variation in reported data. Consequently, a major question is to what extent *in situ* sorption to AC varies among HOCs, sediments and AC types because of the aforementioned factors, and to what extent the use of generic 'activated carbon sorption parameters' is warranted. We are not aware of any earlier study addressing the variation in effectiveness of AC by analyzing datasets from single or multiple site AC amendment trials.

Here, we explore to what extent HOC binding to AC may be generalized for different AC types applied to different natural sediments. Our approach used the concept of multiple domain equilibrium sorption *(4, 15, 20-24)*, applied earlier to distinguish between the respective sorption contributions of amorphous organic matter (AOM) and natural CM. The *in situ* contribution of sorption to activated carbon was separated from total sorption by parameterizing and subtracting the sorption contributions by AOM and BC. A large dataset covering 63 PCBs, 10 PAH, 2 types of AC and 9 sediments was obtained from the literature *(10, 12, 25, 26)*.

Methods

Modeling *in situ* sorption of native hydrophobic organic contaminants to added activated carbon

After addition of AC to contaminated sediment, the AC will compete with the original sediment organic matter phases to establish a new HOC sorption equilibrium. The sorption equilibria can be expressed by common isotherm equations, whose parameters reflect the overall efficiency and quality of the sorbent.

The equilibrium redistribution of HOCs upon addition of powdered AC can be quantified from the decrease relative to the original pore water concentration (C_W^0) after AC addition. Assuming equilibrium and presence of two main sorption domains, i.e. amorphous organic matter carbon (OC) and BC, HOC equilibrium distribution in the sediment bed before AC addition can be defined as:

$$C_{sed} = f_{OC}K_{OC}C_W^0 + f_{BC}K_{BC}\left(C_W^0\right)^{n_{F,BC}} \qquad (1)$$

where C_{sed} (ng/kg) is the concentration sorbed to the total sediment mixture (OC, BC, etc), which is assumed to remain unchanged after AC addition, and f_{OC} is the organic carbon fraction (kg_{OC}/kg_{sed}), f_{BC} is the fraction of BC (kg_{BC}/kg_{sed}), K_{OC} is the organic carbon normalized sorption coefficient for OC (L/kg_{OC}), K_{BC} is the Freundlich adsorption coefficient for BC $(\mu g/kg_{BC})/(\mu g/L)^{nF,BC}$ and $n_{F,BC}$ is the Freundlich exponent for BC. This summation thus accounts for the fact that not only amorphous organic matter (AOM, quantified as OC), but also BC acts as sorbent for HOCs *(3, 4, 14, 27)*. After the addition of AC and allowing sorption to AC to be non-linear as parameterized by the Freundlich isotherm, a new equilibrium state has to satisfy:

$$C_{sed} = f_{OC}K_{OC}C_W^1 + f_{BC}K_{BC}\left(C_W^1\right)^{n_{F,BC}} + f_{AC}K_{AC}\left(C_W^1\right)^{n_{F,AC}} \qquad (2)$$

in which K_{AC} is the Freundlich adsorption coefficient for AC $(\mu g/kg_{AC})/(\mu g/L)^{nF,AC}$, f_{AC} is the fraction of added AC (kg_{AC}/kg_{sed}), C_W^1 is the HOC pore water concentration after AC amendment (ng/L), and $n_{F,AC}$ is the Freundlich exponent for AC. Note that the second and third term in eq 2 may also accommodate linear sorption (through $n_F = 1$) or may be replaced by other non-linear models such as the Langmuir or Polanyi models, if required *(28)*.

Assuming C_{sed} remains the same before and after AC addition, eqs 1 and 2 now can be combined to yield:

$$f_{OC}K_{OC}C_W^0 + f_{BC}K_{BC}\left(C_W^0\right)^{n_{F,BC}} = f_{OC}K_{OC}C_W^1 + f_{BC}K_{BC}\left(C_W^1\right)^{n_{F,BC}} + f_{AC}K_{AC}\left(C_W^1\right)^{n_{F,AC}} \qquad (3)$$

which after rearrangement yields:

$$K_{AC} = \frac{f_{OC}K_{OC}(C_W^0 - C_W^1) + f_{BC}K_{BC}\left[\left(C_W^0\right)^{n_{F,BC}} - \left(C_W^1\right)^{n_{F,BC}}\right]}{f_{AC}\left(C_W^1\right)^{n_{F,AC}}} \qquad (4)$$

Eq 3 shows how for any given C_W^0, the reduced pore water concentration C_W^1, can be calculated from AC dose (f_{AC}), chemical dependent affinity constants for amorphous-, black- and activated carbon ($K_{OC,}$, K_{BC}, K_{AC}) and the Freundlich exponents ($n_{F,BC}$, $n_{F,AC}$). The equation also shows how the effect of AC dose (the third right hand side term) decreases if more organic matter and black carbon (the first and the second right hand side terms) are present in the sediment. Note that eq 3 can only be solved numerically, because of the exponents in the BC and AC terms. *In situ* HOC K_{AC} values, however, can be calculated directly from eq 4 once the other parameters and variables are known. If all concentrations relate to equilibrium, eq 4 returns an equilibrium sorption coefficient. If not, K_{AC} is conditional.

Parameterization of the model

Description of dataset. The *in situ* K_{AC} values were estimated using eq 4 and data for six PCB homologue groups and 10 PAHs in nine different sediments reported earlier by Zimmerman et al. (2004, 2005), Cornelissen et al. (2006), and Sun and Ghosh (2008). Data for PCBs were not reported for individual congeners, so we grouped them as dichlorobiphenyls (di-CB), trichlorobiphenyls (tri-CB), tetrachlorobiphenyls (tetra-CB), pentachlorobiphenyls (penta-CB), hexachlorobiphenyls (hexa-CB), heptachlorobiphenyls (hepta-CB) and octachlorobiphenyls (octa-CB), assuming similar sorption properties per homologue group. Studied PAHs were benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[e]pyrene (BeP), benzo[ghi]perylene (BghiP), benzo[k]fluoranthene (BkF), chrysene (CHR), fluoranthene (FLU), indeno[1,2,3-cd]pyrene (InP), phenanthrene (PHE), and pyrene (PYR). Details of the dataset are provided as supporting information (Table S1). Sum concentrations (ΣC_{sed}) ranged from 0.33 to 87 mg/kg (ΣPCB) and 2.0 to 160 mg/kg (ΣPAHs) and were typically measured using rigorous (sonication, liquid-liquid) extraction techniques. Initial sum concentrations in the pore water ranged from 0.010 to 2.3 µg/L (ΣPCB) and 92 to 620 µg/L (ΣPAH) and were measured *ex situ* directly after liquid-liquid extraction or using passive samplers such as polyoxymethylene (55 µm thickness). After AC amendment, sum concentrations in the pore water were much lower, ranging from 0.004 to 0.55 µg/L (ΣPCB) and 0.0002 to 0.034 µg/L (ΣPAH). Equilibration times after AC amendment ranged from 28 to 180 days (Table S1). To approach true AC-water equilibrium, PAH aqueous phase concentrations were measured after elevation of temperature (60ºC) *(25)*.

Parameterization of the model. Chemical pore water concentrations (C_W^0, C_W^1) and sediment characteristics f_{OC}, f_{BC}, f_{AC}, were all measured (see Table S1).

The K_{OC} values for amorphous carbon were calculated from compound class specific quantitative structure property relationships (QSPRs) taken from van Noort *(29, 30)*. For PCBs the QSPR reads $\mathrm{Log}K_{OC} = 0.53\ (N_{Cl} - 0.33\ N_{ortho}) + 3.27$, where N_{Cl} is the total number of chlorine atoms and N_{ortho} is the number of ortho-chlorines. For PAHs, the QSPR is: $\mathrm{Log}K_{OC} = 1.11\ \mathrm{Log}K_{OW} - 1.14$. $\mathrm{Log}K_{OW}$ values for PCBs and PAHs were taken from Booij et al. *(31)* and Hawker and Connell *(32)*.

BC Freundlich sorption affinity constants for all individual chemicals (K_{BC}) were calculated from the pore water data prior to AC addition (C_W^0), using the dual domain approach as condensed in eq 1, *(4, 20-24)*, which can be rearranged to:

$$K_{BC} = \frac{C_{sed} - f_{OC} K_{OC} C_W^0}{f_{BC} \left(C_W^0\right)^{n_{F,BC}}} \tag{5}$$

Values for C_{sed}, C_W^0, f_{OC}, and f_{BC} were used as published (see Table S1), and K_{OC} values for amorphous carbon were estimated as described above.

As for non-linearity of sorption to BC and AC, three scenarios were followed. The first scenario used a non-linear model approach in which the Freundlich exponents were optimized (i.e. $n_{F,AC} \neq 1$ and $n_{F,BC} \neq 1$) such, that variability in Freundlich affinity constants (K_{BC}, K_{AC}) was minimized. This procedure follows the logic that a Freundlich coefficient that better approaches the true value will lead to more accurate and less variable estimates of the Freundlich affinity constants. Mechanistically, the non-linearity scenario is supported by many observations of curved isotherms at higher concentrations *(3, 4, 33)*. Although values for $n_{F,AC}$ and $n_{F,BC}$ are chemical as well as sorbent specific, literature data show that chemical differences are primarily expressed through the sorption affinity constant *(3, 4, 20, 22, 23)*. Freundlich exponents are affected by surface saturation phenomena which are reported to be similar for structurally similar chemicals *(18)*. Consequently, in the nonlinearity scenarios $n_{F,AC}$ was optimized per chemical class rather than calculated per individual chemical.

The second scenario used a model from Zhang and He *(33)*, that estimates BC Freundlich exponents from sediment BC and TOC content:

$$n_{F,BC} = 0.410 + 0.454e^{-0.028BC/TOC} \qquad (6)$$

where TOC is total organic carbon. Zhang and He *(33)* derived this expression from PHE isotherms to BC. Consequently, this scenario tests to what extent PHE sorption to BC is representative for the wider group of chemicals analyzed in this study. BC and TOC data were used as reported (Table S1) and extracted values were used to calculated $K_{F,BC}$. Because eq 6 was derived from BC sorption data, this scenario was not applied to AC.

The third scenario used a linear sorption model in which the Freundlich exponents were set to 1 (i.e. $n_{F,AC} = n_{F,BC} = 1$). This scenario is supported by recent observations that at very low concentrations, isotherms for CM may approach linearity *(18, 19)* and by the observation that HOC sorption to fouled CM is more linear than to virgin CM *(27)*.

Sensitivity analysis. Following Accardi-Dey and Gschwend *(34)* and Lambert et al. *(24)*, a simple sensitivity analysis was performed by repeating all K_{AC} estimations at $n_{F,AC}$ and $n_{F,BC}$ plus and minus 10% of their optimum values. This provides a rough estimate of the sensitivity of the model outcome i.e. sorption coefficient to variations in the n_F-values and also illustrates the correlation between K_{AC} and n_F.

Results and discussions

In situ black carbon sorption parameters

Scenarios for calculating $n_{F,BC}$. The best fit to the data, that is, the smallest variation in calculated K_{BC} values per chemical, was observed with $n_{F,BC,optimized} = 0.82$ for PCBs and $n_{F,BC,optimized} = 0.83$ for PAHs (Table 1, Scenario 1; Figure 1a). This suggests that *in situ* sorption of PCBs and PAHs to BC was non-linear as was described before *(3, 4)*. The fitted Freundlich exponents lie in the upper range of those previously reported for pure BC, i.e., $n_{F,BC} = 0.6 - 0.8$ *(3, 4, 20, 34-36)*. This means that the current *in situ* sorption is closer to linearity than reported from laboratory studies with pure BC *(27)*. Lower pore water concentration ranges or fouling with OM may explain the difference *(18, 19)*. Variation of the Freundlich exponent by ± 10% did not increase the variation (SD) in the K_{BC} values for both PCBs and PAHs. Therefore, any uncertainty in Freundlich exponents did not significantly affect estimation of PCB and PAH K_{BC} values.

The second scenario used $n_{F,BC}$ values calculated with eq 6, which was originally derived for PHE *(33)*. For this compound, the resulting LogK_{BC} is 7.6 ± 0.2 (Table 1, Scenario 2). This is very close to the value obtained in the first scenario (LogK_{BC} = 7.5 ± 0.2, Table 1), where $n_{F,BC}$ was optimized to obtain minimum variation in resulting K_{BC} values. For the other chemically similar PAHs, e.g. FLU and PYR, the values were also close (difference of 0.1 Log unit), whereas for CHR, BbF, BaP, BeP, PER, InP, and BghiP, the K_{BC} values calculated using eq 6 were identical to those estimated with $n_{F,BC\ optimized}$ (Table 1, Figure S1). Also for PCBs the two scenarios resulted in K_{BC} values that were close (0.1 Log unit difference for di-, tri-, tetra-, penta-, hexa-, and octa-CB, Table 1) or identical (hepta-CB, Table 1).

The third scenario, assuming $n_{F,BC} = 1$, was included for completeness and yields K_{BC} values that are 0 to 0.3 Log units lower than those from the other two scenarios for the calculation of $n_{F,BC}$ (Table 1, Scenario 3). Compared to Scenario 1, the variation (SD) in K_{BC} values, however, increases by a factor 1.5-2 for 9 compounds (di- and penta-CB, PHE, FLU, PYR, CHR, BbF, BeP, PER) whereas the variation decreases only for one compound (tri-CB), also by a factor 1.5. Considering all scenarios, we conclude that the results from the optimized non-linear scenario are to be preferred for the current dataset and therefore are used for further discussion and calculations.

K_{BC} values calculated with $n_{F,BC\ optimized}$. The K_{BC} values per chemical calculated with $n_{F,BC\ optimized}$, varied with SD < 0.3 Log unit (Table 1). This implies that despite the variation in sediment characteristics and methods used, K_{BC} values varied less than a factor 2.5. LogK_{BC} values increase between LogK_{OW} = 4.5 and 6.5 and appear to level off at higher LogK_{OW} values (Figure 1a). This may suggest that sorption for the first mentioned range is hydrophobicity driven partitioning, whereas surface adsorption prevails for the more bulky compounds at higher LogK_{OW}. Individually modeled Log$K_{F,BC}$ values for PCBs were one order of magnitude lower than those for PAHs, which agrees with earlier reported BC sorption constants for these compound classes *(22, 23, 37).*

In situ activated carbon sorption parameters

The K_{BC} values calculated with $n_{F,BC\ optimized}$ were used as input for the calculation of K_{AC} (eq 4). Consequently, the contribution of sorption to BC at the reduced pore water concentration C_W^1 was accounted for using the independently estimated non-linear BC isotherms.

Table 1. BC-water and AC-water Freundlich affinity constants (SD) for PCBs and PAHs, calculated using eq 4 and 5 with $n_{F\ optimized}$ and $n_{F\ optimized}$ ± 10% and n_F- values individually calculated using the exponential model eq 6.

PCBs	**LogK_{OW}**	**n***	**Scenario 1**			**Scenario 2**	**Scenario 3**		**Scenario 1**			**Scenario 3**	
			Optimum LogK_{BC} ($n_{F.BC} = 0.82$)	**LogK_{BC} $n_{F.BC\ opt}$ - 10% ($n_{F.BC} = 0.74$)**	**LogK_{BC} $n_{F.BC\ opt}$ + 10% ($n_{F.BC} = 0.90$)**	**LogK_{BC} $n = 0.410 + 0.454e^{-0.028BC/TOC}$**	**LogK_{BC} ($n_F = 1$)**	**Literature values**	**Optimum LogK_{AC} ($n_{F.AC} = 0.74$)**	**LogK_{AC} $n_{F.AC\ opt}$ - 10% ($n_{F.AC} = 0.67$)**	**LogK_{AC} $n_{F.AC\ opt}$ + 10% ($n_{F.AC} = 0.81$)**	**LogK_{AC} ($n_F = 1$)**	**Literature values**
di-CB	4.9	3	6.3 (0.3)	6.4 (0.2)	6.4 (0.2)	6.4 (0.2)	6.1 (0.5)	5.3[7], 5.2[8]	7.1 (0.1)	7.1 (0.1)	7.2 (0.1)	7.3 (0.3)	
tri-CB	5.5	9	6.6 (0.3)	6.7 (0.4)	6.7 (0.4)	6.7 (0.4)	6.4 (0.2)	5.9[7], 5.9[8]	7.1 (0.4)	7.1 (0.4)	7.1 (0.3)	7.2 (0.4)	7.3-8.1[5]
tetra-CB	5.9	9	7.3 (0.1)	7.4 (0.2)	7.4 (0.2)	7.4 (0.2)	7.0 (0.2)	5.9-6.7[3], 6.3[7], 6.3[8]	7.3 (0.3)	7.4 (0.2)	7.3 (0.3)	7.3 (0.5)	7.0-7.5[5]
penta-CB	6.3	9	7.7 (0.2)	7.7 (0.2)	7.7 (0.2)	7.8 (0.2)	7.5 (0.3)	6.1[3], 6.7[7], 6.7[8]	7.3 (0.3)	7.3 (0.3)	7.3 (0.4)	7.2 (0.5)	7.1-7.8[5]
hexa-CB	6.7	5	8.3 (0.1)	8.4 (0.1)	8.4 (0.1)	8.4 (0.1)	8.1 (0.1)	7.1[7], 7.1[8]	7.8 (0.1)	7.8 (0.1)	7.8 (0.2)	7.7 (0.2)	
hepta-CB	7.1	5	8.6 (0.1)	8.6 (0.1)	8.6 (0.1)	8.6 (0.1)	8.4 (0.1)	7.4[7], 7.5[8]	7.8 (0.1)	7.8 (0.1)	7.7 (0.1)	7.7 (0.1)	
octa-CB	7.5	5	8.5 (0.2)	8.6 (0.1)	8.6 (0.2)	8.6 (0.2)	8.5 (0.2)	7.8[7], 7.9[8]	7.6 (0.3)	7.6 (0.3)	7.6 (0.3)	7.6 (0.3)	
PAHs	**LogK_{OW}**	**n***	**Optimum LogK_{BC} ($n_{F.BC} = 0.83$)**	**LogK_{BC} $n_{F.BC\ opt}$ - 10% ($n_{F.BC} = 0.74$)**	**LogK_{BC} $n_{F.BC\ opt}$ + 10% ($n_{F.BC} = 0.91$)**	**LogK_{BC} $n = 0.410 + 0.454e^{-0.028BC/TOC}$**	**LogK_{BC} ($n_F = 1$)**	**Literature values**	**Optimum LogK_{AC} ($n_{F.AC} = 0.82$)**	**LogK_{AC} $n_{F.AC\ opt}$ - 10% ($n_{F.AC} = 0.74$)**	**LogK_{AC} $n_{F.AC\ opt}$ + 10% ($n_{F.AC} = 0.90$)**	**LogK_{AC} ($n_F = 1$)**	**Literature values**
PHE	4.6	7	7.5 (0.2)	7.6 (0.2)	7.4 (0.2)	7.6 (0.2)	7.3 (0.3)	5.4[1], 5.7[1], 5.9[2], 5.6-6.1[3], 5.8[7], 6.0[8]	7.7 (0.3)	7.7 (0.3)	7.7 (0.3)	8.0 (0.3)	7.8[6]
FLU	5.2	14	7.7 (0.1)	7.8 (0.1)	7.5 (0.2)	7.8 (0.1)	7.4 (0.2)	5.1[4], 6.3[7], 6.5[8]	8.6 (0.3)	8.5 (0.2)	8.6 (0.3)	8.9 (0.3)	8.2[6]
PYR	5.2	14	7.7 (0.1)	7.8 (0.1)	7.5 (0.2)	7.8 (0.1)	7.4 (0.2)	6.3[1], 6.6[1], 6.4[3], 6.3[4], 6.3[7], 6.5[8]	8.6 (0.3)	8.5 (0.2)	8.6 (0.3)	8.9 (0.3)	8.5[6]
CHR	5.8	14	8.6 (0.2)	8.6 (0.2)	8.5 (0.2)	8.6 (0.2)	8.4 (0.1)	7.1[4], 6.9[7], 6.9[8]	8.8 (0.4)	8.7 (0.3)	8.8 (0.3)	9.0 (0.4)	8.7[6]
BbF	5.8	14	8.6 (0.2)	8.6 (0.2)	8.5 (0.2)	8.6 (0.3)	8.4 (0.1)	7.2[4], 6.9[7], 6.9[8]	8.8 (0.4)	8.7 (0.3)	8.8 (0.3)	9.0 (0.4)	8.6[6]
BaP	6.0	7	8.6 (0.3)	8.6 (0.3)	8.5 (0.3)	8.6 (0.3)	8.5 (0.3)	7.3[4], 7.1[7], 7.0[8]	8.5 (0.5)	8.5 (0.5)	8.6 (0.5)	8.8 (0.6)	8.9[6]
BeP	6.4	14	8.6 (0.2)	8.6 (0.2)	8.6 (0.3)	8.6 (0.2)	8.6 (0.3)	7.4[7], 7.3[8]	8.4 (0.5)	8.3 (0.5)	8.6 (0.4)	8.6 (0.6)	
PER	6.4	14	8.6 (0.2)	8.6 (0.2)	8.6 (0.3)	8.6 (0.2)	8.6 (0.3)	7.4[7], 7.3[8]	8.4 (0.5)	8.3 (0.5)	8.6 (0.4)	8.6 (0.6)	
InP	6.6	7	9.0 (0.3)	8.9 (0.3)	9.0 (0.3)	9.0 (0.3)	9.0 (0.3)	8.3[4], 7.6[7], 7.4[8]	8.3 (0.7)	8.2 (0.7)	8.5 (0.6)	8.5 (0.7)	9.2[6]
BghiP	6.9	7	9.0 (0.2)	9.0 (0.2)	9.1 (0.2)	9.0 (0.2)	9.1 (0.2)	7.8[4], 7.9[7], 7.6[8]	8.5 (0.5)	8.4 (0.6)	8.4 (0.7)	8.6 (0.6)	

* number of data on which K_F is based.

[1]*(34)*, [2]*(3)*, [3]*(22)*, [4]*(44)*, [5]*(39)*, [6]*(40)*, [7]*(23)*, [8]*(4)*.

The best fit to the data was observed with $n_{F,AC}$ = 0.74 for PCBs and $n_{F,AC}$ = 0.82 for PAHs. These values are close to the Freundlich exponents that were fitted for BC. The fact that the fit was best with $n_{F,AC} < 1$ means that part of the variability in the dataset indeed relates to non-linear sorption as captured by the Freundlich term in eq 2. The sensitivity analysis showed that changes in $n_{F,AC}$ by ±10% results in negligible (up to 0.1 Log unit) changes in LogK_{AC} values (Table 1). The linear model, however, resulted in significant changes in LogK_{AC} (up to 0.3 Log unit) and an increase in variation (SD) in LogK_{AC}. Therefore, we conclude that the results from the optimized non-linear scenario are to be preferred for AC as well, and therefore are used for further discussion and calculations.

For PCBs, PHE, FLU, PYR, CHR and BbF, SD in corresponding *in situ* LogK_{AC} estimates per chemical is between 0.1 and 0.4. For the higher molecular weight PAHs BaP, BeP, PER, InP and BghiP), SD range from 0.5 to 0.7 (Table 1, Figure 1b). The variability per chemical (SD from 0.1 to 0.7) may reflect the differences in site conditions and types of AC used. The relatively low variation in LogK_{AC} for PCBs and low molecular weight PAHs can be understood if these chemicals are more available for equilibrium redistribution than higher molecular PAHs. After all, the model as condensed in eq 4 assumes that HOCs originally bound to BC, can be redistributed to AC. If (a) high molecular PAHs are distributed more slowly, and (b) the kinetics of this process varies with the type of BC, this will result in a higher variation in apparent LogK_{AC} values for sites with different types of BC, all the more since equilibration times ranged from 28 to 180 days (Table S1). This explanation is supported by literature data from Jonker and Koelmans *(38),* who calculated 'fractions unavailable for equilibrium distribution' (f_{UED}'s) for six native PAHs and seven types of BC. For charcoal, f_{UED}'s were negligible, but for traffic soot, oil soot, wood soot, coal, and diesel soot, f_{UED}'s were approximately 0.5 for PHE and increased with roughly 50% with increasing PAH molecular weight. If their hypothesis of occlusion of PAHs in the soot core holds for the current sediments, 'apparent' K_{BC} values after AC amendment in fact may be overestimated, dependent on the magnitude of the f_{UED}'s. Note that LogK_{AC} values would be overestimated to a similar extent (because BC dominates the numerator in eq 4) so that this speculated bias would not affect our evaluation of AC competitive strength.

In contrast to the LogK_{BC} values (Figure 1a), LogK_{AC} values hardly increase with LogK_{OW} (Figure 1b). Between LogK_{OW} = 4.9 - 6.3 for PCBs and 5.2 - 6.9 for PAHs, the change in LogK_{AC} is not significant (Kruskal-Wallis, $\chi_2(5) = 3.353$, $p = 0.340$ for PCBs and $\chi_2(5) = 4.537$, $p = 0.475$ for PAHs). Consequently, the variability in *in situ* LogK_{AC} values can be captured in a single median value per chemical class. Interquartile ranges are 7.0-7.5 (median 7.2) for PCBs. and 8.3-8.8 (median 8.6) for PAHs. The absence of a dependency of LogK_{OW} agrees with earlier observations for virgin CMs, which can be explained by linear hydrophobic partitioning being much less important for sorption of HOCs to powdered AC than surface sorption *(38).*

The *in situ* K_{AC} estimates are in a good agreement with recent literature data *(39, 40)* and are approximately one to two order of magnitude lower than the distribution coefficients measured earlier for virgin AC *(38)* (Figure 1b).

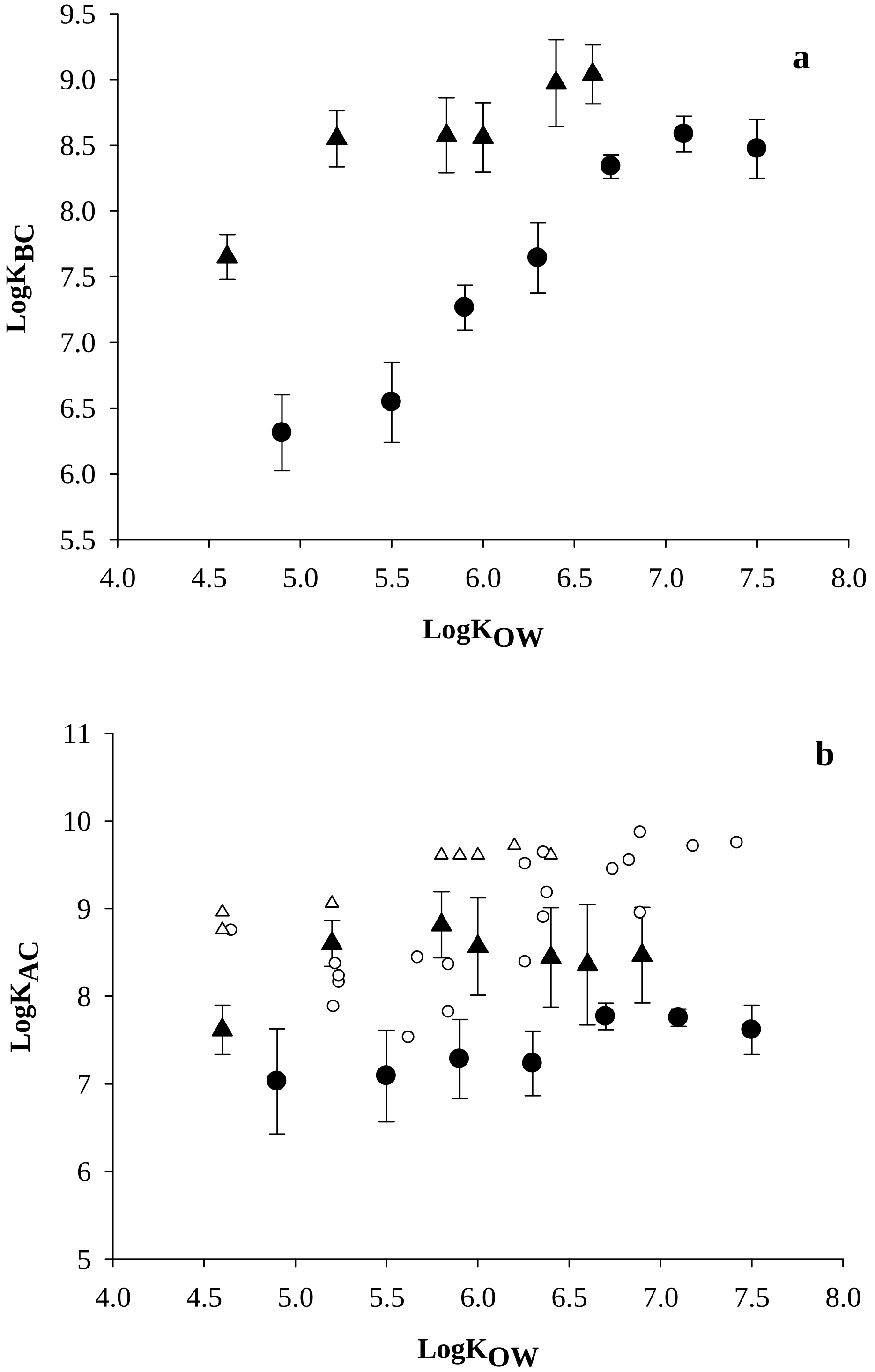

Figure 1. BC-water (a) and AC-water (b) Freundlich affinity constants (SD) for PCBs (circles), and PAHs (triangles), as a function of LogK_{OW}. K_{BC} and K_{AC} are calculated using eqs 4 and 5 with $n_{F.BC}$ = 0.82 and $n_{F.AC}$ = 0.74 for PCBs and $n_{F.BC}$ = 0.83 and $n_{F.AC}$ = 0.82 for PAHs (Table 1). Open symbols are pure AC- water distribution coefficients taken from the literature *(38)*.

This may be explained by the lower concentrations applied in the experiments with pure AC or by 'fouling' of the AC adsorption surfaces by natural organic matter in the sediment *(16, 27, 41-43)*. Fouling played no role in the experiments with virgin AC as this was washed prior to use *(38)*.

Despite the attenuation of HOC sorption, the AC sorbents were sufficiently powerful to reduce the pore water concentrations (Table S1). Interestingly, LogK_{AC} - LogK_{OW} trends and differences between PCBs and PAHs are quite similar for the virgin AC and the *in situ* AC data (Figure 1b).

Using the calibrated model, the relative contributions of OC, BC and AC to total sorption can be estimated using eq 3. The relative importance of sorption to BC and AC is substantial. Before addition of AC, BC accounted for 89 (for octa-CB) to 94% (hexa-CB) and 96 (BghiP) to 99% (PHE) of the total sorption for PCBs and PAHs, respectively (Figure S2 and S3). Addition of AC resulted in a calculated redistribution of chemicals in the system and then BC accounted only for 10 (di-CB) to 45% (octa-CB) and 5 (FLU and PYR) to 39% (BghiP). The added AC, in turn, accounted for 50% (octa-CB) to 90 (di-CB) and for 60% (BghiP) to 95 (FLU and PYR) of the total PCBs and PAHs, respectively (Figure S2 and S3). To compare the sorption strength to BC and AC, a K_{AC}/K_{BC} ratio was calculated for each individual PAH and PCB homologue group. It appeared that the ratio decreases with increasing hydrophobicity of the compounds for both PCBs and PAHs (Figure S4). For PCBs and PAHs, the ratio is higher than 1, i.e. AC is the stronger sorbent, for chemicals with LogK_{OW} < 6.3 and 6.6, respectively. This is favorable from a risk reduction perspective because these chemicals typically are the most bioavailable in aquatic sediments. For PCBs and PAHs with higher LogK_{OW} values, BC seems to be stronger, implying that bulky molecules of compounds with high LogK_{OW} might need more time to reach the AC sorption sites.

Implications for designing an activated carbon dose

The calibrated model now can be used to predict the effectivity of AC amendments given native OM and BC contents of aquatic sediments. Using the above calibrations of K_{AC}, K_{BC}, $n_{F,AC}$ and $n_{F,BC}$, eq 3 can be used to generalize the effect of AC addition on pore water concentrations. This may facilitate the design of AC dosing for PCB and PAH contaminated sediments. To illustrate the reduction of HOC aqueous concentrations under natural conditions, eq 3 was solved numerically for PHE, BaP, and InP as example chemicals. Furthermore, a high and a low sorption scenario were calculated in order to predict the consequences of parameter uncertainty (optimized K_{BC} and K_{AC} ± 95% CI, optimized n_F ± 10%). It appears that even with sorption affinity parameters at the low ends of their uncertainty ranges, the pore water concentrations are significantly reduced (up to 90%) already at AC levels of 1 % (Figure 2 and Figure S5). Furthermore, it appears that the predicted effectivity of AC decreases with increasing hydrophobicity of the PAH. This follows from the fact that binding to AC was modeled identically for these chemicals (i.e.

LogK_{OW} independent K_{AC}), whereas sorption to the competing phases OM and BC was observed to be stronger at higher LogK_{OW}.

Once sufficient field data are available, it will be required to validate the applicability of our conceptual model under such *in situ* conditions.

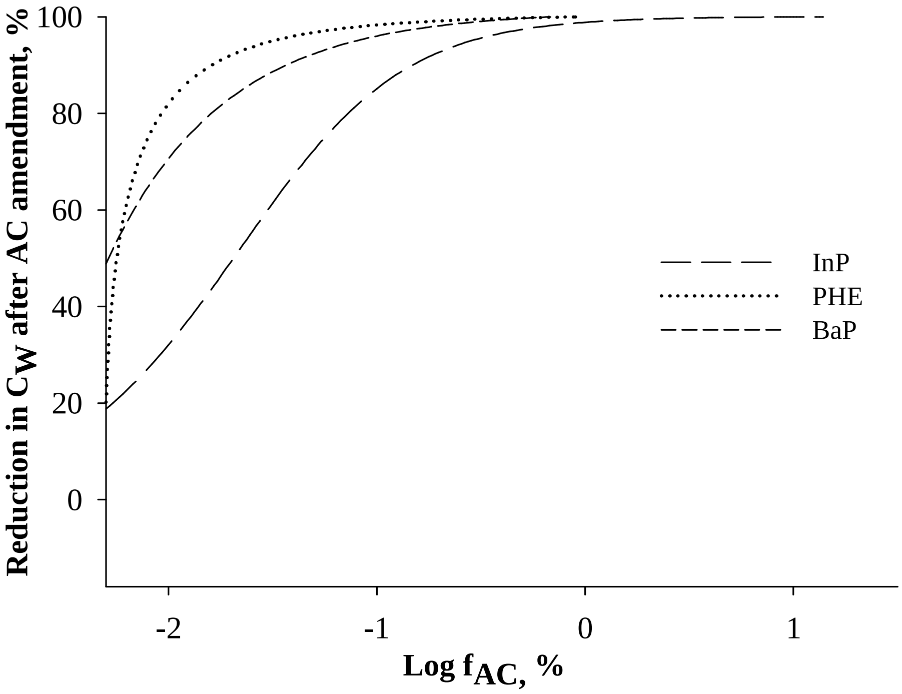

Figure 2. Effect of AC dose on the reduction of PHE (dotted), BaP (short dash), and InP (long dash) aqueous concentrations. The reduction in aqueous concentrations after AC amendment was calculated numerically using eq 3 and the optimized AC binding parameters as presented in Table 1.

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Supporting Information

Table S1. Reported data on AC amendment of sediment systems and individually calculated affinity parameters for *in situ* sorption of hydrophobic organic compounds to BC and AC.

AC	Contact time, d	Sediment type	HOCs	C_{sed}, µg/kg	C_W^0, ng/L	C_W^1, ng/L	OC, %	AC, %	BC, %	logK_{BC}, $n_{F,BC\,opt}$=0.82	logK_{AC}, $n_{F,AC\,opt}$=0.74	Reference
TOG® Calgon Carbon (virgin powdered, bituminous coal, 75–300 µm)	28	Freshwater, sandy	di-CB	10	20	0.1	3.22	1.61	0.64	6.3	6.6	1
			tri-CB	10600	580	50	3.22	1.61	0.64	6.9	7.6	
			tetra-CB	23950	490	180	3.22	1.61	0.64	7.3	7.3	
			penta-CB	8530	60	40	3.22	1.61	0.64	7.6	7.1	
		Freshwater, sandy	di-CB	50	10	0.1	3.70	1.85	0.616	6.0	7.2	
			tri-CB	31230	1550	180	3.70	1.85	0.616	7.1	7.6	
			tetra-CB	40650	700	320	3.70	1.85	0.616	7.5	7.2	
			penta-CB	12040	80	50	3.70	1.85	0.616	7.7	7.1	
		Freshwater, clay/silty	di-CB	840	300	3	5.17	2.585	0.365	6.2	7.2	
			tri-CB	2540	410	6	5.17	2.585	0.365	6.6	7.4	
			tetra-CB	1950	110	10	5.17	2.585	0.365	6.9	7.1	
			penta-CB	670	16	6	5.17	2.585	0.365	7.1	6.7	
		Freshwater, sandy	di-CB	10	0.85	0.16	0.83	0.415	0.258	6.6	7.0	
			tri-CB	40	2.5	1.35	0.83	0.415	0.258	6.9	6.6	
			tetra-CB	110	2.5	1.5	0.83	0.415	0.258	7.3	7.0	
			penta-CB	90	0.5	0.33	0.83	0.415	0.258	7.8	7.3	
TOG® Calgon Carbon (virgin powdered, bituminous coal, 75–300 µm)	28	Marine, sandy	tri-CB	10	1.95	0.01	1.50	3.4	0.20	6.4	6.9	2
			tetra-CB	250	8.8	0.1	1.50	3.4	0.20	7.2	7.5	
			penta-CB	1250	10.2	0.8	1.50	3.4	0.20	8.0	7.6	
			hexa-CB	3423	10.9	2.18	1.50	3.4	0.20	8.4	7.6	
			hepta-CB	3635	5	1.45	1.50	3.4	0.20	8.7	7.7	
			octa-CB	1348	1.25	0.35	1.50	3.4	0.20	8.7	7.7	
	180	Marine, sandy	tri-CB	10	1.95	0.01	1.50	3.4	0.20	6.4	6.9	
			tetra-CB	250	8.8	0.15	1.50	3.4	0.20	7.3	7.5	
			penta-CB	1250	10.2	0.4	1.50	3.4	0.20	7.7	7.6	
			hexa-CB	3423	10.9	1.18	1.50	3.4	0.20	8.4	7.9	
			hepta-CB	3635	5	1.43	1.50	3.4	0.20	8.7	7.8	
			octa-CB	1348	1.25	0.33	1.50	3.4	0.20	8.7	7.8	
TOG® Calgon Carbon (virgin powdered, bituminous coal, 75–300 µm)	28	Marine, sandy	tri-CB	10	2.42	0.38	1.50	0.34	0.20	6.3	6.7	3
			tetra-CB	250	9.4	4.06	1.50	0.34	0.20	7.3	7.1	
			penta-CB	1250	12	6.42	1.50	0.34	0.20	7.6	7.3	
			hexa-CB	3423	16.6	10.1	1.50	0.34	0.20	8.2	7.8	
			hepta-CB	3635	9.33	6.2	1.50	0.34	0.20	8.5	7.9	
			octa-CB	1348	2.6	2	1.50	0.34	0.20	8.4	7.7	
		Marine, sandy	tri-CB	10	2.42	0.01	1.50	1.7	0.20	6.3	7.2	
			tetra-CB	250	9.4	0.13	1.50	1.7	0.20	7.3	7.8	
			penta-CB	1250	12	0.75	1.50	1.7	0.20	7.6	7.7	
			hexa-CB	3423	16.6	2.25	1.50	1.7	0.20	8.2	8.0	
			hepta-CB	3635	9.33	3	1.50	1.7	0.20	8.5	7.8	
			octa-CB	1348	2.6	1	1.50	1.7	0.20	8.4	7.7	
		Marine, sandy	tri-CB	10	2.42	0.01	1.50	3.4	0.20	6.3	6.9	
			tetra-CB	250	9.4	0.13	1.50	3.4	0.20	7.3	7.5	
			penta-CB	1250	12	0.75	1.50	3.4	0.20	7.6	7.4	
			hexa-CB	3423	16.6	2.25	1.50	3.4	0.20	8.2	7.7	
			hepta-CB	3635	9.33	2.25	1.50	3.4	0.20	8.5	7.6	
			octa-CB	1348	2.6	1.38	1.50	3.4	0.20	8.4	7.1	

Table S1. (continued)

AC	Contact time, d	Sediment type	HOCs	C_{sed}, µg/kg	C_W^0, ng/L	C_W^1, ng/L	OC, %	AC, %	BC, %	LogK_{BC}, $n_{F,BC\ opt}$=0.83	LogK_{AC}, $n_{F,AC\ opt}$=0.82	Reference
Sigma-Aldrich (untreated powdered, 37-149 µm)	31^*	Harbour, silty	PHE	1100	16.8	4.9	3.95	0.2	0.25	7.6	8.0	4
			FLU	2930	29.8	3.7	3.95	0.2	0.25	7.8	8.6	
			PYR	3900	54	10.6	3.95	0.2	0.25	7.7	8.3	
			CHR	5400	4.5	2.3	3.95	0.2	0.25	8.8	8.8	
			BbF	7000	8.8	6.2	3.95	0.2	0.25	8.7	8.3	
			BeP	1240	2.1	1.4	3.95	0.2	0.25	8.4	8.1	
			BaP	3800	3.3	3	3.95	0.2	0.25	8.7	7.8	
			PER	1420	0.64	0.63	3.95	0.2	0.25	8.9	7.1	
			InP	2220	0.48	0.47	3.95	0.2	0.25	9.2	7.6	
			BghiP	2030	0.43	0.4	3.95	0.2	0.25	9.2	8.1	
		Harbour, silty	PHE	1100	16.8	2.8	3.95	0.5	0.25	7.6	7.9	
			FLU	2930	29.8	0.79	3.95	0.5	0.25	7.8	8.8	
			PYR	3900	54	2.8	3.95	0.5	0.25	7.7	8.5	
			CHR	5400	4.5	0.5	3.95	0.5	0.25	8.8	9.2	
			BbF	7000	8.8	2.3	3.95	0.5	0.25	8.7	8.7	
			BeP	1240	2.1	0.45	3.95	0.5	0.25	8.4	8.5	
			BaP	3800	3.3	1.03	3.95	0.5	0.25	8.7	8.7	
			PER	1420	0.64	0.32	3.95	0.5	0.25	8.9	8.5	
			InP	2220	0.48	0.33	3.95	0.5	0.25	9.2	8.5	
			BghiP	2030	0.43	0.25	3.95	0.5	0.25	9.2	8.7	
		Harbour, silty	PHE	1100	16.8	0.98	3.95	2	0.25	7.6	7.7	
			FLU	2930	29.8	0.6	3.95	2	0.25	7.8	8.3	
			PYR	3900	54	1.2	3.95	2	0.25	7.7	8.2	
			CHR	5400	4.5	0.14	3.95	2	0.25	8.8	9.1	
			BbF	7000	8.8	0.49	3.95	2	0.25	8.7	8.8	
			BeP	1240	2.1	0.13	3.95	2	0.25	8.4	8.5	
			BaP	3800	3.3	0.3	3.95	2	0.25	8.7	8.6	
			PER	1420	0.64	0.07	3.95	2	0.25	8.9	8.7	
			InP	2220	0.48	0.14	3.95	2	0.25	9.2	8.6	
			BghiP	2030	0.43	0.12	3.95	2	0.25	9.2	8.6	
		Harbour, silty	PHE	1100	16.8	1.4	3.95	4	0.25	7.6	7.3	
			FLU	2930	29.8	0.17	3.95	4	0.25	7.8	8.5	
			PYR	3900	54	0.25	3.95	4	0.25	7.7	8.5	
			CHR	5400	4.5	0.42	3.95	4	0.25	8.8	8.4	
			BbF	7000	8.8	0.25	3.95	4	0.25	8.7	8.7	
			BeP	1240	2.1	0.05	3.95	4	0.25	8.4	8.5	
			BaP	3800	3.3	0.1	3.95	4	0.25	8.7	8.8	
			PER	1420	0.64	0.03	3.95	4	0.25	8.9	8.8	
			InP	2220	0.48	0.06	3.95	4	0.25	9.2	8.7	
			BghiP	2030	0.43	0.06	3.95	4	0.25	9.2	8.6	
		Harbour, sandy/silty	PHE	6200	128	3.9	6.50	2	0.9	7.6	8.0	
			FLU	24000	171	1.3	6.50	2	0.9	7.8	8.6	
			PYR	24000	261	2.3	6.50	2	0.9	7.7	8.3	
			CHR	31000	21	0.35	6.50	2	0.9	8.8	8.8	
			BbF	29000	18.4	0.57	6.50	2	0.9	8.7	8.3	
			BeP	5400	4.2	0.11	6.50	2	0.9	8.4	8.1	
			BaP	22000	9.8	0.32	6.50	2	0.9	8.7	7.8	
			PER	4000	1.3	0.15	6.50	2	0.9	8.9	7.1	
			InP	8000	1.18	0.11	6.50	2	0.9	9.2	7.6	
			BghiP	8000	0.88	0.11	6.50	2	0.9	9.2	8.1	

Table S1. (continued)

AC	**Contact time, d**	**Sediment type**	**HOCs**	**C_{sed}, µg/kg**	**C_W^0, ng/L**	**C_W^1, ng/L**	**OC, %**	**AC, %**	**BC, %**	**LogK_{BC}, $n_{F,BC\ opt}$=0.83**	**LogK_{AC}, $n_{F,AC\ opt}$=0.82**	**Reference**
Sigma-Aldrich (untreated powdered, 37-149 µm)	31[*]	Harbour, sandy	PHE	1100	59	2.17	1.58	2	0.12	7.5	7.4	4
			FLU	1600	59	0.25	1.58	2	0.12	7.6	8.4	
			PYR	1700	59	0.4	1.58	2	0.12	7.7	8.2	
			CHR	1730	8	0.1	1.58	2	0.12	8.4	8.7	
			BbF	890	6	0.09	1.58	2	0.12	8.2	8.5	
			BeP	640	1.8	0.04	1.58	2	0.12	8.5	8.6	
			BaP	300	2.8	0.04	1.58	2	0.12	8.0	8.3	
			PER	490	0.59	0.02	1.58	2	0.12	8.8	8.7	
			InP	180	0.45	0.02	1.58	2	0.12	8.4	8.3	
			BghiP	310	0.36	0.02	1.58	2	0.12	8.8	8.5	
		Harbour, sandy	PHE	70	3.8	0.02	1.91	2	0.09	7.4	7.9	
			FLU	470	37	0.02	1.91	2	0.09	7.4	8.8	
			PYR	700	48	0.02	1.91	2	0.09	7.5	8.9	
			CHR	300	1.8	0.02	1.91	2	0.09	8.3	8.6	
			BbF	170	0.98	0.02	1.91	2	0.09	8.3	8.3	
			BeP	50	0.21	0.02	1.91	2	0.09	8.3	7.7	
			BaP	130	0.33	0.02	1.91	2	0.09	8.6	8.2	
			PER	60	0.21	0.02	1.91	2	0.09	8.4	7.8	
			InP	40	0.05	0.02	1.91	2	0.09	8.7	7.4	
			BghiP	50	0.05	0.02	1.91	2	0.09	8.8	7.5	

Benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[e]pyrene (BeP), benzo[ghi]perylene (BghiP), benzo[k]fluoranthene (BkF), chrysene (CHR), fluoranthene (FLU), indeno(1,2,3-cd)pyrene (InP), phenanthrene (PHE), and pyrene (PYR)

[1]*(10)*, [2]*(12)*, [3]*(26)*, [4]*(25)*

[*]at 60° C followed by 47 d at 22° C

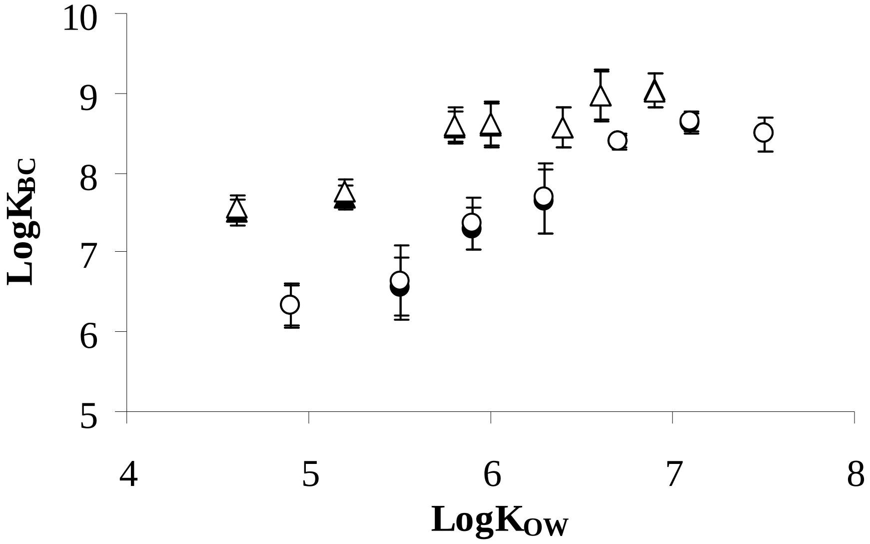

Figure S1. BC-water Freundlich affinity constants (SD) for PCBs (circles) and PAHs (triangles), calculated using eq 4 with optimized n_F (closed symbols), and n_F calculated using the exponential model eq 6 (open symbols).

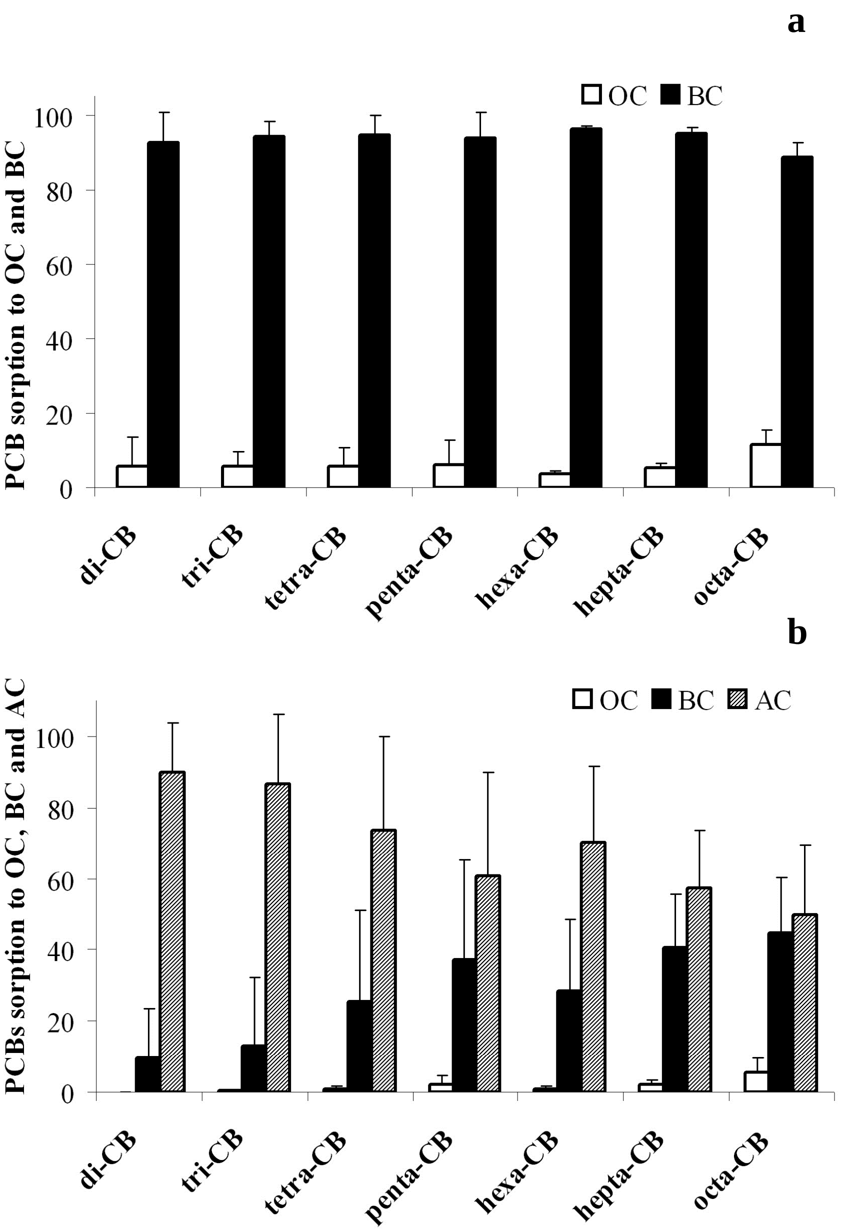

Figure S2. The relative contributions of OC (open bars), BC (black) and AC (diagonal striped) to total sorption of PCBs a) before and b) after AC addition.

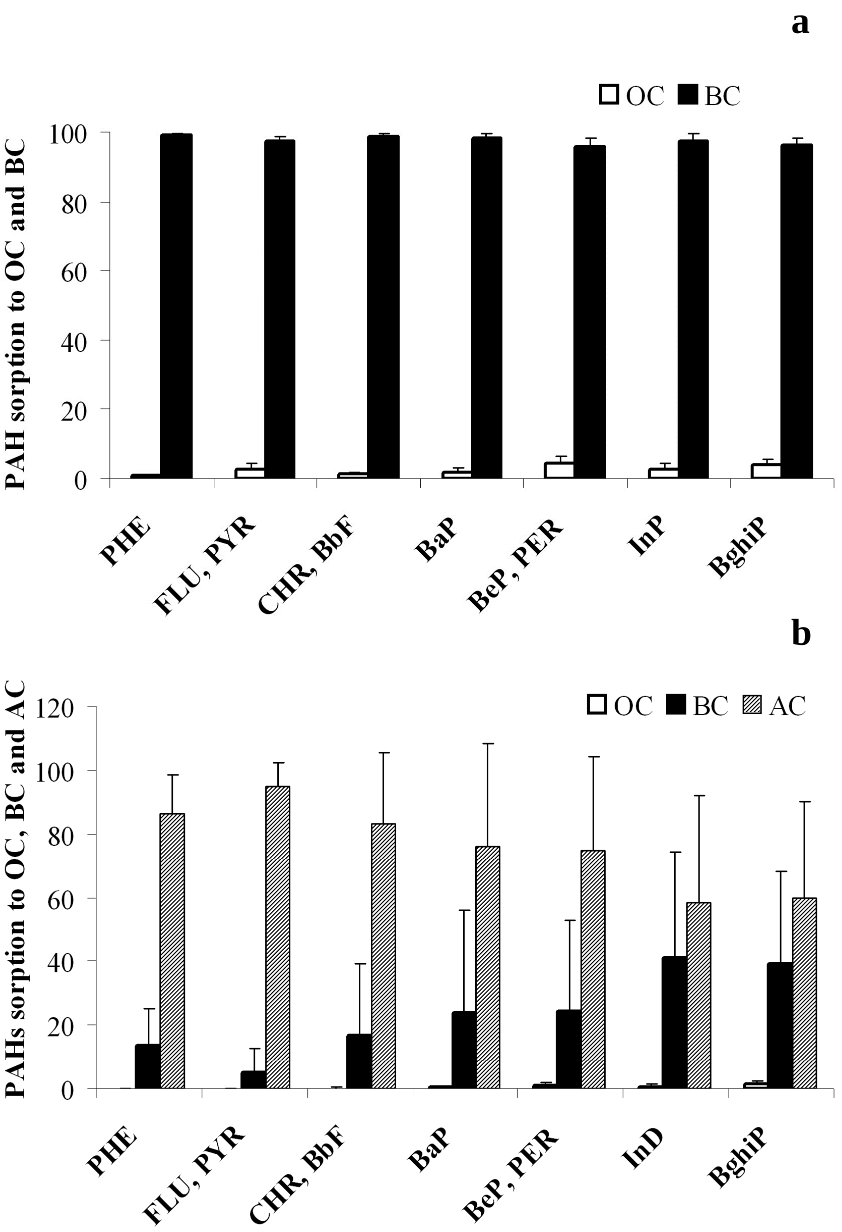

Figure S3. The relative contributions of OC (open bars), BC (black) and AC (diagonal striped) to total sorption of PAHs a) before and b) after AC addition.

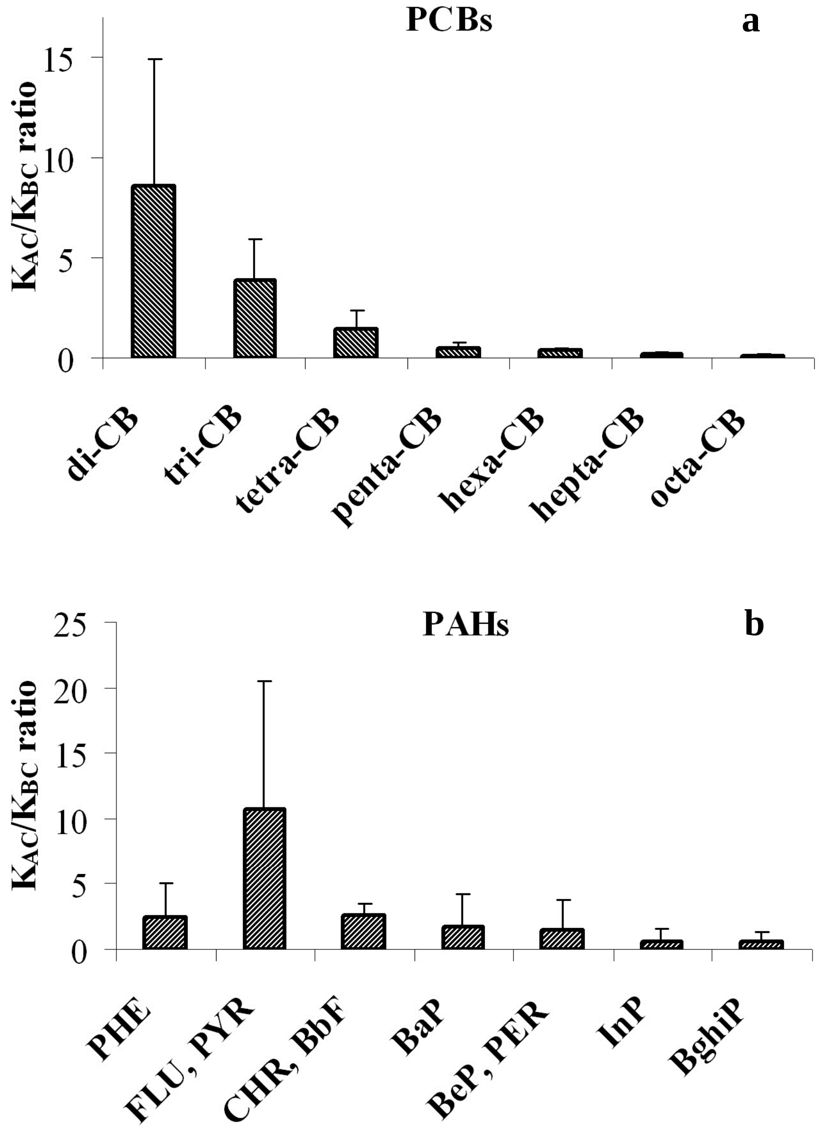

Figure S4. K_{AC}/K_{BC} ratio for PCBs (a) and PAHs (b) calculated using data from Table 1.

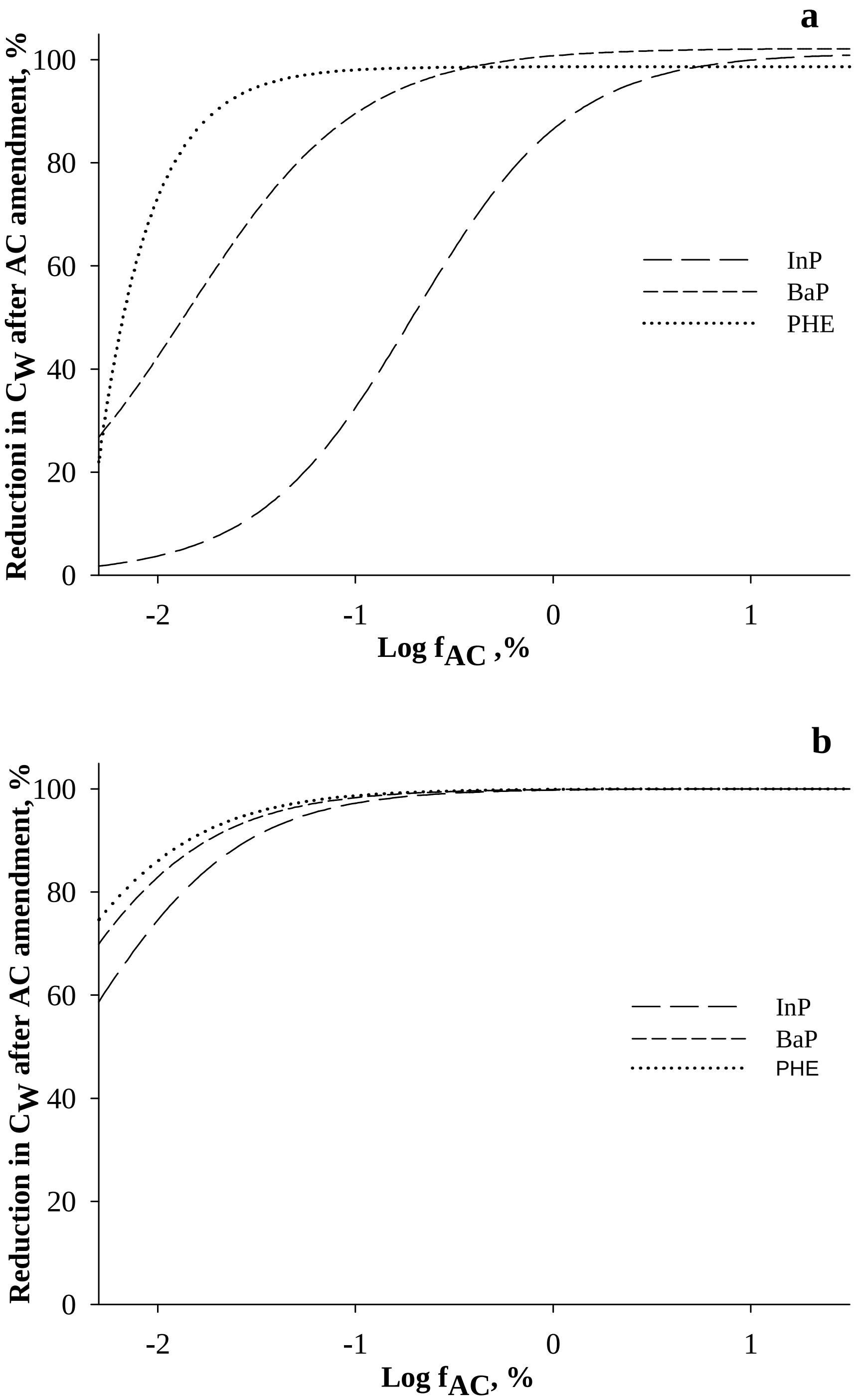

Figure S5. Effect of AC dose on reduction of PHE (dotted), BaP (short dash), and InP (long dash) aqueous concentrations. C_W reduction has been estimated using sorption affinity parameters leading to a) minimum (optimized K_{BC} and K_{AC} - 95% CI, optimized n_F - 10%) and b) maximum (optimized K_{BC} and K_{AC} + 95% CI, optimized n_F + 10%) sorption. Reduction in aqueous concentrations after AC amendment was calculated numerically using eq 3 and optimized AC binding parameters given in Table 1.

CHAPTER 4

BIOTURBATION AND DISSOLVED ORGANIC MATTER ENHANCE CONTAMINANT FLUXES FROM SEDIMENT TREATED WITH POWDERED AND GRANULAR ACTIVATED CARBON

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Abstract

Sediment amendment with activated carbon (AC) is a promising technique for *in situ* sediment remediation. To date it is not clear whether this technique sufficiently reduces sediment-to-water fluxes of sediment-bound hydrophobic organic chemicals (HOCs) in the presence of bioturbators. Here, we report polychlorobiphenyl (PCB) pore water concentrations, fluxes, mass transfer coefficients, and survival data of two benthic species, for four treatments: no AC addition (control), powdered AC addition, granular AC addition and addition and subsequent removal of GAC (sediment stripping). AC addition decreased mass fluxes but increased apparent mass transfer coefficients due to dissolved organic carbon (DOC) facilitated transport across the benthic boundary layer (BBL). In turn, DOC concentrations depended on bioturbator activity which was high for the PAC tolerant species *A. aquaticus* and low for AC sensitive species *L. variegatus*. A dual BBL resistance model combining AC effects on gradients, DOC facilitated transport and biodiffusion was evaluated against the data and showed how the type of resistance differs with treatment and chemical hydrophobicity. Data and simulations illustrate the complex interplay between AC and contaminant toxicity to benthic organisms, and how differences in species tolerance affect mass fluxes from sediment to the water column.

Introduction

Contaminated sediments may pose a risk for the ecological quality of surface waters *(1, 2)*. Various remediation strategies like dredging, *in situ* capping and *in situ* treatment have been developed to reduce the risk associated with contaminated bed sediment. Such strategies often aim at reducing the fluxes of hydrophobic organic chemicals (HOC) from the bed sediment to the overlying water, making them less available for uptake by aquatic organisms and accumulation in the food web *(3)*. Consequently, sediment to water transfer is an important endpoint when developing, evaluating or comparing contaminated sediment remediation alternatives.

Adding activated carbon (AC) to sediment has been proposed as a remediation technique to reduce HOC release to the overlying water *(4, 5)*. AC is known to bind sediment-bound HOC strongly and to efficiently reduce their bioavailable fractions *(6, 7)*. Most earlier studies addressed the effectiveness of powdered activated carbon (PAC), whereas granular activated carbon (GAC), i.e. activated carbon with a particle size >300µm, has been studied less frequently *(8)*. A recently proposed *ex situ* technique, referred to as ‘sediment stripping’, uses addition and subsequent removal of GAC to actively clean the sediment without leaving substantial traces of AC *(8)*. Sediment-to-water fluxes of HOCs are an important endpoint to assess the relative effectiveness of such treatments *(3)*. HOC fluxes are hypothesized to decrease if carbon phases like PAC or GAC are present in sediment *(9, 10)*. Such fluxes, however, may also be affected by bioturbation. Bioturbation may increase the fluxes by mixing of particles and pore water *(11, 12)*. It has been shown that in low-energy environments, bioturbation is likely to be of equal importance as particle resuspension transport or to even dominate the contaminant movement in the upper sediment layers *(13-15)*. The mechanism behind bioturbation-driven release of contaminants from sediment includes upward transport of contaminants sorbed primarily to the sediment particles, i.e. to the sediment-water interface, followed by contaminants desorption to the interfacial water with subsequent diffusion through the benthic boundary layer (BBL) to the overlying water *(16)*. Additionally, it may be hypothesized that bioturbation decreases the thickness of the BBL and affects dissolved organic carbon (DOC) concentrations, processes that both affect the fluxes of HOCs.

To date, it is not clear how the presence of AC and occurrence of bioturbation interact. Bioturbation may increase fluxes such that AC addition may be less effective than anticipated. On the other hand, added carbon phases like AC may have negative impacts on the habitat quality and benthic organisms therefore may reduce their activity *(10, 17)*. Several studies have reported negative effects on growth and survival of benthic organisms. Koelmans and Jonker *(10)* showed that addition of black carbon (BC) reduced bioturbation, which together with BC's sorption capacity might constitute a 'double lock' on sediment bound contaminants, thus decreasing exposure for benthic invertebrates. Important current questions are: whether this mechanism also is relevant for AC, and for different AC alternative treatment scenarios, like PAC addition, GAC addition or sediment stripping. Furthermore, it is important to know whether bioturbation can reduce the effectiveness of sediment remediation with AC.

The primary aim of this study was to assess the effectiveness of four remediation scenarios: (a) no treatment (control), (b) addition of powdered AC, (c) mixing with granular AC, and (d) sediment stripping with granular AC. Endpoints were pore water concentrations in the treated sediments, as well as sediment-water fluxes, the latter through measurement of chemical mass released from the bed and *in situ* sediment-to-water mass transfer coefficients (K_L), which express the rate of contaminant release from the sediment bed *(9, 10, 14, 18, 19)*. The second aim was to investigate the effect of bioturbation on the effectiveness of the four remediation scenarios and to further develop models that integrate the different processes.

Sediments treated according to the four scenarios were taken from a field remediation trial experiment running at the experimental facility the Sinderhoeve (Renkum, The Netherlands). Pore water concentrations were accurately measured using negligible depletion passive sampling *(20)*, whereas laboratory flux measurements followed the methodology recently developed by Koelmans et al *(9, 10)*, using Empore disks as a sink for HOCs in the overlying water. Flux measurements included treatments with two bioturbators, i.e. the sediment dweller *Lumbriculus variegatus* and the waterlouse *Asellus aquaticus*. To test the impact of AC treatment on bioturbation activity, the survival of *L. variegatus* and *A. aquaticus* in the test sediment was checked using 28-d laboratory bioassays. Measured fluxes were interpreted mechanistically using mass transport models.

Materials and Methods

Chemicals and materials

Details on chemicals, materials, and pretreatment of materials are provided as Supporting Information.

Activated carbon treatments

Sediments were taken from a field scale remediation trial at the Sinderhoeve facility (Renkum, The Netherlands). For this field experiment, contaminated freshwater sediment was dredged from The Biesbosch National Park, The Netherlands, in the second half of 2011. Organic carbon content, f_{OC} was 0.0471±0.0016 (n=3). $\sum_{11}$PCB concentration in the Biesbosch sediment was 700 µg/kg, and $\sum_{10}$PAH concentration was 11 mg/kg (Table S1). These values as well as concentrations of metals, total petroleum hydrocarbons and DDT in the sediment were above threshold effect levels *(21, 22)*. Forty four tons of the dredged material (d.w. 53%, bulk density 1.7 t/m^3) was transported to the experimental facility Sinderhoeve, Renkum, The Netherlands, where four 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. and homogenized. After 4 h, 25% of the sediment was pumped into ditch 1 (untreated sediment) and 25% of the sediment into ditch 2. The sediment in ditch 2 was amended with 170 kg PAC to obtain 4% d.w. in the upper 10 cm of the sediment (PAC sediment). Granular activated carbon (340 kg) was added to the remaining 50% of the Biesbosch sediment and mixed 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 mixed for two days (in total 48 h), after which the GAC was sieved out with a 1 mm sieve. The latter procedure thus 'strips' the HOCs from the sediment in 48 h, after which GAC also is removed by sieving. The resulting stripped sediment (25% of the original sediment quantity) 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. The sediment in all ditches was allowed to settle for four days before sampling.

A representative mixed sample was taken from each ditch using a PVC core sampler (4 cm inner diameter) and on the same day transported to the laboratory. The mixed sediment samples were homogenized with an electrical stirrer for 10 min, after which the sediment was diluted with water from the corresponding ditch to achieve a liquid solid ratio of 5, which is comparable to the conditions in the ditches. The resulting slurry was homogenized mechanically and then divided in eight representative subsamples using a Retsch sample-divider. Three samples, each made by pooling two subsamples from the sample-divider together, were transferred to 2.5 L brown colored bottles, which were shaken horizontally (120 rpm) at room temperature for 28 d. One subsample was used for the survival experiment and one for a determination of PCB concentrations in the sediment and pore water.

Determination of PCB concentrations in pore water

Pore water concentrations were measured using polyoxymethylene (POM) negligible depletion passive sampling *(20)*. The details are provided as Supporting Information. PCB aqueous concentrations were calculated from the concentrations measured in the sampler (C_{POM}) using previously published POM-water equilibrium partition coefficients K_{POM} *(23, 24)*.

Organisms

Asellus aquaticus was collected from the (uncontaminated) Duno pond in Doorwerth (The Netherlands), using a sampling bucket. In the laboratory, organisms were sorted to groups with a size range 4-7 mm, which were kept in aerated copper free water in a white bucket in a climate-controlled room at 18 ºC. Prior to the bioassays and flux experiments, organisms were fed dry poplar leaves collected in the field. *Lumbriculus variegatus*, cultivated in house, was kept in reared glass aquaria at 18 °C. Chlorine-free cellulose served as substrate, and the aquaria were continuously flushed with copper free water. Once a week, the organisms were fed with pulverized flake fish food.

Survival experiment

Survival of *A. aquaticus* and *L. variegatus* in the untreated, PAC, GAC, and stripped sediment was tested with whole-sediment bioassays following previously published procedures *(17)*. Briefly, 10 individuals were added to beakers with 1 cm wet sediment and 200 ml (for *A. aquaticus*) and 50 ml (for *L. variegatus*) copper-free water. The beakers were aerated and *A. aquaticus* were fed dry poplar leaves over a 28-d period. The experiment was performed in triplicate in a climate-controlled room at 18°C with a 12:12 light:dark cycle. Survival was determined by gently transferring the beaker content to a tray and counting living organisms.

Flux experiment

Flux measurements followed previously published set up and procedures *(9, 10)*. This method uses a setup with sediment and overlying water in which Empore disks (ED) are placed. The disks act as a sink for HOCs in the water and induce a flux from the sediment to the overlying water. Disks are replaced from time to time and analyzed for HOCs, from which fluxes and mass transfer coefficients can be calculated *(9, 10)*. In short, after the 28-d equilibration period, the sediment samples from the brown bottles were transferred to 12 PVC cylindrical cores (three cores per AC treatment; height 60 cm, inner diameter 6 cm). After settling for one week, 10 individuals of *L. variegatus* were added to one core per AC treatment (“no AC”, “PAC”, “GAC” and “stripped”) and 10 individuals of *A. aquaticus* were added to another four cores. Per core, two Empore disks were placed, one directly above the other into a frame made of stainless steel gauze (mesh size 1 mm) (Figure S1, Supporting Information), which then was connected to a stirring rod. Gauze frames were designed such to keep the disk surfaces fully open to the overlying water and were positioned at a distance of 10 cm from the sediment surface. The twelve stirring rods were connected by a chain driven by one stirring motor to ascertain equal stirring conditions in the cores. Stirring of the overlying water occurred by rotation of the disks at the highest possible rate before sediment resupension occurred (30 rpm). Empore disks were replaced in the overlying water at incremental time intervals after 0.17 (4 h), 1, 2, 7, 14, 28, 42, and 56 d. Nephelometric turbidity (NTU) in every core was measured on a weekly basis using a portable turbidity meter (Aquafluor^{TM}, Turner designs, Sunnyvale, CA, USA). Because overlying water could not be sacrificed for DOC measurements, turbidity was used as a proxy for dissolved organic carbon (DOC), assuming 1 NTU ≈ 1 mg/L DOC *(25)*.

Chemical analysis

Empore disks and untreated sediment were extracted using an Accelerated Solvent Extractor (ASE 350, Dionex, USA) and then cleaned following the procedure described in Jonker and Koelmans *(20)*. PCB concentrations in sediment, Empore disks, and POM were determined using GC-ECD. Details on the chemical and instrumental analyses are provided as Supporting Information.

Data analysis

The flux of PCBs from the sediment pore water to the overlying water (Φ_{sed}, μg/m^2/d), can be described as a product of the concentration gradient between pore- and overlying water, and the sediment-to-water mass transfer coefficient (K_L^*, m/d) *(9, 10, 26)*:

$$\phi_{sed} = K_L^*\left(C_{PW} - C_{OW}\right) \quad (1)$$

where C_{PW} and C_{OW} (ng/L) are the concentrations in pore water and overlying water, respectively. The reciprocal of K_L^* can be interpreted as the overall transport resistance, which is the sum of the transport resistances relating to molecular diffusion in the sediment bed, transport across the BBL, and bioturbation. If molecular diffusion in the sediment bed is not rate-limiting, $1/K_L^*$ equates to *(12)*:

$$\frac{1}{K_L^*} = \frac{1}{\kappa} + \frac{h}{D_b K_d \rho_b} \quad (2)$$

The term $h/D_bK_d\rho_b$ accounts for the impact of bioturbation where h (m) is the average bioturbation depth in the sediment bed, D_b is a biodiffusion coefficient, representing particle diffusivity in the bed (m^2/d), K_d is the sediment-to-water partition coefficient (L/kg) and ρ_b is the dry density of the particles (kg/L) *(12)*. If BC and/or AC is present in sediment, K_d can be approximated as *(27)*:

$$K_d = f_{OC}K_{OC} + f_{BC}K_{F,BC}C_{PW}^{nF,BC-1} + f_{AC}K_{F,AC}C_{PW}^{nF,AC-1} \quad (3)$$

in which f_{OC}, f_{BC} and f_{AC} are the organic carbon, black carbon and activated carbon fraction of the sediment, K_{OC} the organic carbon normalised partition coefficient, $K_{F,BC}$ and $K_{F,AC}$ the Freundlich adsorption coefficients for BC and AC respectively, and $n_{F,BC}$ and $n_{F,AC}$ are the Freundlich exponents for sorption to BC and AC respectively. The parameter κ is the water-side BBL mass transfer coefficient (m/d). If DOC is present in the water, transport of DOC associated HOCs may contribute to the overall BBL mass transport. Based on a model analysis provided by Ter Laak et al *(28)* we derived the following expression for κ (derivation provided as Supporting Information):

$$\kappa = K_L + K_L^{DOC} K_{DOC}[DOC] \tag{4}$$

where κ now is the apparent DOC-inclusive mass transfer coefficient (m/d), K_L is the mass transfer coefficient of freely dissolved PCBs (m/d), K_L^{DOC} is the mass transfer coefficient of DOC-bound PCB (m/d), K_{DOC} is the DOC-water partition coefficient (L/kg) and [DOC] is the concentration of DOC in the aqueous phase (kg/L).

Apart from the flux in eq 1, the Empore disk in the overlying water induces an additional flux Φ_{ED} (ng/m^2/d) from the overlying water to the disk:

$$\phi_{ED} = K_L^{ED}\left(C_{OW} - \frac{C_{ED}}{K_d^{ED,C18}}\right) \tag{5}$$

where K_L^{ED} (m/d) is the apparent mass transfer coefficient for HOC transfer from the overlying water to the Empore disk, C_{ED} is the concentration in the C_{18} phase on the Empore disk (ng/kg) and $K_d^{ED,C18}$ is the PCB C_{18} Empore disk-to-water equilibrium partition coefficient (L/kg). Note that the apparent K_L^{ED} may account for DOC facilitated transport like K_L in eq 4, that is, $K_L^{ED} = K_{L,wateronly}^{ED} + K_L^{DOC} K_{DOC}[DOC]$. The effect of the serial fluxes on the HOC concentration change in the overlying water can be calculated by combining the right side of eqs 1 and 5 and correcting for sediment surface area (A_{sed}, m^2), Empore disk surface area (A_{ED}, m^2), and overlying water volume (V_{OW}, m^3). This yields a mass balance equation for the overlying water, which can be complemented with similar mass balance equations for the pore water and the Empore disks. These equations were published before *(9, 10)* and are provided as Supporting Information. The model was fitted to the cumulative masses of PCBs extracted by the Empore disks, which yields estimates of the mass transfer coefficient for the Empore disk K_L^{ED}, the pore water concentration at time zero $C_{PW,\,t=0}$, and K_L^* *(9, 10)*. In most cases the model fitted the data well (Figures S9-S20). In case of PCB detection limit problems for individual Empore disk extractions, accurate fits could not be obtained. Further details on the model equations and fitting procedure are provided as Supporting Information.

Pilot experiments with phenanthrene and free floating Empore disks, resulted in K_L^{ED} of 3.3 m/d in pure water (Figure S2). The currently optimized K_L^{ED} values averaged 20 m/d (interquartile (IQR) range 4.9-43 m/d) (Table S2), which is a factor of 6 higher than the value obtained from the pilot test and ~100 times higher than previously reported values of 0.18 and 0.24 m/d for PCBs and PAH *(9, 10)*. The individual K_L^{ED} values varied among systems and congeners but showed no trend with either PCB hydrophobicity or turbidity (multiple regression, $p = 0.181$) (Table S7).

Treatment effects on partition coefficients were tested using one-way ANOVA followed by Tukey's post-hoc test ($p = 0.05$) using PASW Statistics 17.0 (SPSS, Chicago, IL, USA). Non-linear and multiple linear regression analyses were performed in Microsoft Excel 2010 (Microsoft Corporation, Redmond, WA, USA).

Results and discussions

Effects of AC treatment on PCB pore water concentrations and sediment-water partitioning

Here we discuss the efficiency of the treatments PAC addition, GAC addition and sediment stripping in reducing pore water concentrations and increasing sorption to the sediment, as compared to the control. Treated sediments were equilibrated for 28 d after which pore water concentrations were determined. Sediment treatments with PAC, GAC, and sediment stripping with GAC resulted in reductions of aqueous Σ_{18}PCB concentrations of 100, 85 and 93%, respectively. For Σ_{13}PAH these concentration reductions were 100, 93, and 97%. Treatment effectiveness generally was higher for PAH than for PCB (Figure S3 and S4), 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 *(27, 29)*. At equal dosages, i.e. 4% d.w., PAC reduces the aqueous concentrations more efficiently than GAC because of the larger external surface area of the sorbent and the short intra- and interparticle diffusive path lengths *(30)*. Note that we used equilibration for 28 d, which may not have resulted in full equilibrium, especially for the GAC treatment. Still, these pore water concentrations can be regarded as a proxy for longer term equilibration results of remediation with AC. After all, 28 d of shaking will accelerate the exchange and transport processes that occur in the sediment at the Sinderhoeve field site, and thus mimics a much longer post remediation state.

The organic carbon-normalized sediment–water distribution coefficients (LogK_{OC}) were calculated from the organic carbon content (f_{OC}), PCB concentrations in sediment (C_{sed}) and POM-SPE based pore water concentration (C_{PW}). The resulting values were observed to increase linearly with LogK_{OW} according to LogK_{OC} = (1.53 ± 0.05)LogK_{OW} – (3.35 ± 0.35) (R^2=0.993; Figure S5). LogK_{OW} values were taken from van Noort *(31)*.

Effects of sediment treatment with activated carbon on survival of *A. aquaticus* and *L. variegatus*. Prior to the flux experiments the tolerance of bioturbators in Biesbosch sediment was assessed using whole sediment bioassays. Test duration of the bioassays with *A. aquaticus* was designed at 28 d. However, mortality of the organisms was already observed after 21 d, so the assay was terminated after 21 d of exposure. The bioassay with *A. aquaticus* revealed a decrease in survival in all treatments (10-35%, Figure S6). Survival followed the order PAC sediment > GAC sediment / stripped sediment > untreated sediment (Figure S6), with % survivors in untreated sediment being statistically lower than in all AC-treated sediments (one-way ANOVA, F (3, 8) = 14.556, $p = 0.001$). This again confirms the positive effect of AC treatments on habitat quality for *A. aquaticus (17)*. However, in this case mortality still occurred in the AC treatments, which may have been caused by negative effects of AC in combination with PCB, PAH and metal toxicity *(17, 32)*. In contrast to *A. aquaticus, L. variegatus* survived at all treatments and the number of individuals were not statistically different between treatments (one-way ANOVA, F (3, 8) = 1.323, p = 0.333) (Figure S6). From the bioassay results it was concluded that both species survived sufficiently long to enable studying the impact of bioturbation on sediment water exchange of HOCs.

Effects of bioturbation and AC treatment on turbidity. Turbidity in the overlying water was measured as a direct indicator of bioturbation. In the systems without bioturbators, average turbidity was low, except in the PAC sediment (Figure S7 and S8). The high turbidity in the PAC treatment was caused by suspended fine AC particles, which were observed in the overlying water. In the presence of *A. aquaticus*, turbidity was enhanced in all systems, which is attributed to bioturbation. In the presence of *L. variegatus*, turbidity was enhanced only in untreated and in stripped sediment, i.e. the systems without AC particles in the sediment. We explain the lack of turbidity enhancement in the PAC and GAC treated sediments by a reduction in bioturbation activity.

This reduction was not caused by mortality because survival was 100% for this species (Figure S6). However, negative AC particle effects have been reported for *L. variegatus*, such as reduction of egestion rate and lipid content *(33-35)*. Koelmans and Jonker *(10)* reported a reduction in bioturbation activity of *Limnodrilus* sp. in sediments to which black carbon was added. Recently, effects of PAC on population density of *L. variegatus* under field conditions have been reported *(36)*. Therefore, sublethal effects on the activity of the species are plausible and may have caused a decrease in bioturbation activity.

PCB mass fluxes. PCB uptake by the Empore disks showed an initial stage during which the chemicals were extracted from the overlying water, followed by a second, slower uptake stage, which was related to release from the sediment bed (Figure 1, Figure S9-S20). The quantity present in the overlying water at time zero was negligible compared to the total extracted quantity (i.e. $Q_{ED} >> Q_{PW,t=0}$). This implies that the extracted PCBs originated from the sediment, which is an important prerequisite for the later assessment of K_L^*. In systems with bioturbators, the cumulative curves were more linear than in non-bioturbated systems (Figure 1).

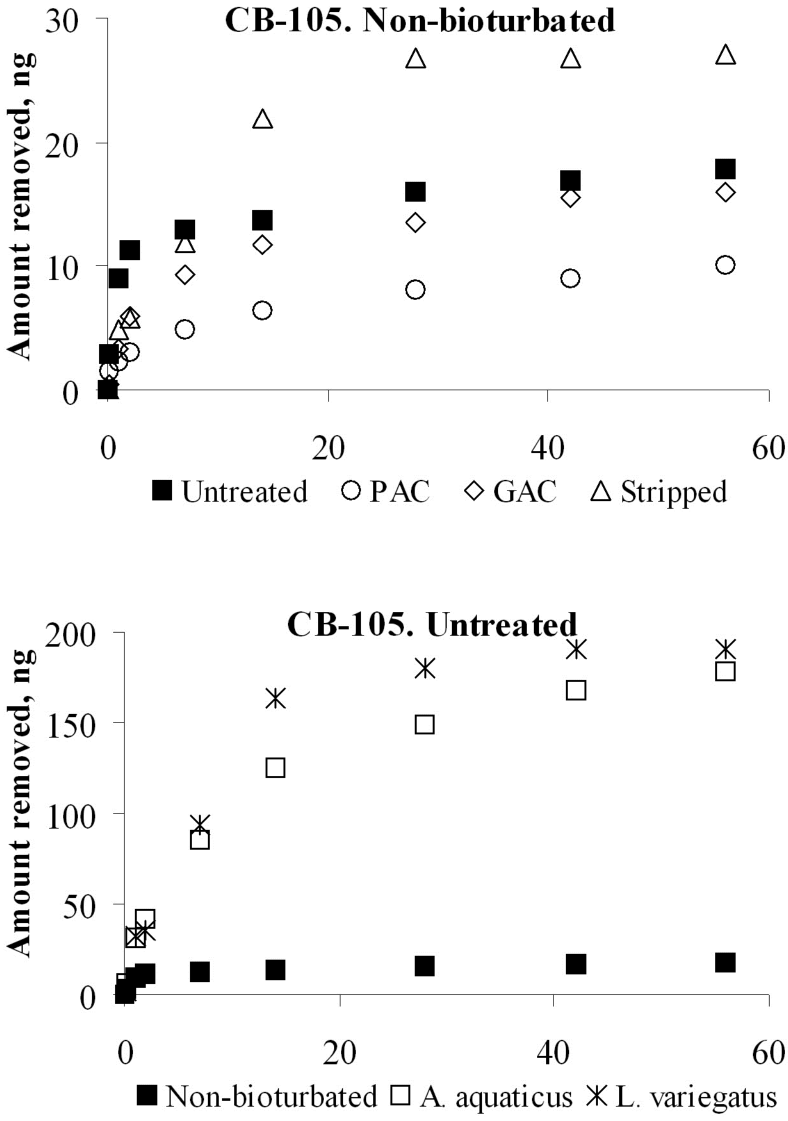

Figure 1. Measured removed cumulative amount of CB-105 from overlying water (a) in untreated, PAC, GAC, and stripped Biesbosch sediment in the absence of bioturbators and (b) in untreated sediment in the presence of *A. aquaticus* and *L. variegatus*.

This phenomenon was observed previously *(10)* and shows that bioturbation causes higher PCB release rates from the sediment. Released quantities followed the order PCB-44 >20 >18 >105 >28 >118 >138 > 31 >180 >153>155 >209 >170 >194 >204, which is roughly the order of increasing PCB hydrophobicity (Table S3). In the systems without bioturbators, PCB removal in PAC treated sediment was up to 4 times lower, which is explained by the lower pore water concentrations C_{PW} in the presence of PAC (Table S3), causing a lower gradient for transport to the overlying water (eq 1). In the GAC treated and stripped sediment, the removed amounts were not always lower than in untreated sediment (Table S3). This lack of clear treatment effect for GAC and stripped sediment may relate to sediment heterogeneity or lack of equilibrium. Compared to GAC, PAC has a much higher surface area and is better dispersed thus causing fast equilibration with the PCBs. In the short term, treatment effects thus can be expected especially for this treatment. The presence of *A. aquaticus* in untreated, PAC, GAC, and stripped sediment increased the amount extracted by the Empore disks by 74, 1.6, 11 and 10 times, respectively, compared to the same treatments without animals. In the presence of *L. variegatus* the increase was a factor of 30, 2.6, 4.8 and 2.7, respectively. Remarkably, the factor increase is the least for the treatment in which HOC sorption affinity was highest (PAC). This suggests that mobilization by bioturbation may have been effectively blocked by increased binding. It is unlikely that these differences between extracted amounts can be explained by decreased bioturbation. After all, the relative differences between extracted amounts occur already in the first stage of release, at time scales for which the bioassays showed no negative effects.

Modeled pore water concentrations. Estimates of the initial pore water concentration ($C_{PW,\, t=0}$) decreased among treatments in the order untreated > GAC > stripped > PAC sediment (Table S4), which agrees very well with the results of POM-SPE experiment. However, the estimated values were 2-50 times higher than those measured with the POM passive samplers (Figure S21). POM-SPE detects truly dissolved PCB concentrations whereas the modelling yields apparent total aqueous phase concentrations, which may include DOC bound PCBs. Consequently, we hypothesize that the difference is explained by the presence of DOC-bound PCBs in the pore water. DOC would increase apparent pore water concentrations dependent on the quantity of DOC and the PCB binding constant *(37, 38)*. Multiple regression analysis showed that the fitted pore water concentrations $C_{PW,\, t=0}$ significantly correlated with the measured turbidity (NTU) as a proxy for DOC in the test systems (p = 0.019) as well as with LogK_{OW} as a proxy for the PCB-DOC binding constant (p = 0.030) (Table S7), which confirms the hypothesis. Because the animal and AC treatments were shown to have substantial effects on turbidity, they also affected the initial apparent dissolved concentrations in the pore waters. The relative increase in pore water concentration in the presence of DOC can be defined as follows:

$$\frac{C_{PW}^{POM}}{C_{PW,t=0}^{*}} = \frac{C_{PW}^{POM}}{C_{PW}^{POM} + C_{DOC}[DOC]} = \frac{1}{1 + K_{DOC}[DOC]} \qquad (6)$$

in which C_{PW}^{POM} (µg/L) is the truly dissolved PCB concentration measured with POM passive samplers, C_{DOC} is the concentration of PCB associated with DOC (µg/kg), [DOC] is the DOC concentration approximated from NTU (kg/L) and K_{DOC} = C_{DOC}/C_{PW}^{POM} is the DOC-water partition coefficient (L/kg). Eq 6 was used to estimate DOC-water partition coefficients (LogK_{DOC}, L/kg). The resulting LogK_{DOC} values were positively correlated with LogK_{OW} (Figure 2, p = 0.010, 0.008, 0.023 for untreated, GAC, and stripped sediment, respectively). The regressions were statistically different from each other, which implies that DOC binding properties differed among treatments. Such differences are plausible because differences in bioturbation and presence of AC fines may have resulted in variations in DOC composition among the treatments. The regression for untreated sediment, LogK_{DOC} =0.96 LogK_{OW}+0.26, can be assumed to reflect binding to amorphous organic matter and is close to previously published regressions of PCBs to DOC or humic acids *(39, 40)*. This analysis supports the hypothesis that the observed difference between truly dissolved and apparent aqueous concentrations is explained from binding to DOC. The fraction of aqueous PCB concentration bound to DOC was calculated from:

$$F_{DOC} = \frac{K_{DOC}[DOC]}{1 + K_{DOC}[DOC]} \qquad (7)$$

and ranged from 37 (CB-52) to 99 % (CB-194, 204) and increased with increasing LogK_{OW} (Figure S22). Apparent LogK_{OC}^{*} values calculated with the apparent $C_{PW,\,t=0}$ values appeared to be up to two Log units lower than those based on truly dissolved C_{PW} values measured with POM-SPE (Figure S5), an effect known in the literature as the ‘third phase’ effect *(37, 38)*.

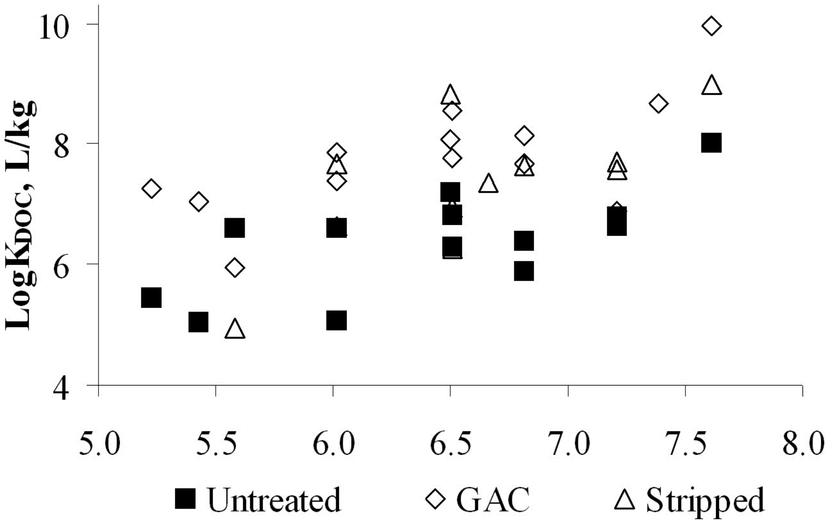

Figure 2. Dissolved organic carbon – water sorption coefficients (LogK_{DOC}, L/kg) of PCBs in untreated, GAC, and stripped sediment calculated using eq 2.
LogK_{DOC} = (0.79 ± 0.25) LogK_{OW} + (1.2 8± 1.63), R^2 = 0.471, p = 0.010 (for untreated sediment),
LogK_{DOC} = (0.74 ± 0.24) LogK_{OW} + (2.92 ± 1.57), R^2 = 0.454, p = 0.008 (for GAC sediment),
LogK_{DOC} = (0.96±0.36) LogK_{OW} + (0.89±2.43), R^2=0.420, p=0.023 (for stripped sediment).

Effects of sediment treatment and bioturbation on mass transfer coefficients for sediment water exchange. PCB K_L^* values for untreated sediment without bioturbators showed no trend with hydrophobicity and had a median 0.067 m/d (IQR range 0.05-0.078) (Table S5). This range agrees very well to previously reported values for systems were BBL transport was rate limiting (Table S6). The fact that no trend with hydrophobicity was observed is also consistent with transport being rate limited in the BBL because molecular diffusivities in water have limited range *(9)*. However, our present values are not consistent with intra- or interparticle diffusion in the sediment bed because hydrophobicity should have a large impact on the effective diffusivity governing these in-bed processes. Therefore, we conclude that transport in the BBL and not in-bed diffusion was rate limiting, which also supports the assumption underlying eq 2.

The K_L^* values for PAC, GAC, and stripped sediment systems without bioturbators were partly in the above range, but also much higher values up to 483 m/d were estimated, especially for more hydrophobic PCBs (Table S5). Because the treated sediments generally were more turbid than the untreated system without bioturbation, the higher values may relate to colloid or DOC facilitated mass transfer of the PCBs across the BBL *(28, 41, 42)*, a hypothesis which also is consistent with the positive trend between K_L^* and LogK_{OW} and the high values observed for K_L^{ED}.

The K_L^* values for systems with bioturbators were up to two times higher than K_L^* values for non-bioturbated systems. It is not likely that animal activity would affect the gradient in eq 1, because mixing in the overlying water already occurred by the Empore disk stirrer and pore water PCB concentrations are not supposed to drop given the negligible depletion of the sediment top layers in this type of flux experiments *(9, 10)*. Consequently, we explain this as an effect of bioturbation on the thickness of the BBL or by an increase in sediment porosity enhancing advective processes at the sediment interface and thus facilitating PCB transport to the overlying water *(11)*. However, bioturbation also contributed to turbidity so these higher K_L^* values also may be explained from DOC facilitated mass transfer. The differences in K_L^* values between AC treatments with *A. aquaticus* were not so pronounced. For worms, however, K_L^* values were elevated for systems with worms in untreated sediment, but not for the systems with the sediments treated with PAC (Table S5). This again can be explained with decreased biological activity of *L. variegatus* in the systems with AC-treated sediment which resulted in decreased PCB mass transfer. This absence of K_L^* enhancement in the *L. variegatus* worm treatments matches with the absence of turbidity enhancement in these systems, with was discussed above and explained from sublethal effects of AC or generally black carbon on activity of the worms *(10)*.

From the above observations we conclude that the enhancement of mass transfer across the BBL may have been driven by DOC facilitated transport. Just like for the effect of DOC on apparent solubility enhancement described above, transport enhancement would depend on the DOC concentration and the affinity of the PCBs for the DOC. This was tested using multiple regression analysis, which revealed a significant correlation between LogK_L^* and LogK_{OW} (p = 0.0002), thus confirming the hypothesis. The dependence of LogK_L^* on measured turbidity (LogNTU) as a proxy for DOC was not significant (p = 0.146) (Table S7). Several factors may explain the lack of significance for NTU. First, NTU is a rough proxy for DOC in the systems, which most probably was a mixture of humic acids and natural colloids from the sediment and resuspended fines from the AC treated sediments, which may have varied over time and among cores. Furthermore, the range of NTU values was less than that of the LogK_{OW} values. Finally, variability in modelled K_L^* values was considerable and may have been larger than that for modelled $C_{PW,t=0}$ values, for which the NTU dependence was significant.

Mechanistic interpretation of mass transfer coefficients. The detected dependence of K_L^* on LogK_{OW} may also be mechanistically explained by evaluation of eqs 1-4. Combination of eq 2 and 4 and simplification yields:

$$\frac{1}{K_L^*} = \frac{1}{K_L + K_L^{DOC} K_{DOC}[DOC]} + \frac{h}{D_b K_d \rho_b} = \frac{1}{K_L + K_L^{DOC} NTU 10^{-6} 10^b K_{OW}^a} + \frac{\lambda}{K_d} \qquad (8)$$

in which b and a are intercept and slope of the linear relationship LogK_{DOC}= aLogK_{OW}+b, DOC/NTU an empirical ratio between [DOC] and NTU, and λ is $h/D_b\rho_b$. This equation was evaluated using our measured median K_L of 0.067 m/d, measured treatment specific b and a estimates (Figure 2) and measured K_d values (Figure S5), and [DOC]≈NTU·10^{-6} *(25, 43)*. Values for K_L^{DOC} were taken as 0.02K_L, based on data provided by Ter Laak et al, showing a more or less constant ratio of 0.02±0.01 between stagnant boundary layer diffusivities for DOC-bound and freely dissolved PCBs *(28)*. The factor $h/D_b\rho_b$ (=λ) was estimated as 11060 (d/m)·(L/kg) based on a typical bioturbation depth of h=3 cm, a sediment density ρ_b of 1.5 kg/L and an average biodiffusion coefficient D_b of 1.81·10^{-6} m^2/d *(44)*. Using this parameterization, a theoretical scenario analysis of the dependence of K_L^* on LogK_{OW} indicates that the transport resistance in the BBL is rate limiting for the PAC and stripped treatments, whereas for the untreated and GAC treatment also biodiffusion plays a role, especially for the less hydrophobic congeners (LogK_{OW}<6) (Figure 3). From this evaluation we conclude that no term in eq 8 can be a priori neglected and that the processes molecular diffusion, DOC facilitated transport and biodiffusion all are potentially relevant in the interpretation of the fluxes from the treated sediments.

Consequently, the full model as condensed in eq 8 was tested quantitatively by fitting the (composite) parameters K_L^{DOC} and λ against the data. The other parameters were set at the values mentioned above, which were all independently measured or taken from the literature. Measured and modeled K_L^* values were not normally distributed and spanned 5 orders of magnitude and therefore were Log-transformed. The model fit (2 parameters and 46 observations) was highly significant (F-test, p = 0.0147), despite the scatter in the data (Figure S23). The estimate for the apparent K_L^{DOC} was 0.00173 m/d (0.00036 - 0.01260, 90%CI). This is lower than the K_L value for dissolved PCB (0.068 m/d), which can be explained from the humic aggregate associated PCBs having lower diffusivities in the BBL than freely dissolved PCBs *(28)*. The factor K_L^{DOC}/K_L is 0.025, which agrees very well to the 0.02±0.01 K_L^{DOC}/K_L ratio calculated from the data by Ter Laak et al *(28)*. The estimate for the composite variable λ (=$h/D_b\rho_b$) was 11030 (d/m)·(L/kg) (1105 – 51592, 90% CI), which also has a high uncertainty, yet is practically identical to the value of 11060 (d/m)·(L/kg) which was calculated above using independent measured and literature data. From this analysis we conclude that the new integrated model is consistent with the data and that DOC facilitated transport as well as biodiffusion affected the mass transfer of PCBs.

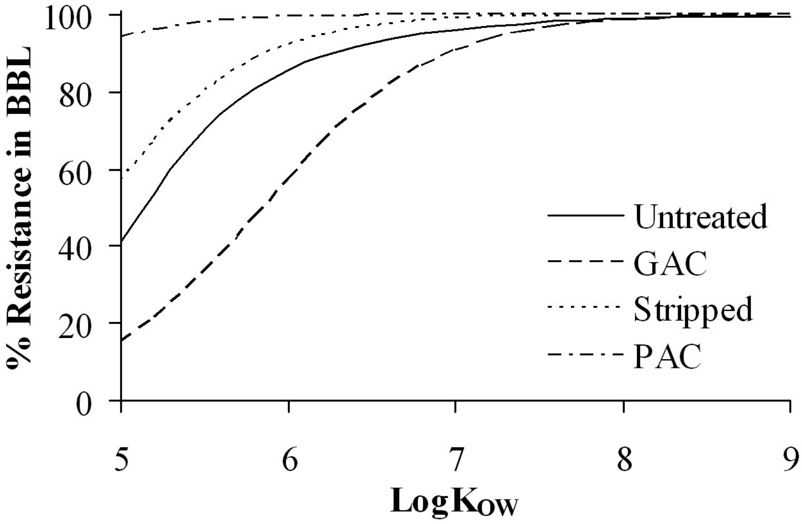

Figure 3. Percentage resistance to PCB transport in the BBL calculated with eq 8, as a function of PCB hydrophobicity, for the four remediation scenarios.

Implications

The present study showed that sediment treatment with AC decreased pore water concentrations and fluxes of PCBs. The efficiency of the AC-treatments decreased in the order PAC > sediment stripping > GAC. This improvement of sediment quality increased the survival of *A. aquaticus*, whereas *L. variegatus* was tolerant to all treatments. The presence of bioturbators may lead to increased turbulence, increased fluxes and thus decreased efficiency of sediment treatment with AC if the bioturbators, such as *A. aquaticus*, are tolerant to AC. If bioturbators are not tolerant to AC as was the case for *L. variegatus* in PAC sediment, AC might cause a decrease activity of the organisms and no enhancement of the flux occurs. Sediment stripping, i.e. addition-removal of GAC, did not have a negative effect on the test species, which is an advantage of this remediation technique. AC treatments and bioturbation substantially enhanced mass transfer coefficients by DOC facilitated transport of HOC through the BBL. Consequently, this process should be taken into account when evaluating the effectiveness of AC treatment or in the risk assessment of contaminated sediments, since traditional pore water concentration alone may underestimate mass fluxes and bioavailability.

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Supporting Information

Methods details

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 obtained from Norit Activated carbon, Amersfoort, The Netherlands. Empore^{TM} disks with a diameter of 47 mm and coated with a C_{18} phase with a volume (V_{ED}^{C18}) of 144 µm were obtained from J.T. Baker, The Netherlands. Prior to use, the disks were cleaned with 10 ml methanol using a vacuum filter and then air dried. Polyoxymethylene sheets (POM; thickness 76 µm) were obtained 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. 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 were obtained from Promochem (Wesel, Germany). CB-72 was obtained from Ultra Scientific (North Kingstown, RI, USA). 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), sodium azide (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) Nonopure water.

Determination of PCB concentrations in pore water. PCB concentrations in sediment pore water were determined using the POM-SPE method *(20)*. An amount of wet sediment, corresponding to about 10 g of dry weight, was brought into a full glass 50 mL bottle and the bottle was filled with an aqueous solution of sodium azide (50 mg/L) and calcium chloride (0.01 M) in Millipore 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. Then, the pieces of POM were recovered, cleaned with wet tissue, and extracted with acetonitrile. Finally, internal standard (CB-209) was added. PCB aqueous concentrations were calculated from the concentrations measured in the sampler (C_{POM}) using previously published POM-water equilibrium partition coefficients K_{POM} *(23, 24)*.

Chemical analysis. Empore disks were extracted twice with 20 ml methanol using an Accelerated Solvent Extractor (ASE 350, Dionex, USA). Extracts were concentrated to 1 mL, exchanged to hexane, and cleaned over Al_2O_3/silica gel columns. Eluates were concentrated to 1 mL, desulpherized using Cu powder in the ultrasonic bath, and exchanged to iso-octane. Eluates were reduced to 0.2 mL and the internal standard (CB-143) was added. Recoveries and experimental and analytical blanks (three per every 12 samples) were used in the analysis.

The recoveries ranged 85.3(±3.2) – 113(±3.9)%. Data were corrected for blanks. Untreated sediment (approximately 1 g d.w.) was extracted with 70 ml hexane/acetone (3:1 v/v) using ASE, and then cleaned following the same procedure as for Empore disks. The sediment analysis was done in triplicate with relative SD of 3.7%.

Instrumental analysis. PCB concentrations in sediment and Empore disks were measured by splitless injection of 1 µL of sample in an upgraded HP5890 series GC 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 ^{63}Ni electron capture detectors. The injector and detector temperatures were 250 and 325 °C, respectively. Carrier gas was N_2 (1 mL/min). 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.

Estimating sediment-water mass transfer coefficients K_L

The contaminant flux from the sediment bed in the laboratory sediment core systems (Φ_{sed}, µg/m^2/d), can be described as the product of the overall apparent sediment-to-water mass transfer coefficient (K_L^*) and the concentration gradient between pore water (C_{PW}, µg/m^3) and overlying water (C_{OW}, µg/m^3) *(9, 26)*:

$$\phi_{sed} = K_L^*\left(C_{PW} - C_{OW}\right) = \frac{1}{\frac{1}{\kappa} + \frac{h}{D_b K_d \rho_b}}\left(C_{PW} - C_{OW}\right) \tag{1}$$

The right hand side of eq 1 quantifies two resistances against sediment-water transfer: an in-bed resistance described by $h/D_bK_d\rho_b$ and a benthic boundary layer (BBL) mass transfer resistance $1/\kappa$, where h (m) is the average bioturbation depth in the sediment bed, D_b is a biodiffusion coefficient representing particle diffusivity in the bed (m^2/d), K_d is the sediment-to-water partition coefficient (L/kg), ρ_b is the dry density of the particles (kg/L), and κ is the water-side DOC-inclusive benthic boundary layer mass transfer coefficient (m/d).

When an Empore^{TM} disk is present in the overlying water the additional flux Φ_{ED} (m/d) from the overlying water to the disk can be defined as:

$$\phi_{ED} = K_L^{ED}\left(C_{OW} - \frac{C_{ED}}{K_d^{ED,C18}}\right) \tag{2}$$

where K_L^{ED} (m/d) is the mass transfer coefficient for HOC transfer from the overlying water to the Empore disk, C_{ED} is the concentration in the Empore disk (ng/kg) en $K_d^{ED,C18}$ is the HOC disk to water equilibrium partition coefficient (L/kg). The effect of the serial fluxes on the HOC concentration change in the overlying water can be calculated by combining the right side of eqs 1 and 2 and correcting for sediment surface area (A_{sed}, m^2), Empore disk surface area (A_{ED}, m^2), and overlying water volume (V_{OW}, m^3) *(9, 10)*:

$$\frac{dC_{OW}}{dt} = \frac{K_L^{*} A_{sed}}{V_{OW}}\left(C_{PW} - C_{OW}\right) + \frac{K_L^{ED} A_{ED}}{V_{OW}}\left(\frac{C_{ED}}{K_d^{ED,C18}} - C_{OW}\right) \tag{3}$$

The concentration change in the Empore disks can be modeled as:

$$\frac{dC_{ED}}{dt} = \frac{K_L^{ED} A_{ED}}{V_{ED}^{C18}}\left(C_{OW} - \frac{C_{ED}}{K_d^{ED,C18}}\right) \tag{4}$$

in which V_{ED}^{C18} is a volume of an octadecylsilica (C_{18}) phase of the Empore disk. For the pore water, a similar mass balance can be defined:

$$\frac{dC_{PW}}{dt} = \frac{K_L^{*} A_{sed}}{V_{PW}}\left(C_{OW} - C_{PW}\right) \tag{5}$$

where V_{PW} is the apparent pore water volume. The total quantity of HOCs extracted with Empore disk (Q_{ED}) can be calculated from the modelled C_{ED} values (eq 4) *(9, 10)*:

$$Q_{ED} = C_{ED} V_{ED}^{C18} \tag{6}$$

The parameters A_{sed}, A_{ED}, V_{OW}, and V_{ED}^{C18} are known from the experimental conditions. At time zero, concentrations in the initially mixed pore and overlying water can be assumed equal ($C_{OW,t=0} = C_{PW,t=0} = C_0$). The apparent pore water volume (V_{PW}) stands for the volume of water required to contain the initial sediment-bound HOC (Q_T) minus HOC mass in the overlying water that can be estimated as $V_{PW} = (Q_T - V_{OW}C_0)/C_0$ *(9, 10)*. $K_d^{ED,C18}$ were taken from the literature *(45)*.

Eqs 3–6 were numerically solved in Microsoft Excel, using an Euler integrator and variable time step. At the Empore disk replacement times, modeled values for C_{ED} were reset to zero. K_L^{ED}, K_L^{*}, and C_0 were optimized by fitting Q_{ED} to the measured values using the Excel Solver tool with scaling of parameters and a relative least squares criterion.

Equilibrium partition coefficients were calculated as the ratio of the PCB concentrations in sediment and the initial concentration in the pore water from the model fitting ($C_{PW,t=0}$) or from the POM-SPE measurements.

The DOC-inclusive mass transfer coefficient κ can be expressed as a function of DOC concentration as follows. In the absence of bioturbation and when DOC-associated PCBs contribute to the exchange of PCBs across the BBL, the overall contaminant flux from the bed will be *(28)*:

$$\phi_{sed} = K_L\left(C_{PW} - C_{OW}\right) + K_L^{DOC}\left(C_{PW}^{DOC} - C_{OW}^{DOC}\right) \tag{7}$$

where K_L is the mass transfer coefficient of freely dissolved PCBs (m/d), K_L^{DOC} is the mass transfer coefficient of DOC-bound PCB (m/d), C_{PW}^{DOC} and C_{OW}^{DOC} (ng/L) are the concentrations of DOC-sorbed PCBs in pore and overlying water, respectively. Assuming linear partitioning between DOC and water *(40, 46)*, $C^{DOC} = K_{DOC} C_W[\mathrm{DOC}]$, where K_{DOC} is the DOC-water sorption coefficient (L/kg), and [DOC] is the concentration of DOC in the aqueous phase (kg/L). Eq 7 now can be rewritten to yield:

$$\phi_{sed} = (K_L + K_L^{DOC} K_{DOC}[DOC])(C_{PW} - C_{OW}) \qquad (8)$$

where $K_L + K_L^{DOC} K_{DOC}[DOC] = \kappa$ is the apparent DOC-inclusive BBL mass transfer coefficient.

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

	C, mg/kg	**Threshold effect level^a, mg/kg**		**C, µg/kg**	**Threshold effect level^a, µg/kg**
PAHs			**PCBs**		
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[*a*]anthracene	1.2	0.07	CB-31	43 (1.2)	
Chrysene	1.4	0.11	CB-44	14 (0.7)	
Benzo[*k*]fluoranthene	1.0	0.06	CB-52	82 (1.2)	
Benzo[*a*]pyrene	1.1	0.09	CB-101	75 (4.1)	
Benzo[*ghi*]perylene	0.78		CB-105	17 (0.8)	
Indeno[1,2,3-*cd*]pyrene	0.64		CB-118	29 (0.7)	
∑PAHs	**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	**∑PCBs**	**700 (28)**	**22**
Total petroleum hydrocarbons	**700**		**TOC, %**	**5.86 (0.51)**	**-**
∑DDT/DDE/DDD	**0.22**	**0.0045**	**BC, %**	**1.15 (0.19)**	-

[a] ref *(21)*

Table S2. PCB mass transfer coefficient (K_L^{ED} , m/d) for untreated, PAC, GAC, and stripped sediment, with and without bioturbators, viz. *A. aquaticus* and *L. variegatus*.

Treatment	**Untreated**			**PAC**			**GAC**			**Stripped**			**Average (SD)**	**Median (25th/75th percentile)**
PCB	**N**	**A**	**L**	**N**	**A**	**L**	**N**	**A**	**L**	**N**	**A**	**L**		
CB-18	6.397	54.52	7.047	45.30	29.54	52.82	n.a.	17.15	55.20	41.60	54.24	53.64	**35 (22)**	**43 (15/54)**
CB-20	19.71	56.16	8.755	50.34	52.94	33.86	7.779	5.375	27.13	n.a.	64.76	10.30	**31 (22)**	**27 (9.5/52)**
CB-28	11.79	5.192	30.15	n.a.	0.508	42.73	0.867	6.402	n.a.	33.58	2.176	51.40	**18 (19)**	**9.1 (2.9/33)**
CB-29	9.464	47.49	6.145	0.212	51.82	11.20	0.054	n.a.	18.05	1.200	31.76	25.62	**18 (19)**	**11 (3.7/29)**
CB-31	9.753	53.45	7.268	49.98	51.95	38.00	18.32	11.01	55.44	9.565	3.56	55.16	**30 (22)**	**28 (9.7/52)**
CB-44	10.00	n.a.	10.63	49.46	51.99	54.39	53.50	n.a.	55.29	13.50	n.a.	53.53	**39 (21)**	**52 (13/54)**
CB-52	11.58	15.41	0.532	n.a.	4.960	51.51	1.929	n.a.	n.a.	1.274	17.11	40.93	**16 (18)**	**12 (1.9/17)**
CB-105	13.70	2.808	39.30	29.79	17.56	46.87	24.63	43.79	53.23	36.33	50.61	53.14	**34 (17)**	**38 (23/48)**
CB-118	23.51	6.256	43.90	9.228	2.474	43.40	n.a.	4.474	4.507	29.98	49.30	41.58	**22 919)**	**16 (4.5/42)**
CB-138	2.913	17.16	1.227	n.a.	37.26	41.30	1.000	31.24	3.547	33.80	2.356	n.a.	**17 (17)**	**10 (2.5/33)**
CB-149	n.a.	15.64	1.435	27.50	0.530	24.81	0.468	n.a.	5.590	2.872	18.42	n.a.	**11 (11)**	**5.6 (1.4/18)**
CB-153	13.88	12.46	n.a.	15.66	25.63	5.033	2.099	33.70	16.13	0.901	0.172	27.99	**14 (11)**	**14 (3.6/21)**
CB-155	16.38	48.84	44.16	10.06	n.a.	54.13	34.87	n.a.	56.72	3.047	47.43	10.00	**30 (22)**	**35 (10/48)**
CB-170	26.47	21.87	0.809	10.47	14.80	4.744	36.13	22.72	22.42	3.875	0.475	0.415	**14 (12)**	**13 (3.1/22)**
CB-180	20.07	21.98	1.596	21.26	n.a.	32.95	n.a.	29.02	26.59	2.808	28.12	7.259	**19 (11)**	**22 (10/28)**
CB-194	24.37	53.45	50.55	n.a.	2.951	46.21	n.a.	45.06	54.38	1.647	4.881	n.a.	**28 (24)**	**35 (3.4/49)**
CB-204	n.a.	n.a.	36.78	0.020	2.658	43.77	2.675	24.52	n.a.	0.687	28.58	47.19	**21 (20)**	**25 (2.7/37)**
CB-209	n.a.	n.a.	0.828	22.16	n.a.	38.61	32.23	0.777	53.53	49.75	2.289	12.38	**42 (21)**	**22 (2.3/39)**
Average (SD)	**15(6.9)**	**29(21)**	**17(19)**	**24(18)**	**22(21)**	**37(16)**	**13(17)**	**21(15)**	**34(21)**	**16(17)**	**24(22)**	**33(20)**		
Median (25th/75th percentile)	**14 (9.9/20)**	**22 (14/51)**	**7.3 (1.4/37)**	**22 (10/41)**	**16 (2.6/41)**	**42 (33/47)**	**2.1 (0.8/25)**	**23 (6.4/31)**	**27 (17/55)**	**3.9 (1.6/34)**	**18 (2.4/47)**	**41 (11/52)**		

"N" relates to the non-bioturbated systems, "A" to the systems with *A. aquaticus* and "L" to the systems with *L. variegatus*.

Table S3. Cumulative PCB quantities removed, ng, from untreated, PAC, GAC, and stripped sediment, with and without bioturbators, viz. *A. aquaticus* and *L. variegatus*.

	Untreated			**PAC**			**GAC**			**Stripped**		
	N	**A**	**L**	**N**	**A**	**L**	**N**	**A**	**L**	**N**	**A**	**L**
CB-18	18.6	180	69.5	7.17	6.65	18.7	7.04	11.1	9.67	8.05	20.6	10.7
CB-20	40.8	34.4	20.4	44.3	18.6	47.8	30.3	30.3	17.8	20.3	45.2	42.2
CB-28	16.1	128	38.5	11.6	9.45	11.9	13.4	23.3	10.5	8.90	38.5	18.6
CB-29	16.3	93.4	121	34.6	8.02	32.1	46.3	39.3	52.1	34.6	62.6	15.4
CB-31	10.2	51.1	50.9	5.99	3.37	8.29	6.45	7.98	6.35	4.27	11.4	8.03
CB-44	45.5	332	161	26.9	20.1	70.4	23.8	91.8	45.2	17.4	124	46.5
CB-52	17.5	380	111	13.4	7.08	17.8	18.5	29.1	23.1	18.9	29.0	13.3
CB-105	17.8	179	191	10.1	10.8	18.9	16.0	81.5	29.1	27.1	135	42.8
CB-118	16.1	155	129	8.44	12.2	14.6	20.8	88.0	30.0	33.2	120	45.4
CB-138	15.7	212	130	8.37	8.78	9.78	18.7	75.4	24.9	17.7	124	27.3
CB-149	28.7	373	249	14.9	17.0	21.6	34.7	133	47.1	51.6	279	56.4
CB-153	11.9	278	176	10.2	12.7	12.1	14.3	92.5	38.9	40.8	181	36.7
CB-155	6.26	54.5	63.6	6.47	8.79	12.2	8.89	38.7	14.5	16.3	61.9	23.6
CB-170	5.51	29.9	19.2	7.77	2.08	4.78	7.17	19.2	3.71	9.03	23.2	8.81
CB-180	9.95	67.2	46.8	7.99	6.88	8.20	6.40	39.5	11.9	18.5	57.4	19.4
CB-194	2.42	180	14.6	4.47	3.69	5.38	6.41	15.6	4.65	7.20	17.6	12.4
CB-204	3.22	9.50	7.24	0.83	1.31	1.04	0.64	7.12	3.11	4.14	7.06	4.33
CB-209	3.74	9.44	7.11	3.65	4.43	0.73	2.05	6.55	1.73	2.63	4.68	2.93

“N” relates to the non-bioturbated systems, “A” to the systems with *A. aquaticus* and “L” to the systems with *L. variegatus*.

Table S4. Pore water concentration at time zero ($C_{PW,\ t=0}$, ng/L) in untreated, PAC, GAC, and stripped sediment, with and without bioturbators, viz. *A. aquaticus* and *L. variegatus*.

	Untreated			**PAC**			**GAC**			**Stripped**		
	N	**A**	**L**	**N**	**A**	**L**	**N**	**A**	**L**	**N**	**A**	**L**
CB-18	9.009	6.892	69.70	0.348	0.738	0.919	n.a.	7.870	2.681	0.805	3.058	5.455
CB-20	26.37	13.01	12.17	22.64	1.195	2.918	14.92	21.86	3.592	n.a.	14.81	23.76
CB-28	7.497	47.82	9.199	n.a.	n.a.	0.291	6.169	8.779	n.a.	0.858	23.13	3.626
CB-29	9.072	8.369	35.85	23.86	1.455	1.492	172.6	n.a.	0.736	22.34	0.579	9.892
CB-31	4.469	1.766	33.74	1.980	0.507	0.444	0.670	6.607	1.865	3.835	10.25	3.539
CB-44	26.31	n.a.	103.9	16.14	4.290	5.245	3.214	n.a.	12.57	11.42	n.a.	14.13
CB-52	6.981	7.424	143.1	n.a.	2.772	0.305	53.60	n.a.	n.a.	8.241	5.371	6.229
CB-105	9.320	84.51	7.537	1.004	1.497	0.956	2.359	11.45	3.617	1.000	2.728	2.989
CB-118	4.951	14.26	2.415	0.603	4.872	0.536	n.a.	8.244	10.90	0.600	2.740	1.727
CB-138	4.958	3.017	40.23	n.a.	0.079	0.344	10.00	2.468	2.425	0.168	13.42	n.a.
CB-149	n.a.	6.049	62.48	0.166	n.a.	1.281	n.a.	n.a.	2.303	7.641	3.613	n.a.
CB-153	2.241	5.702	n.a.	0.199	0.135	2.826	4.706	3.032	0.508	12.33	243.5	0.360
CB-155	4.071	4.225	1.531	0.602	n.a.	0.673	0.884	n.a.	1.853	11.04	1.916	8.062
CB-170	0.575	0.358	7.515	0.123	0.656	1.327	0.062	0.527	0.047	0.886	10.65	10.41
CB-180	1.708	0.801	10.06	0.105	n.a.	0.400	n.a.	1.210	0.123	2.505	0.558	1.399
CB-194	1.239	4.877	0.195	n.a.	1.711	0.238	n.a.	1.251	0.956	3.385	2.833	n.a.
CB-204	n.a.	n.a.	0.067	43.86	0.641	0.024	0.405	0.209	n.a.	n.a.	0.067	0.050
CB-209	n.a.	n.a.	2.706	0.186	n.a.	0.006	0.176	0.251	0.276	0.270	4.520	0.056

“N” relates to the non-bioturbated systems, “A” to the systems with *A. aquaticus* and “L” to the systems with *L. variegatus*.

Table S5. Apparent PCB mass transfer coefficient (K_L^*, m/d) for untreated, PAC, GAC, and stripped sediment, with and without bioturbators, viz. *A. aquaticus* and *L. variegatus*.

	Untreated			**PAC**			**GAC**			**Stripped**			**Average**	SD	**Median**	25th percentile	75th percentile
	N	**A**	**L**	**N**	**A**	**L**	**N**	**A**	**L**	**N**	**A**	**L**					
CB-18	0.012	3.842	0.014	2.412	0.892	2.498	0.000	0.079	0.168	0.800	0.472	0.082	**0.939**	1.277	**0.320**	0.063	1.272
CB-20	0.077	0.137	0.077	0.089	1.553	2.315	0.126	0.009	0.345	n.a.	0.166	0.091	**0.453**	0.756	**0.126**	0.083	0.255
CB-28	0.071	0.277	0.277	n.a.	0.000	8.172	1.089	0.135	n.a.	0.987	0.128	0.305	**1.144**	2.498	**0.277**	0.130	0.816
CB-29	0.045	0.989	0.382	71.35	0.386	15.88	134.0	n.a.	427.3	0.164	273.4	0.059	**84.00**	142.5	**0.989**	0.273	102.7
CB-31	0.059	4.426	0.072	0.184	0.506	2.780	1.163	0.044	0.158	0.004	0.028	0.112	**0.795**	1.396	**0.135**	0.055	0.670
CB-44	0.053	n.a.	0.072	0.066	0.317	1.392	0.554	n.a.	0.212	0.053	n.a.	0.196	**0.324**	0.433	**0.196**	0.066	0.317
CB-52	0.076	125.1	0.037	n.a.	0.241	13.85	0.002	n.a.	n.a.	0.444	0.484	0.093	**15.60**	41.33	**0.241**	0.076	0.484
CB-105	0.067	0.218	4.218	0.883	0.810	2.512	0.576	5.961	0.643	5.108	11.07	1.466	**2.794**	3.288	**1.175**	0.626	4.441
CB-118	0.316	5.173	15.37	6.445	0.357	4.232	0.000	0.991	0.285	31.29	8.298	3.984	**6.395**	9.029	**4.108**	0.347	6.908
CB-138	0.185	380.0	3.367	n.a.	136.4	4.616	0.500	192.2	11.61	248.8	49.12	n.a.	**102.7**	132.9	**30.36**	3.679	178.3
CB-149	n.a.	328.8	5.361	203.7	0.000	2.585	0.000	n.a.	44.12	6.042	409.6	n.a.	**111.1**	161.3	**6.042**	2.585	203.7
CB-153	0.046	379.4	n.a.	258.2	284.5	0.618	0.708	164.6	537.2	18.19	649.9	256.9	**231.8**	224.6	**256.9**	9.448	331.9
CB-155	0.057	1.291	10.12	2.152	0.000	2.152	0.976	n.a.	0.629	0.102	5.710	0.248	**2.130**	3.121	**0.976**	0.175	2.152
CB-170	0.013	331.0	4.128	483.8	0.222	0.490	258.0	303.5	228.5	13.19	649.9	0.048	**189.4**	222.9	**120.9**	0.423	310.4
CB-180	0.078	327.9	7.640	218.1	0.000	3.001	0.000	233.1	301.4	9.071	307.9	6.524	**117.9**	144.1	**8.355**	2.270	250.2
CB-194	0.134	6.728	28.98	n.a.	0.222	3.080	0.000	18.50	0.292	0.386	1.636	n.a.	**5.996**	9.891	**1.011**	0.240	5.816
CB-204	n.a.	n.a.	150.9	158.3	0.183	8.836	62.80	324.0	n.a.	0.000	305.2	43.6	**117.1**	126.7	**62.80**	8.836	158.3
CB-209	n.a.	n.a.	4.923	0.970	0.000	134.7	1.265	0.885	0.421	0.788	0.020	423.7	**56.77**	135.6	**0.928**	0.513	4.009
Average	**0.086**	**126.3**	**13.88**	**100.5**	**23.69**	**11.87**	**25.66**	**95.69**	**103.6**	**19.73**	**157.2**	**49.17**					
SD	0.077	166.9	36.08	146.4	72.52	30.96	67.14	128.1	180.4	59.65	231.5	122.8					
Median	**0.067**	**5.173**	**4.128**	**4.428**	**0.279**	**2.891**	**0.565**	**5.961**	**0.629**	**0.800**	**8.298**	**0.248**					
25th percentile	0.049	1.140	0.077	0.905	0.046	2.361	0.000	0.135	0.288	0.164	0.472	0.092					
75th percentile	0.077	328.3	7.640	192.3	0.734	7.283	1.144	192.2	136.3	9.071	305.2	5.254					

“N” relates to the non-bioturbated systems, “A” to the systems with *A. aquaticus* and “L” to the systems with *L. variegatus*.

Table S6. Literature HOC sediment-to-water mass transfer coefficients K_L^* values for untreated sediment without bioturbators

HOCs	K_L^* m/d	Reference
PCBs	0.03-0.19	Erickson et al. *(14)*
DDE, DDD, PCBs	0.07-0.53	Granberg et al. *(47)*
TCDD	0.1	Valsaraj et al. *(26)*
PAHs	0.01 – 0.1	Koelmans et al *(9)*
PCBs	0.03, 0.14	Connolly et al. *(48)*

Table S7. Parameters and statistics of multiple regression analyses used to study the effect of hydrophobicity (LogK_{OW}) and turbidity (LogNTU) on PCB pore water concentration (Log$C_{PW,t=0}$), PCB mass transfer coefficient for the empore disk (K_L^{ED}), and PCB sediment-to-water mass transfer coefficient (Log K_L^*).

	Statistics	Log$C_{PW,t=0}$	Log K_L^{ED}	Log K_L^*
R^2		0.052	0.018	0.087
ANOVA	d.f.	2, 185	2, 185	2, 185
	F	32.34	1.726	8.786
	p	$8.5 \cdot 10^{-13}$	0.181	0.0002
Intercept	Value	39.35	1.820	-4.109
	(SE)	(15.49)	(0.410)	(0.879)
	t	2.541	4.440	-4.674
	p	0.012	$1.54 \cdot 10^{-5}$	$5.7 \cdot 10^{-6}$
LogK_{OW}	Slope	-5.168	-0.111	0.617
	(SE)	(2.362)	(0.061)	(0.130)
	t	-2.188	-1.827	4.741
	p	0.030	0.069	$4.25 \cdot 10^{-6}$
LogNTU	Slope	0.050	-0.023	0.198
	(SE)	(0.021)	(0.063)	(0.135)
	t	2.366	-0.360	1.462
	p	0.019	0.719	0.146

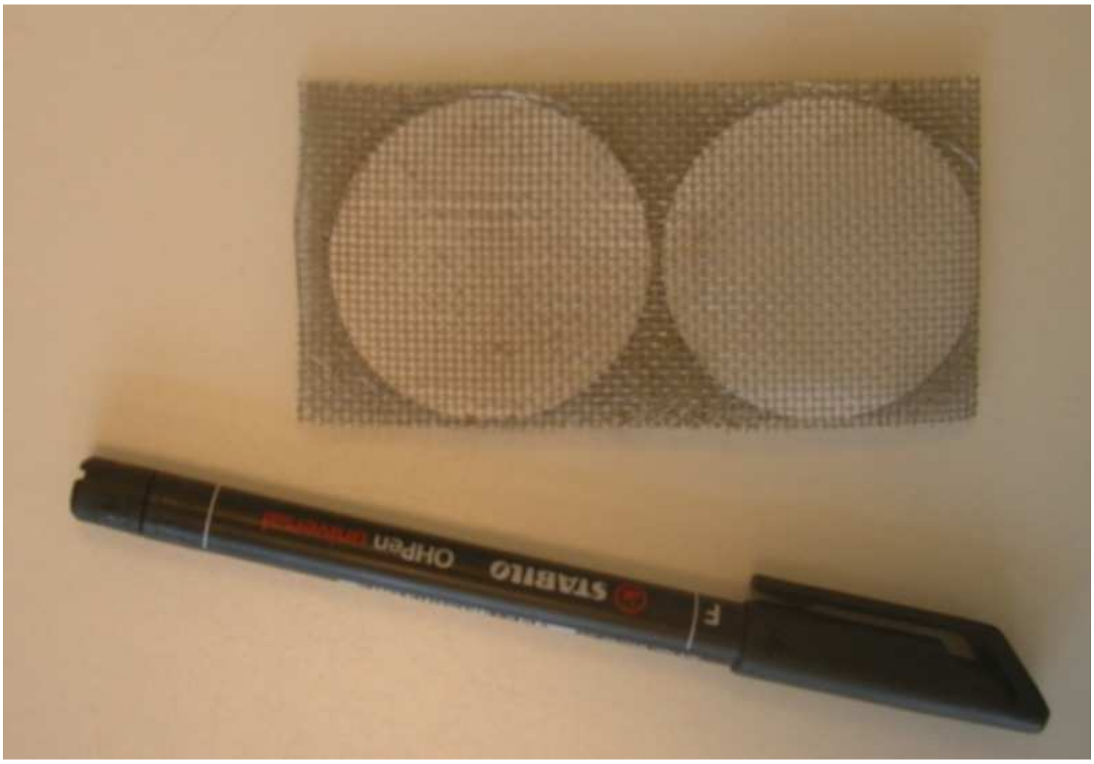

Figure S1. Empore disks mounted in a stainless steel frame as used in the flux experiment.

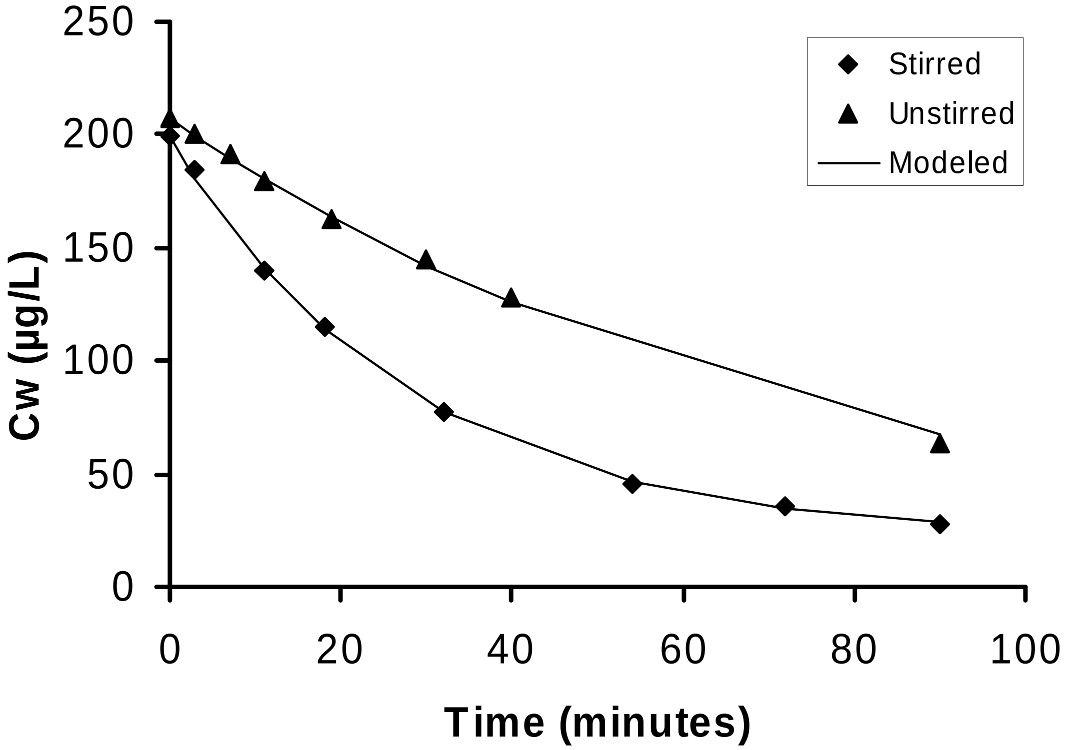

Figure S2. Result of pilot test to determine the extraction efficiency of Empore disks in pure water. Graph shows the decrease of phenanthrene (PHE) concentration in water (C_W) upon addition of an Empore disk, under stirred and unstirred conditions. Solid lines represent model fits to the data, see below. Removal from the aqueous phase was measured in aqueous subsamples of about 2 ml in a quartz-glass cuvette using a Perkin-Elmer LS50B fluorimeter at an excitation wavelength 250 nm and an emission of 366 nm. Mass transfer rate constants for uptake into the disks were calculated using a two-compartment (water and disk) reversible kinetic model *(49)*:

$$C_W = \frac{C_{W,t=0}}{k_{ED} + k_b}\left(k_b + k_{ED}e^{-(k_{ED}+k_b)t}\right)$$

where $C_{W,t=0}$ is the PHE concentration at time zero, k_{ED} is the forward (to the disk) first order uptake rate constant and k_b is the rate constant for the opposite (backward) process. Fitted k_{ED} was 46.1 d^{-1} for the stirred and 18 d^{-1} for the unstirred system. Assuming transport through the laminar boundary layer at the disk surface is rate limiting, k_{ED} (d^{-1}) equates to K_L^{ED} A_{ED}/V_{OW}. With a double sided disk surface of $3.47 \cdot 10^{-3}$ m^2 and water volume $0.25 \cdot 10^{-3}$ m^3 this yields mass transfer coefficients K_L^{ED} of 1.3 and 3.3 m/d^{-1} for the non-stirred and stirred systems respectively.

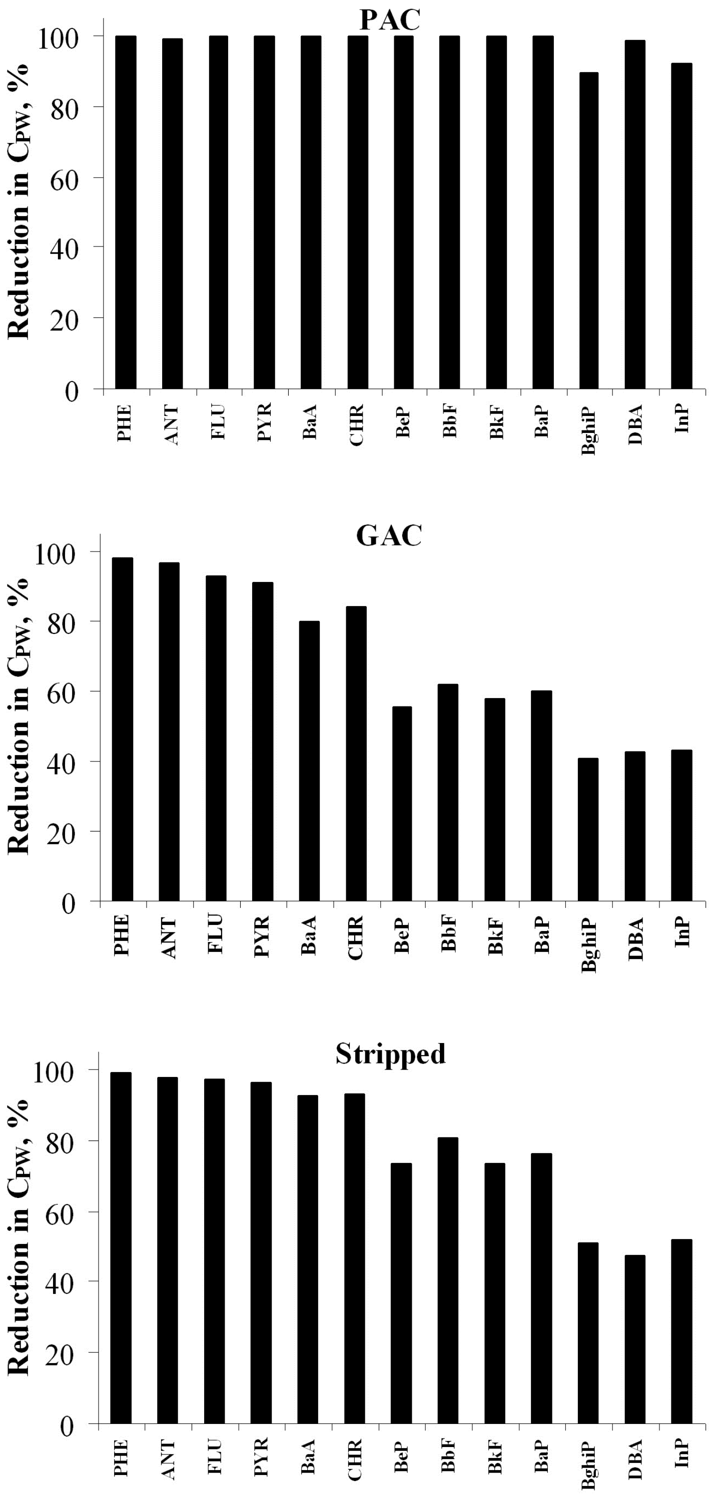

Figure S3. Relative reduction of equilibrium pore water concentration of PAHs in Biesbosch sediment treated with AC according to the following scenarios: (a) capping with PAC, (b) mixing with GAC, and (c) stripping with GAC.

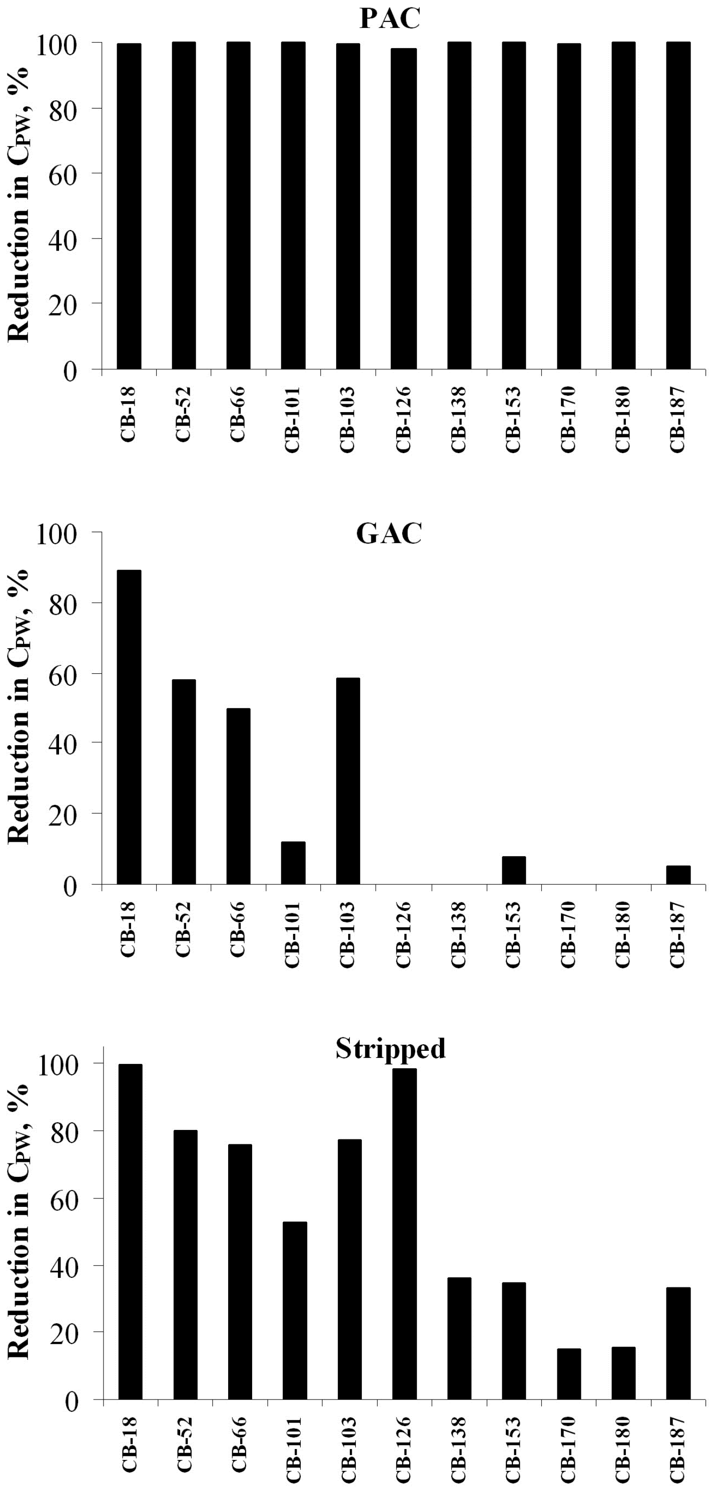

Figure S4. Relative reduction of equilibrium pore water concentration of PCBs in Biesbosch sediment treated with AC according to the following scenarios: (a) capping with PAC, (b) mixing with GAC, and (c) stripping with GAC.

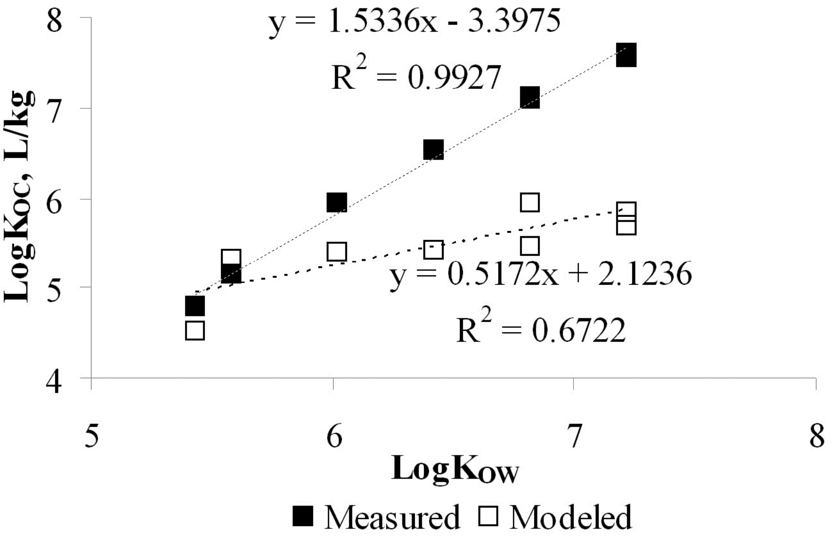

Figure S5. Organic carbon-normalized sediment–water distribution coefficients (LogK_{OC}) as a function of LogK_{OW}, calculated as C_{sed}/C_Wf_{OC} with C_W measured (closed symbols, measured with POM-SPE) and C_W modeled (open symbols).

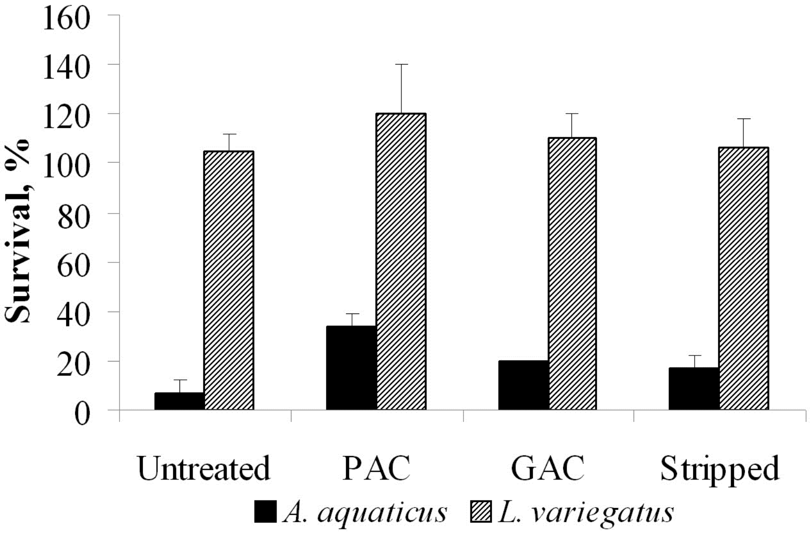

Figure S6. Survival (SD, n = 3) of *A. aquaticus* and *L. variegatus* after 21-and 28-d exposure respectively. Exposure was to Biesbosch sediment treated with AC according to the following scenarios: mixing with PAC, mixing with GAC, and sediment stripping with GAC.

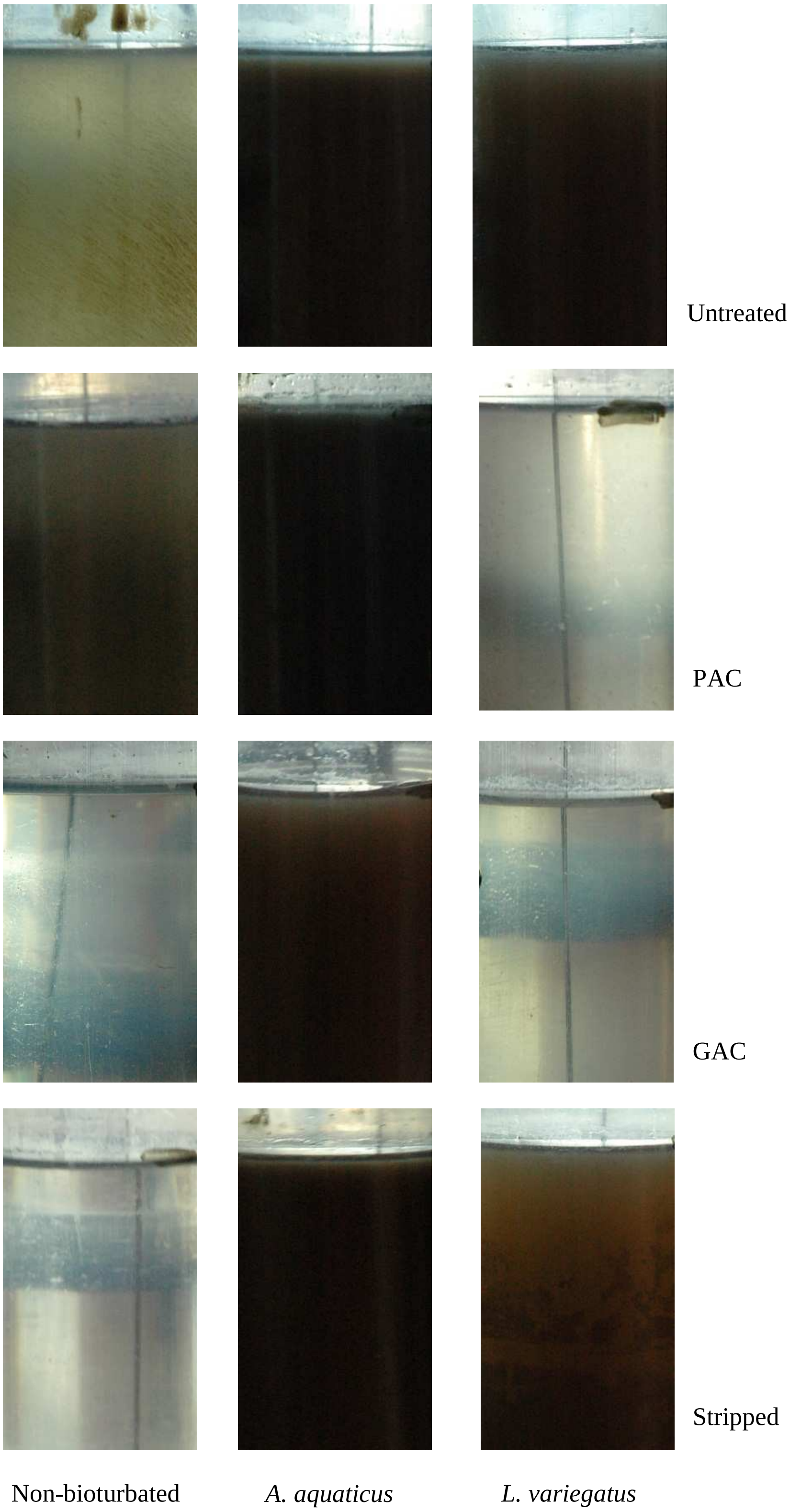

Figure S7. Appearance of the test systems in the flux experiment. Transparent systems show the stirring rods to which the Empore disks were connected.

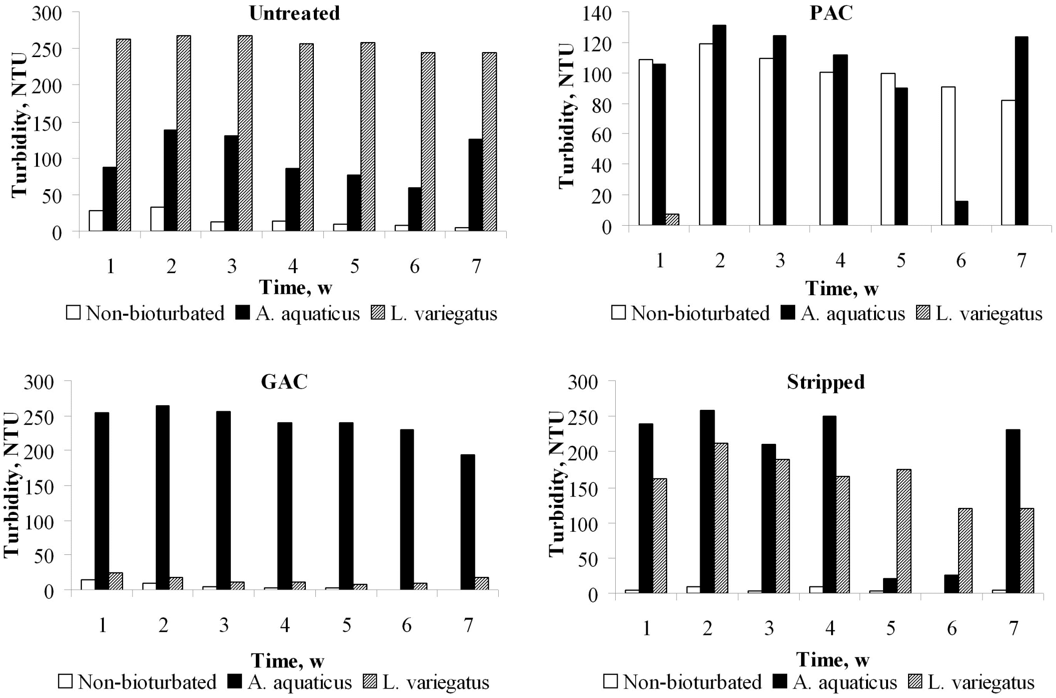

Figure S8. Effect of sediment treatments PAC addition, GAC addition and sediment stripping on turbidity in the absence and presence of bioturbators, viz. *A. aquaticus and L. variegatus*.

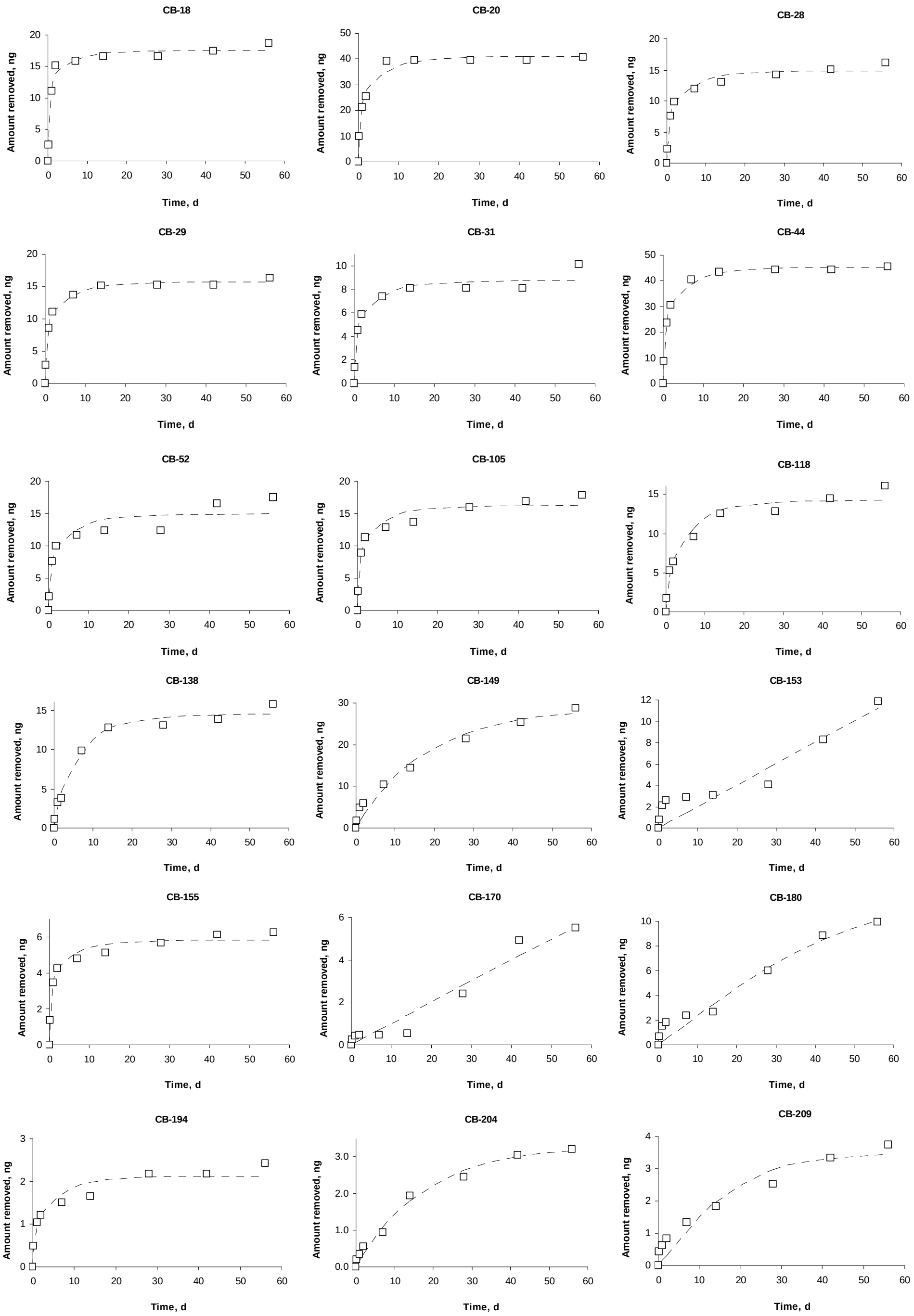
CB-18
CB-20
CB-28
CB-29
CB-31
CB-44
CB-52
CB-105
CB-118
CB-138
CB-149
CB-153
CB-155
CB-170
CB-180
CB-194
CB-204
CB-209

Figure S9. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for untreated non-bioturbated sediment.

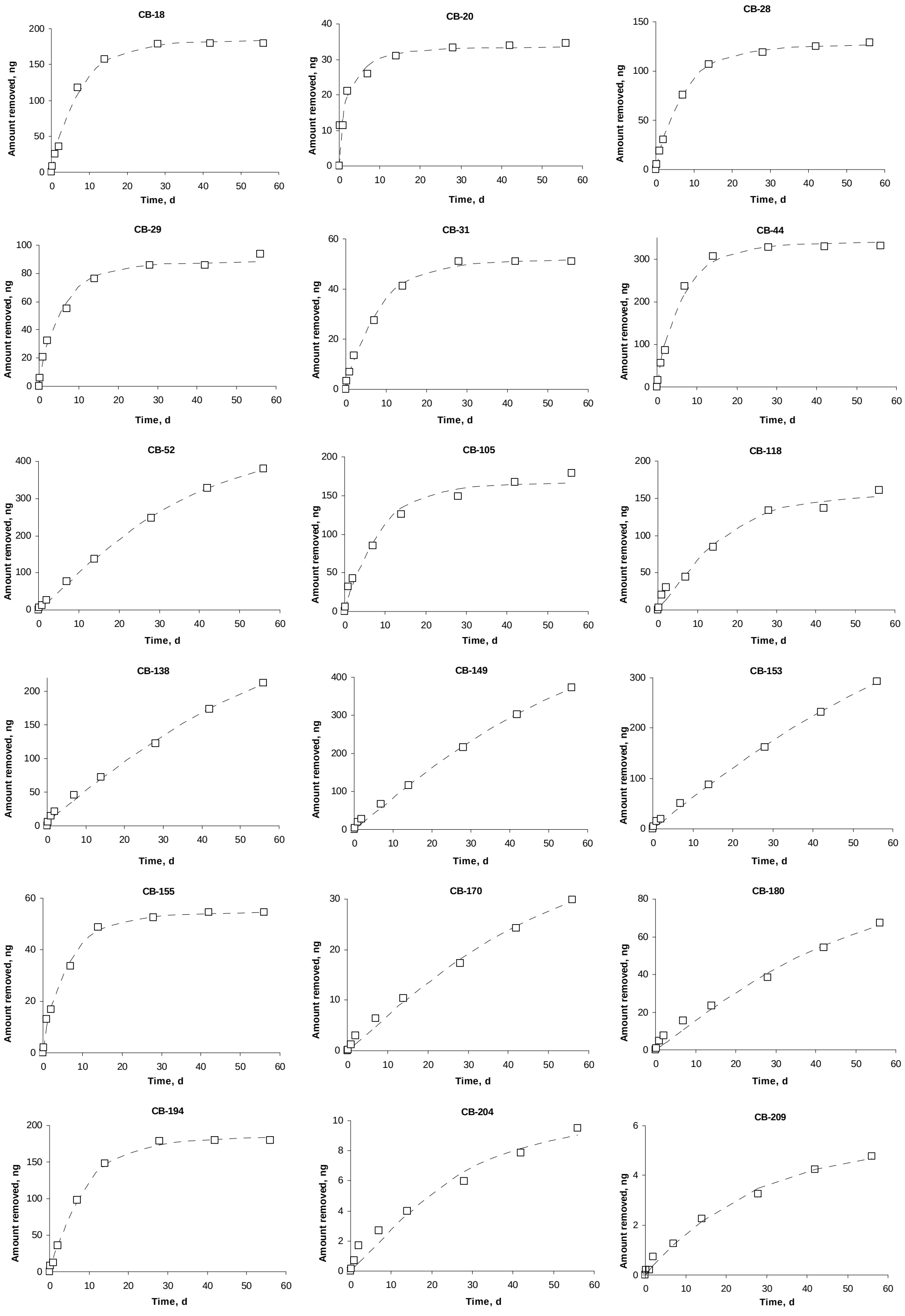

Figure S10. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for untreated sediment with *A. aquaticus*.

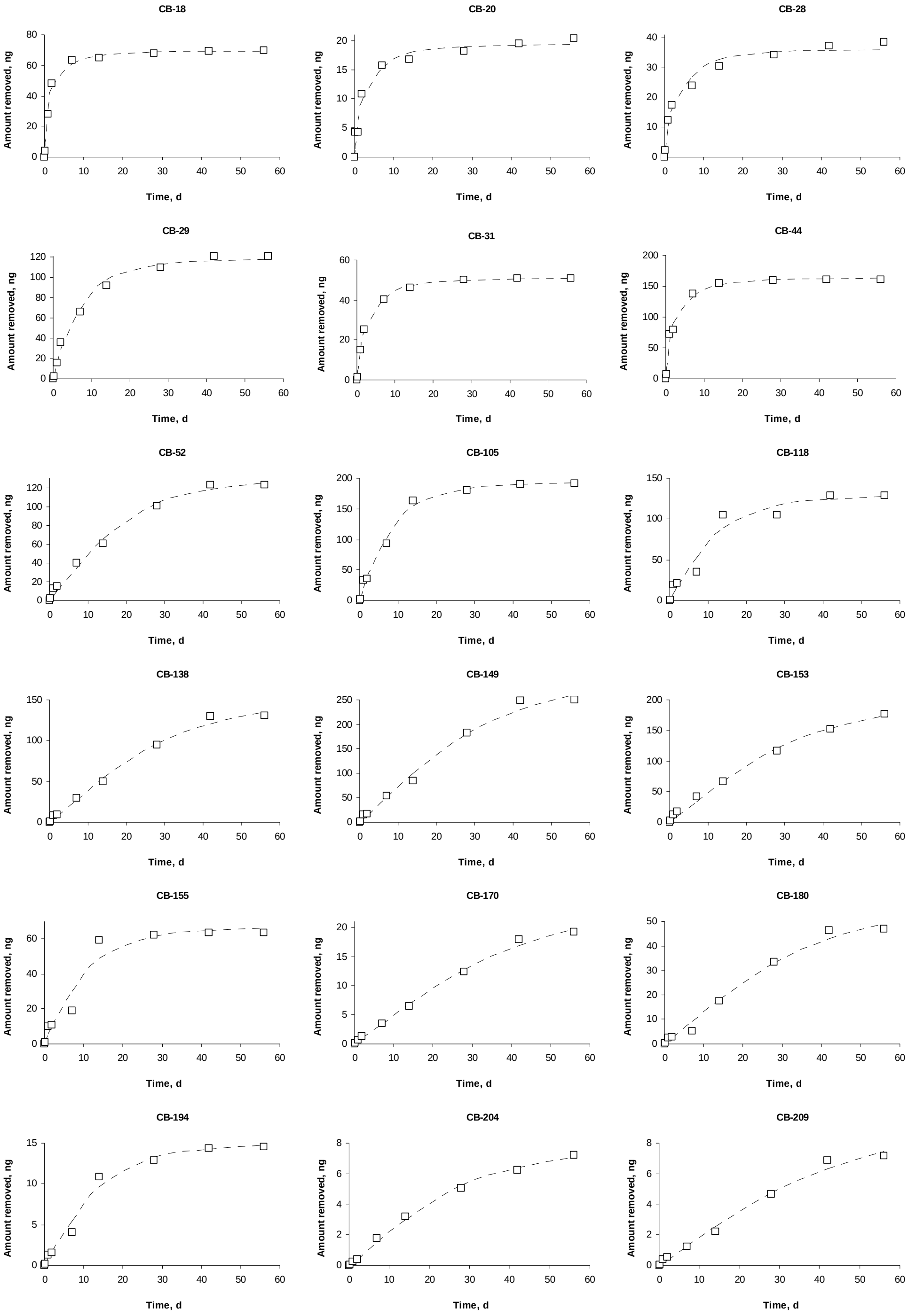

Figure S11. Measured (markers) and modeled (lines) extracted mass of PCBs from overlying water using Empore disks, for untreated sediment with *L. variegatus*.

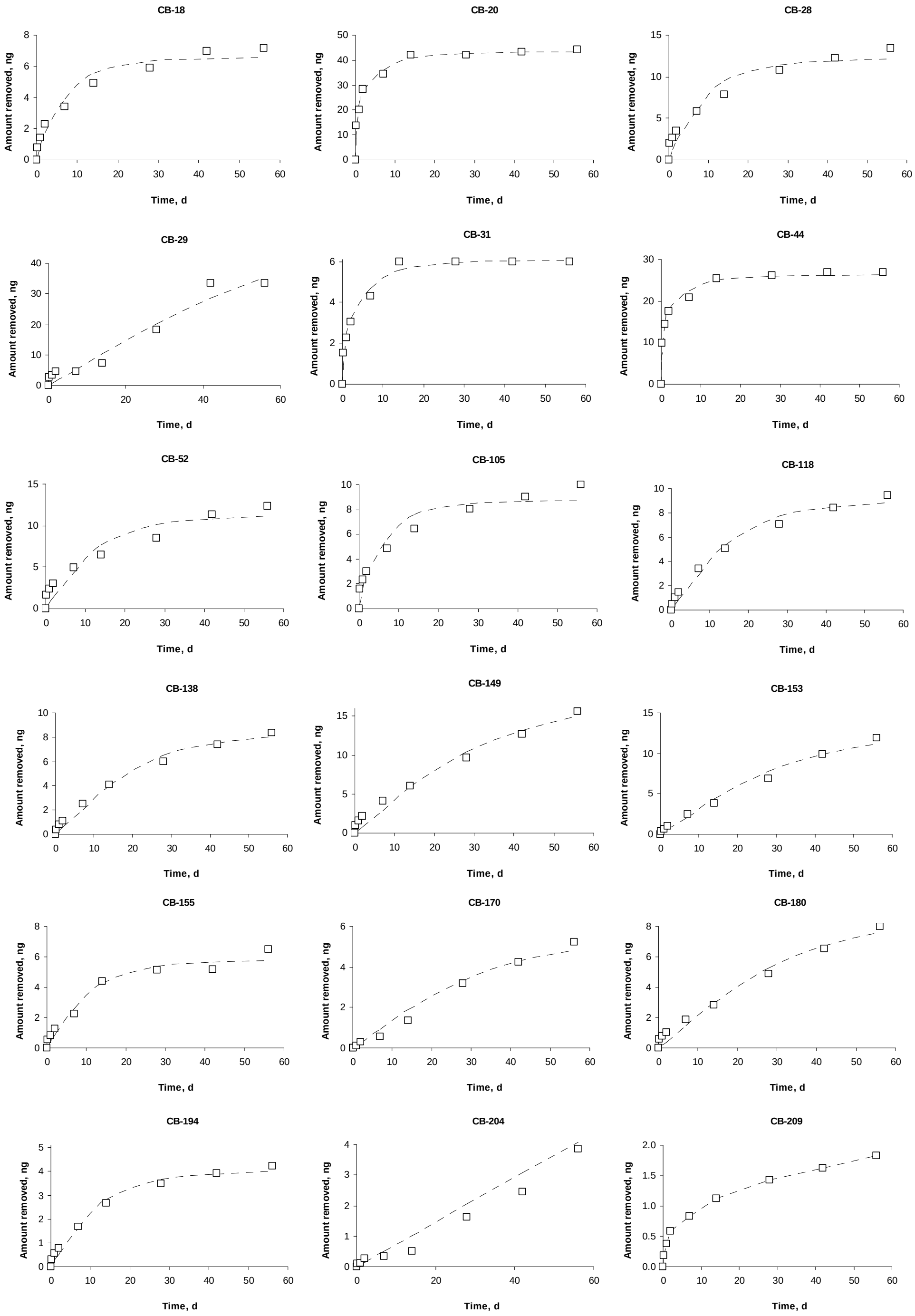

Figure S12. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for non-bioturbated PAC sediment.

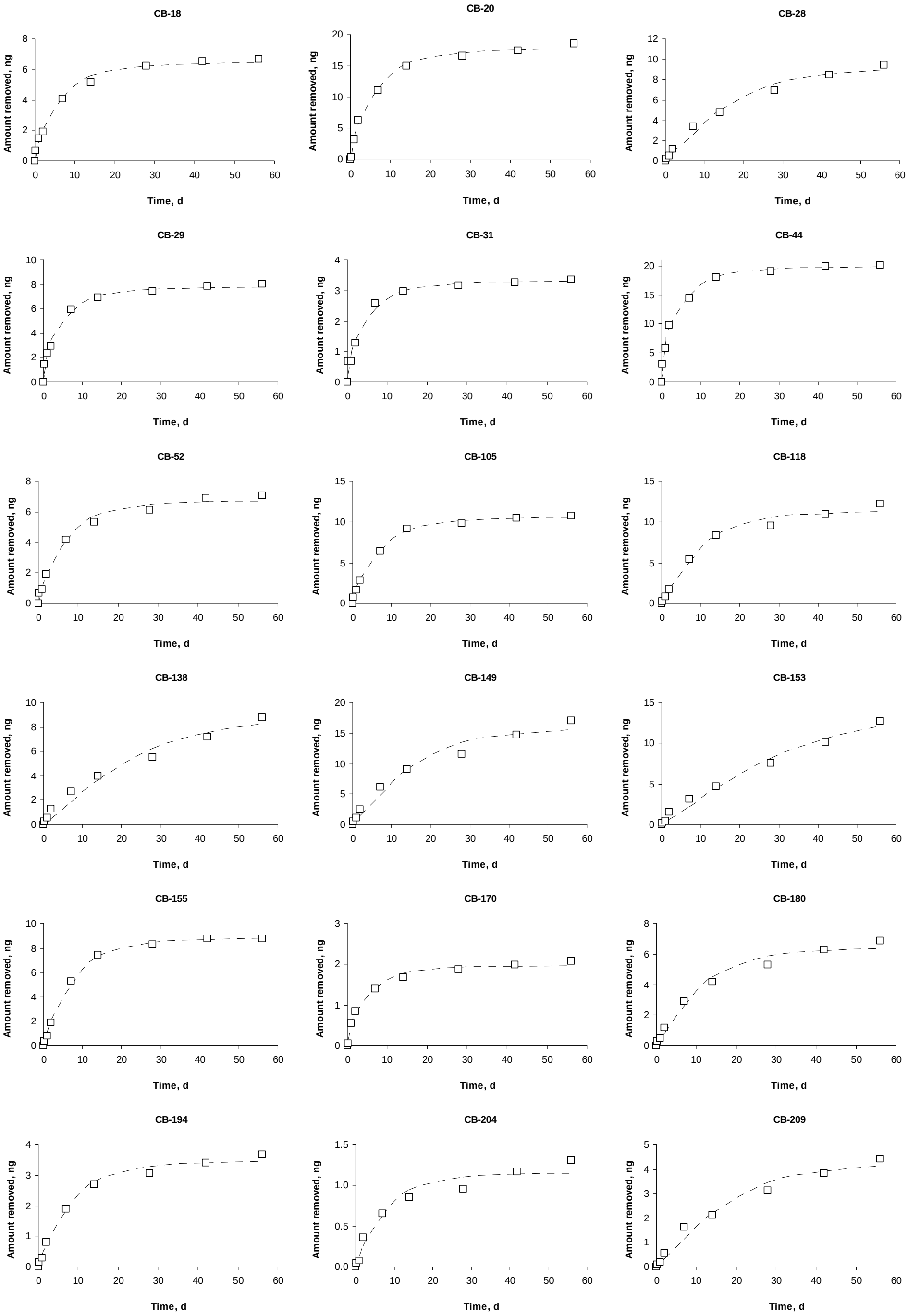

Figure S13. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for PAC sediment with *A. aquaticus*.

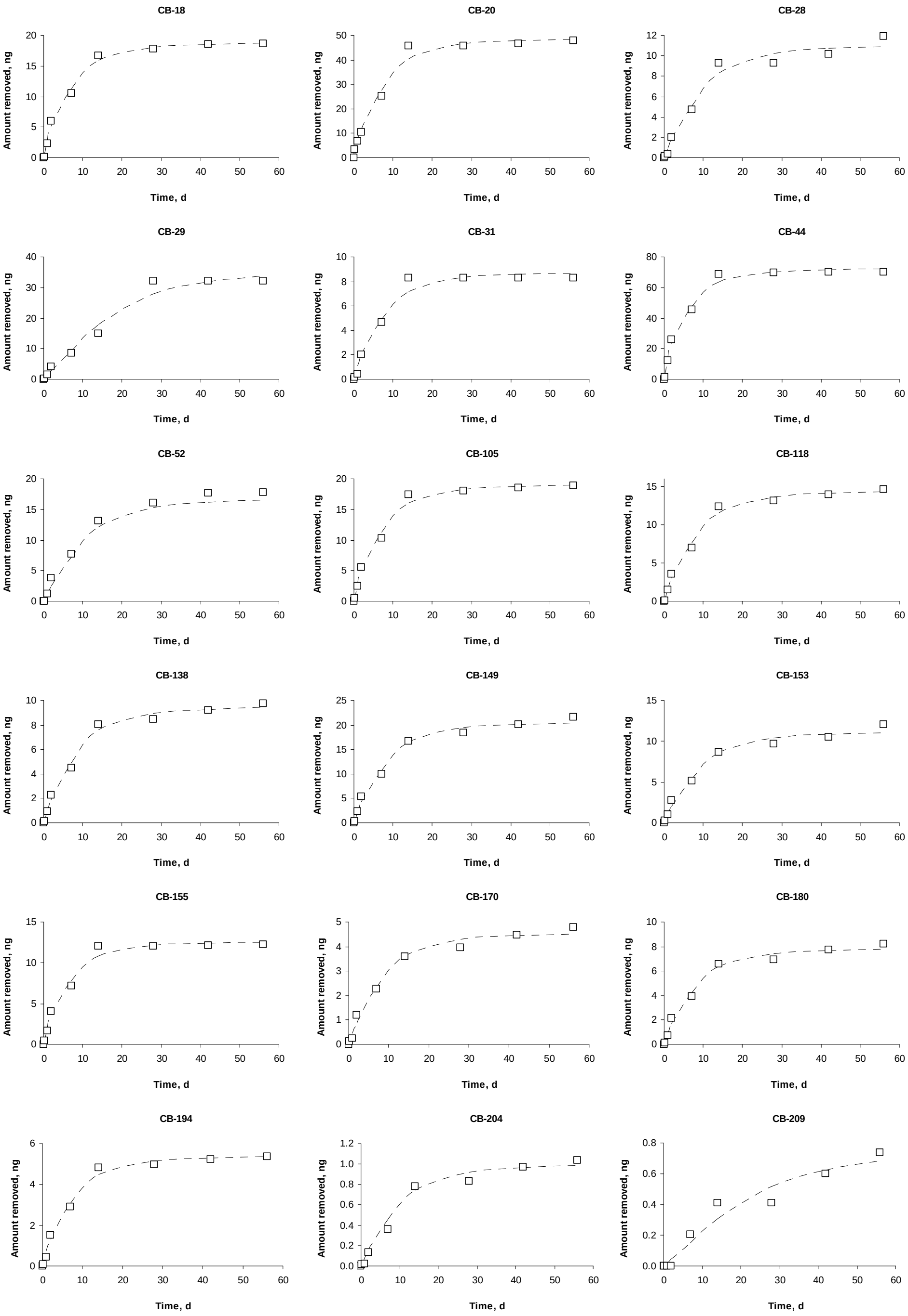

Figure S14 Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for PAC sediment with *L. variegatus*.

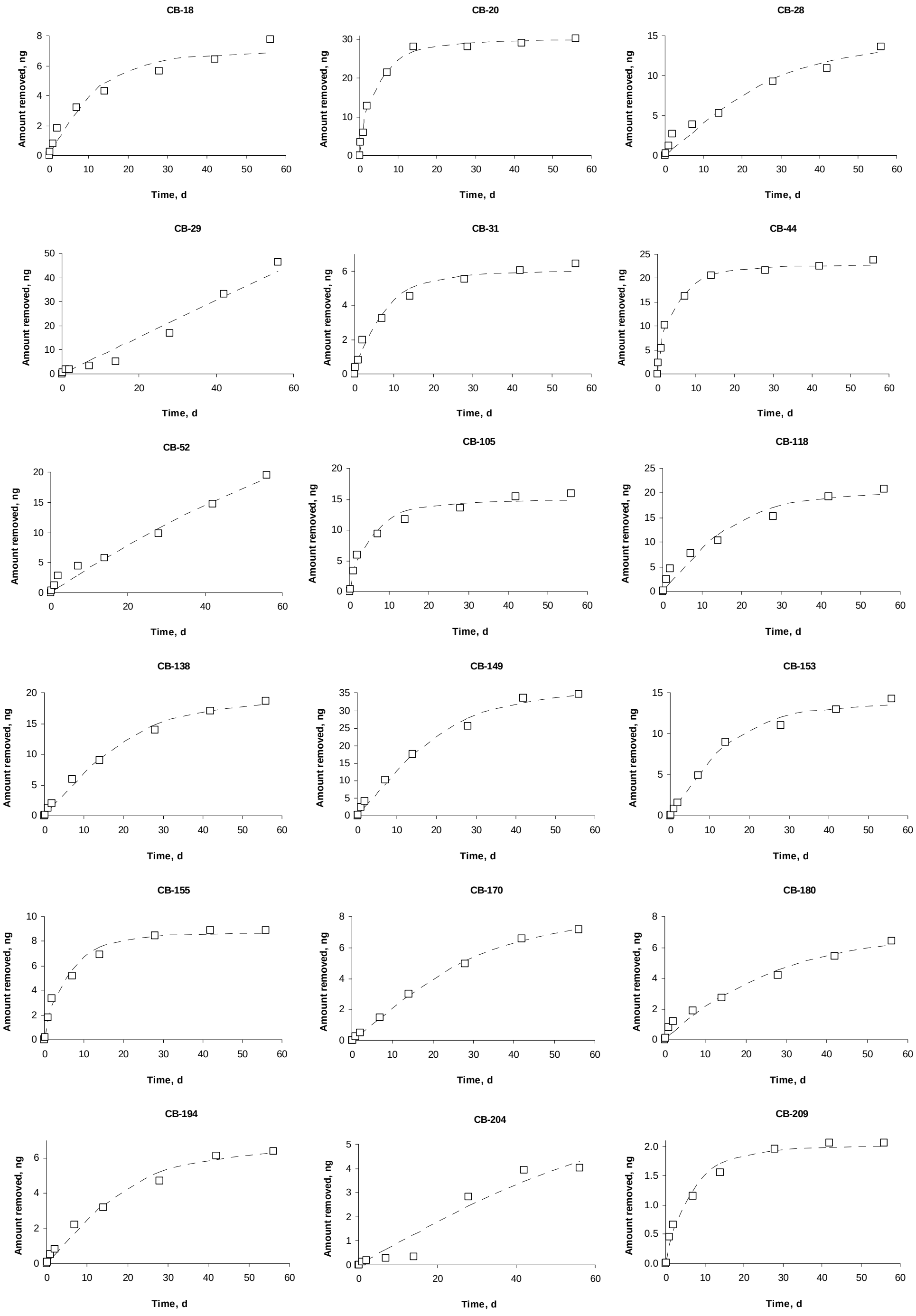

Figure S15. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for non-bioturbated GAC sediment.

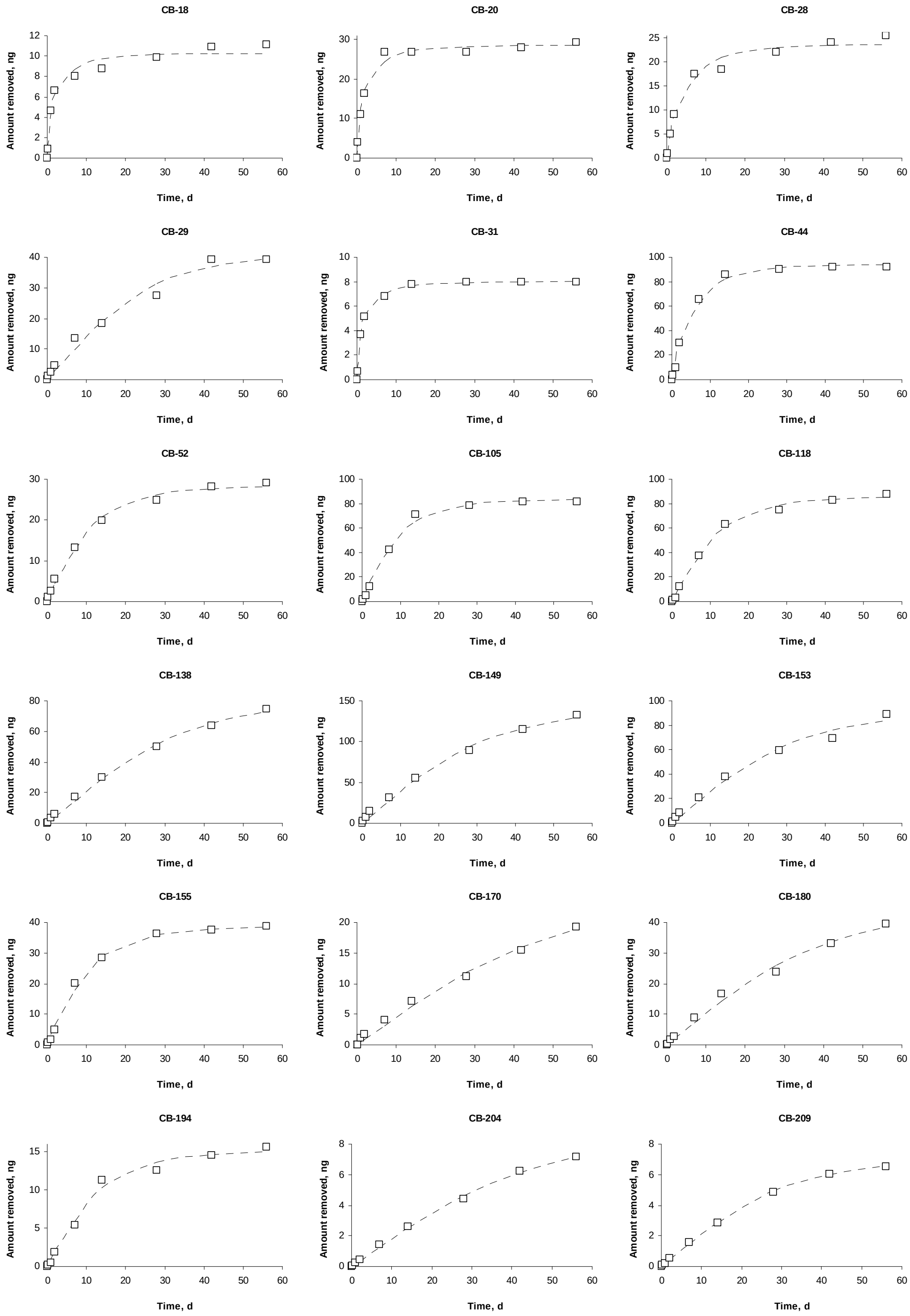

Figure S16. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for GAC sediment with *A. aquaticus*.

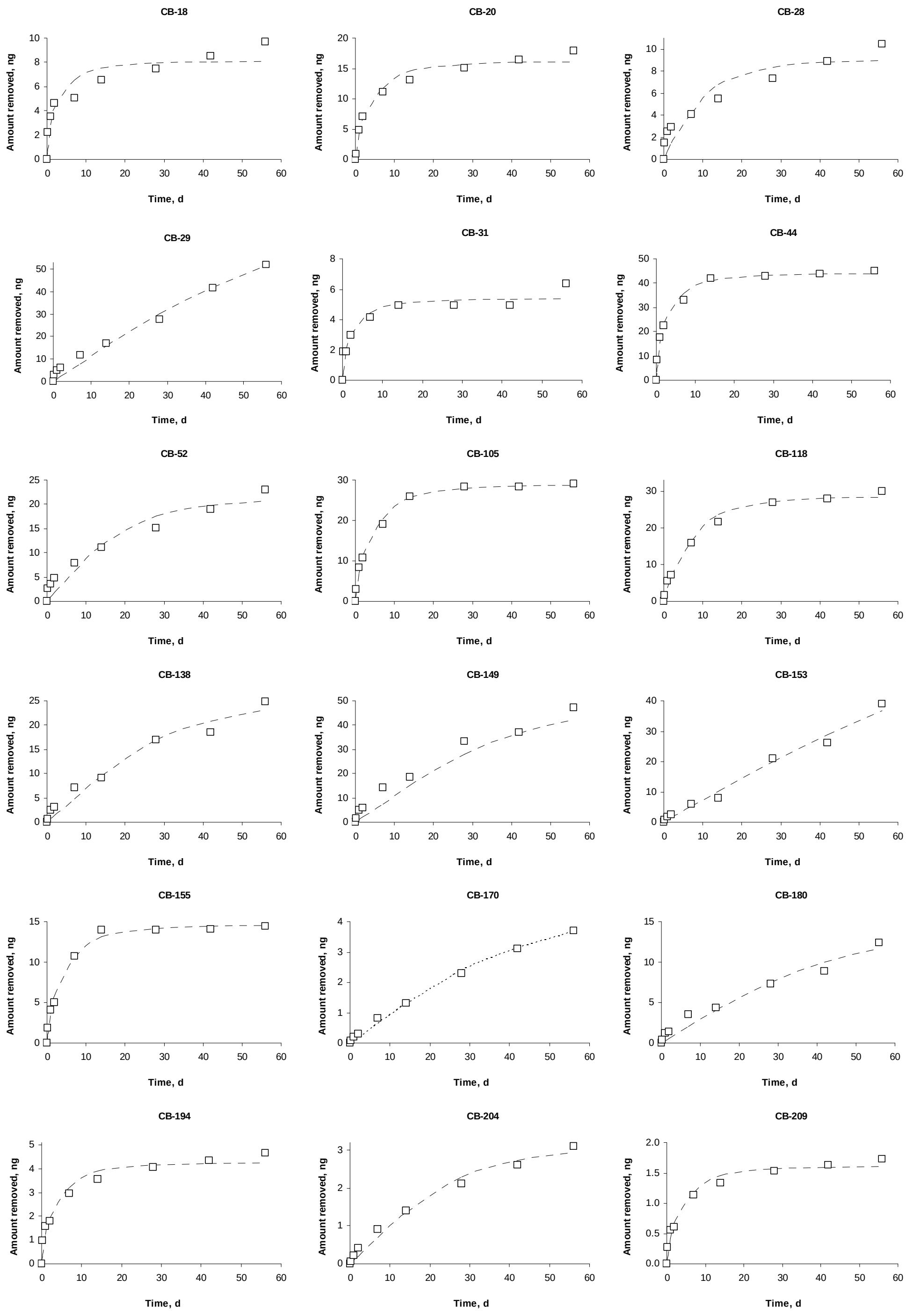

Figure S17. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for GAC sediment with *L. variegatus*.

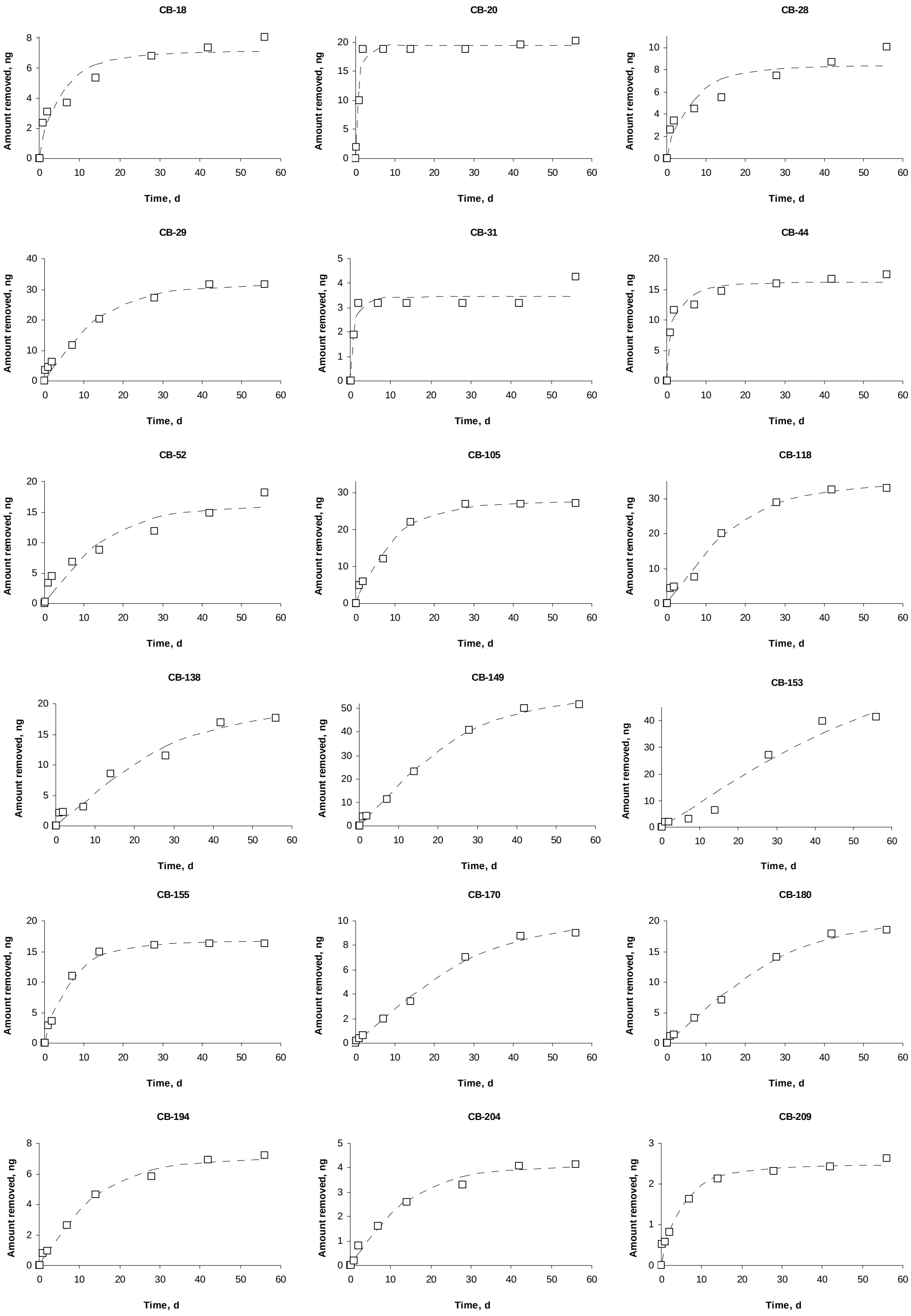

Figure S18. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for non-bioturbated stripped sediment.

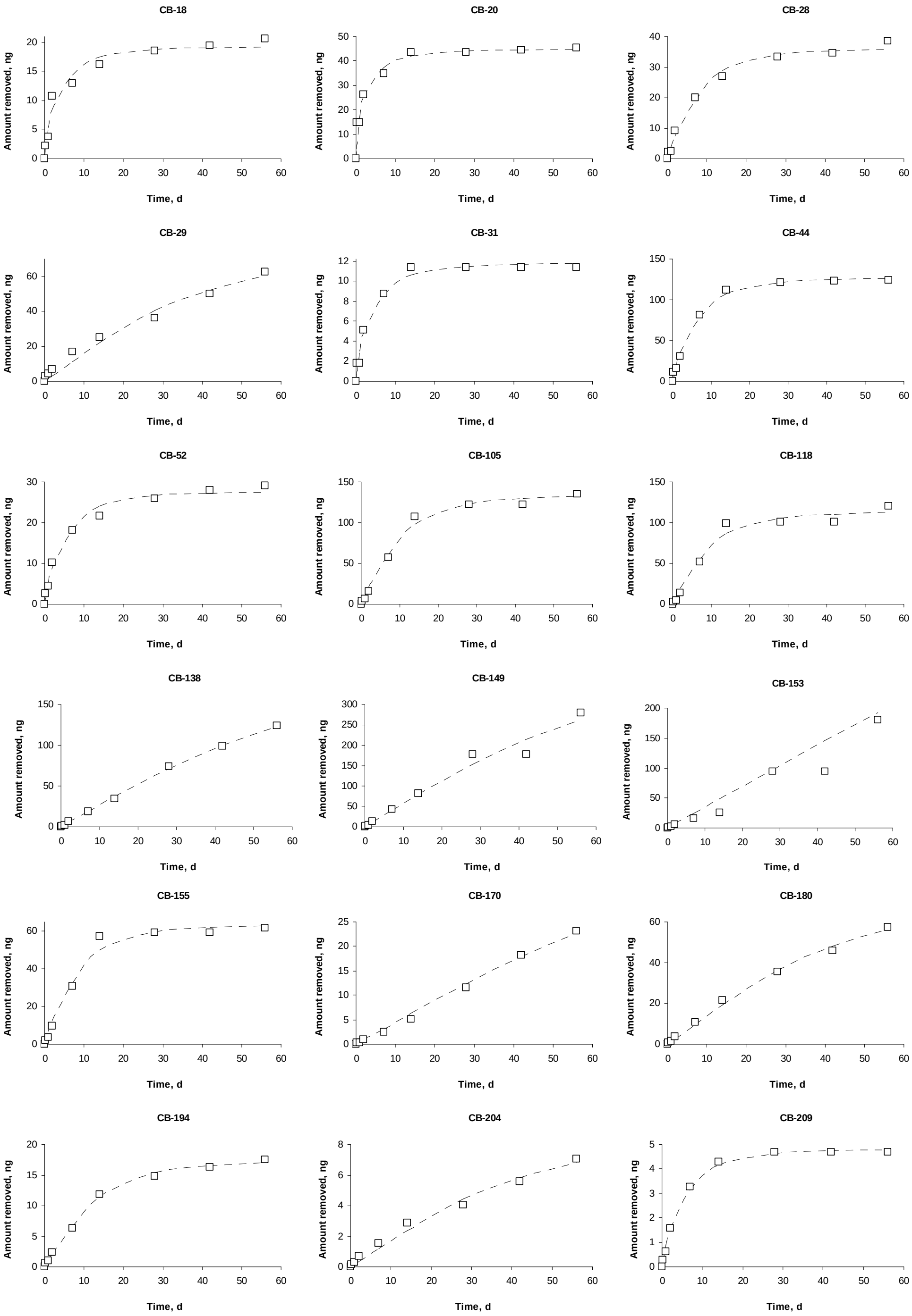

Figure S19. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for stripped sediment with *A. aquaticus*.

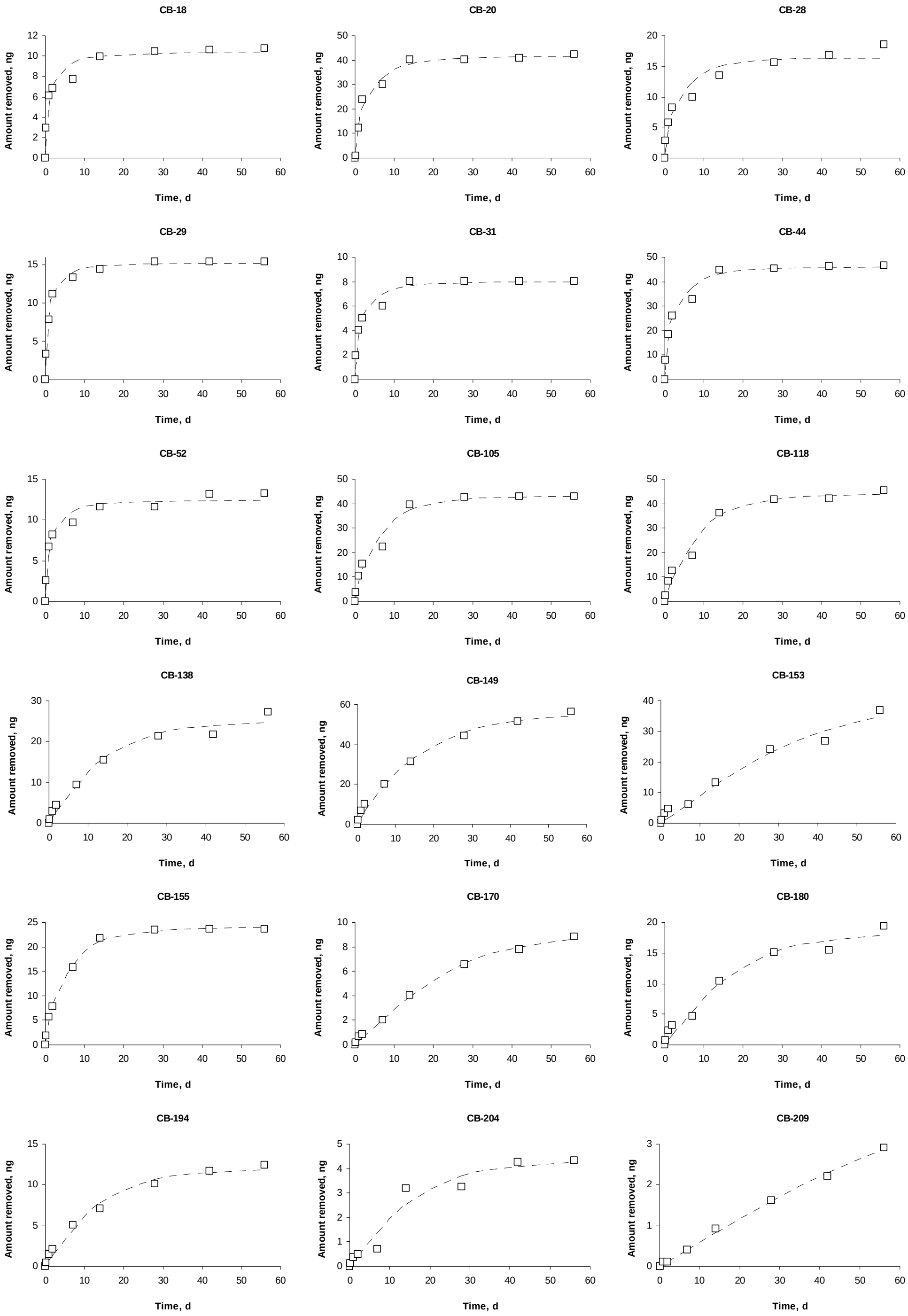

Figure S20. Measured (marker) and modeled (line) extracted mass of PCBs from overlying water using Empore disks, for stripped sediment with *L. variegatus*.

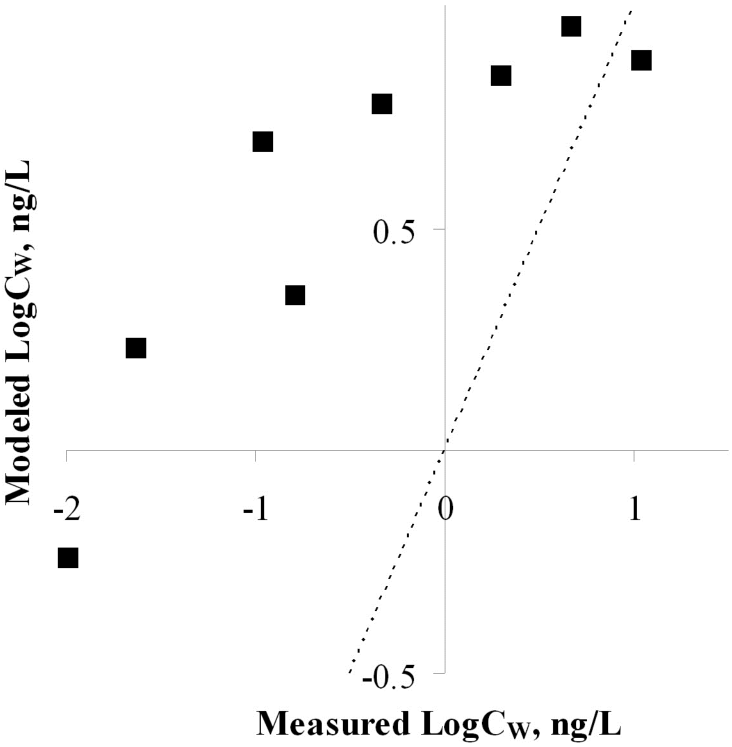

Figure S21. Measured LogC_{PW} vs. modeled LogC_{PW} in untreated Biesbosch sediment for selected PCBs. The dashed line is the 1:1 line.

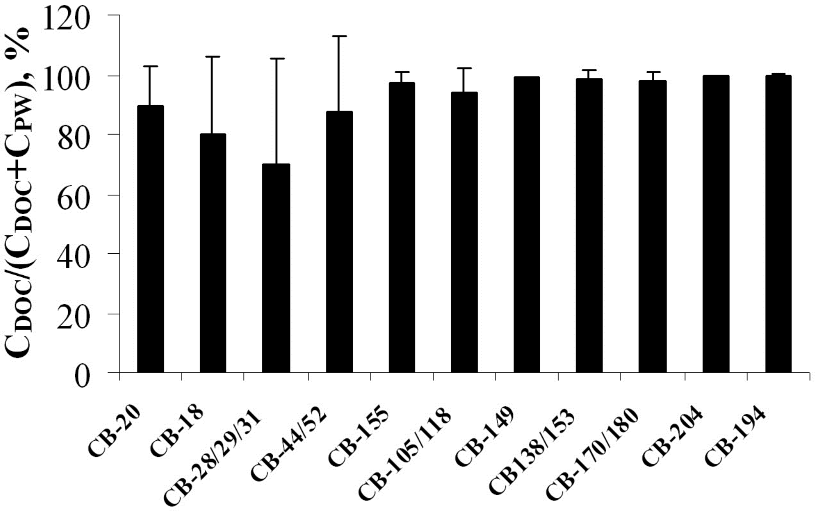

Figure S22. Percentage of PCB sorbed to DOC.

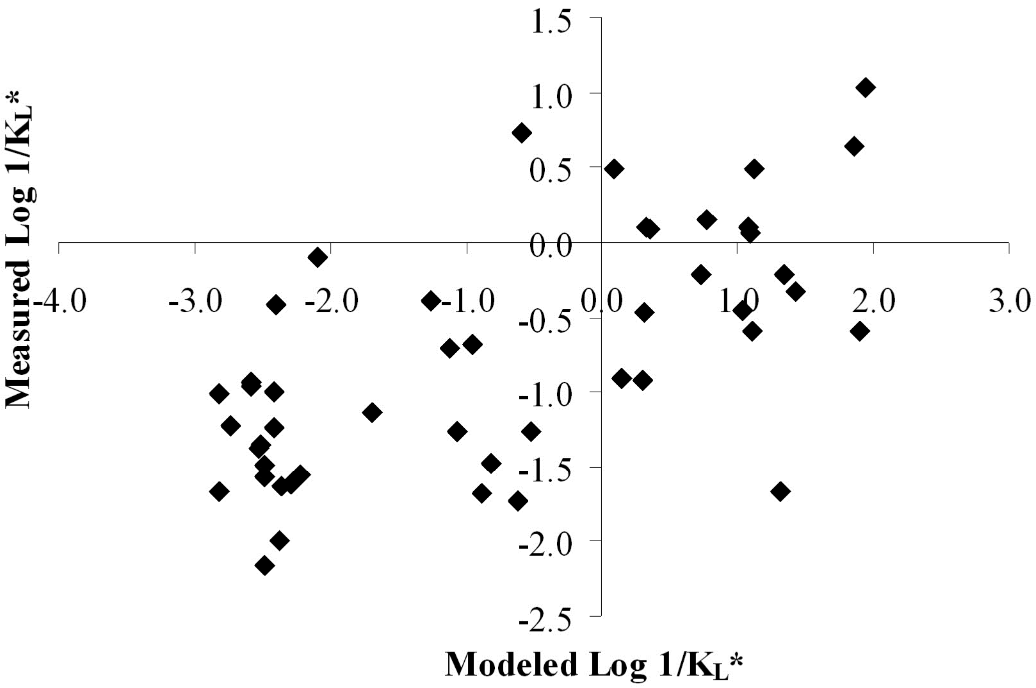

Figure S23. Measured overall transport resistance $1/K_L^*$ vs. modelled $1/K_L^*$ (eq 8 with optimized parameters K_L^{DOC} and λ).

CHAPTER 5

ECOTOXICOLOGICAL EFFECTS OF ACTIVATED CARBON AMENDMENTS ON MACROINVERTEBRATES IN NON-POLLUTED AND POLLUTED SEDIMENTS

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Abstract

Amendment of contaminated sediment with activated carbon (AC) is a remediation technique that has demonstrated its ability to reduce aqueous concentrations of hydrophobic organic compounds. The application of AC, however, requires information on possible ecological effects, especially effects on benthic species. Here, we provide data on effects of AC addition on locomotion and ventilation, sediment avoidance, mortality and growth of two benthic species, *Gammarus pulex* and *Asellus aquaticus*, in clean versus polycyclic aromatic hydrocarbon (PAH) contaminated sediment. Exposure to PAH was quantified using 76 µm polyoxymethylene passive samplers. In clean sediment, AC amendment caused no behavioral effects on both species after 3–5 days exposure; no effect on the survival of *A. Aquaticus*, moderate effect on the survival of *G. pulex* (LC_{50}=3.1% AC) and no effects on growth. In contrast, no survivors were detected in PAH contaminated sediment without AC. Addition of 1% AC, however, resulted in a substantial reduction of water exposure concentration and increased survival of *G. pulex* and *A. aquaticus* by 30 and 100% in 8 days and 5 and 50% after 28 days exposure, respectively. We conclude that AC addition leads to substantial improvement of habitat quality in contaminated sediments and outweighs ecological side effects.

Introduction

Aquatic sediments polluted with hydrophobic organic compounds (HOCs) such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) may become a source of secondary pollution, thus posing a risk to aquatic organisms *(1, 2)*. Traditional remediation methods include dredging of polluted sediment with subsequent deposition of dredged material in sediment storage facilities or *in situ* capping with clean materials. These methods focus on remediation of the total concentration of contaminants and are thus usually laborious, time-consuming, and expensive. Moreover, they may lead to complete physical deterioration of benthic habitats and benthic communities. An *in situ* technique based on addition of carbonaceous materials (CM), like activated carbon (AC), to contaminated sediments has recently been suggested as an alternative to dredging. Many studies have demonstrated high effectiveness of CM application to reduce the bioavailable fractions of HOCs *(3-6)*, the bioaccumulation of HOCs *(3, 6-9)* and thus the toxicity of sediment-bound HOCs *(10, 11)*. Notwithstanding this advantageous effect, however, it has been shown that CM itself may have some negative effects on aquatic organisms *(6, 8, 9, 12)*, raising the question to what extent the addition of AC to sediments can be considered ecologically safe.

In previous studies, many organisms exposed to sediment amended with 2-4% AC showed high survival *(9, 11-14)*. As for growth inhibition, some studies demonstrated no effects of AC addition, or only mild effects, for the clam *Corbicula fluminea* and the mussel *Mytilus edulis (7, 14)*. The greatest effects seem to occur in worms. Growth reductions have been reported for *Neanthes arenaceodentata (9)*, whereas lipid content and egestion rate reductions have been observed in *Lumbriculus variegatus (6, 12)*. These studies have mainly focused on the effects of AC on sediment-dwelling benthic organisms, assuming them to be the most sensitive benthic species, since they are exposed to CM via direct contact and ingestion of CM particles. Many sediment-dwelling organisms, however, acquire their food and oxygen from the overlying water, so the effects of CM on species inhabiting the bottom sediment and overlying water should not be overlooked.

Previous work on effects of AC focused on traditional endpoints such as mortality or growth, but behavioral changes may occur at much lower concentrations than those inhibiting survival and growth, and may reveal negative impacts that would otherwise be missed *(15)*.

Therefore, the objective of this study was to assess possible effects of AC amendment on two contrasting benthic species under laboratory conditions, using a suite of behavioral and traditional endpoints. To our knowledge, no earlier studies addressed the effects of AC on macroinvertebrate behavioral endpoints such as macroinvertebrate locomotion and ventilation. *Gammarus pulex* and *Asellus aquaticus* were selected as test organisms because they (a) are common invertebrates in freshwater habitats, (b) differ in sensitivity to pollutants of various types, and (c) have different species-specific properties in terms of behavior, feeding strategies, and uptake routes, complementing those of previously studied aquatic organisms, and thus providing better representation of benthic communities. Furthermore, these species are an important food source for predatory invertebrates, fish, and waterfowl and thus play an important role in the benthic-pelagic coupling of the food chain transfer of HOCs. Impacts of AC amendment were tested using sediment taken from uncontaminated versus highly contaminated sites. Our whole-sediment AC toxicity tests with clean sediment used locomotion, ventilation, avoidance, growth and mortality as endpoints. Because of the acute toxicity, our tests with contaminated sediment used only mortality as a toxicological endpoint. In the latter tests, aqueous HOC exposure was accurately determined using polyoxymethylene (POM) passive samplers. The required HOC POM-to-water partition coefficients were obtained by extrapolation from coefficients measured at a range of methanol-water mixtures.

Materials and methods

Chemicals and materials

Virgin powdered coal based activated carbon Norit SAE Super was obtained from Norit Activated Carbon (Amersfoort, The Netherlands). To mimic the long-term condition of AC in field applications, AC was washed prior to experiments, as described previously by Jonker et al. *(12)*. Briefly, demineralized water with AC was heated to 100°C for 30 min while stirring. After AC had been allowed to settle, the overlying water was decanted, and the procedure was repeated twice. Finally, AC was dried at 105°C overnight.

Polyoxymethylene (POM) film (76 µm thickness) was purchased from CS Hyde Company, Lake Villa, IL, USA. Following previously published procedures, POM passive samplers were prepared by cutting the film into strips (70 mg each) and cold-extracting them with hexane (30 min) and methanol (3x30 min), after which they were air-dried *(16)*.

Acenaphthene (ACE), acenaphthylene (ACY), 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), ethanol (Merck, Darmstadt, Germany; p.a.), acetonitrile (Lab-Scan, Dublin, Ireland; HPLC grade), calcium chloride (Merck; p.a), sodium azide (Aldrich; 99%), 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 (Barnstead). To prevent photodegradation of PAH, brown or aluminum foil covered glassware was used.

Organisms

Gammarus pulex were collected in the spring and summer of 2009 from a non-contaminated brook (Heelsumse Beek, Heelsum, The Netherlands). *Asellus aquaticus* were collected from a non-contaminated pond (Duno pond, Doorwerth, The Netherlands). Organisms were transferred to the laboratory and kept in white buckets filled with aerated copper-free water in a climate-controlled room at 18°C and 12:12 h light:dark cycle. Organisms were fed on dry poplar leaves which were collected in the field. Prior to the experiments, organisms were acclimatized for a month and sorted to obtain a group of organisms with a narrow body size range (4–7 mm).

Sediments

Uncontaminated freshwater sediment was sampled at Station Veenkampen, Wageningen, The Netherlands, using a sampling bucket. The natively contaminated sediment was taken from a previously stored batch, which had originally been dredged from Petroleum Harbor (PH), Amsterdam, The Netherlands. An overview of the concentrations of PAHs, PCBs, and metals is provided as Supporting Information (Table S1 and S2). The sediments were passed over 2 mm sieves, homogenized and amended with AC to obtain AC concentrations of 0, 1, 3, 6, 15, and 30% (d.w.). Subsequently, sediments were homogenized on a roller bank for 48h and stored at 4° C in the dark for 2 months until use.

Toxicity tests

Motility patterns measured with Multispecies Freshwater Biomonitor (MFB). Movements were measured using a Multispecies Freshwater Biomonitor (MFB), following previously published procedures *(15, 17)*. The MFB measures different types of behavior (e.g. locomotion, ventilation, feeding) of aquatic species by recording changes in a high frequency alternating current caused by the movements of organisms in the MFB chambers. Locomotion and ventilation generate currents of different frequencies, viz. <2.5 Hz and 2.5-8 Hz, respectively. Effects of AC addition on *G. pulex* and *A. aquaticus* in Veenkampen sediment were tested using two exposure times: 1 and 5 days. Prior to the experiment, MFB test chambers were placed in PVC aquaria (15x15 cm) filled with aerated Cu-free water. Beakers (50 mL) were filled with a 1 cm layer of sediment and a 3 cm layer of Cu-free water, after which the systems were left for 24 h to allow the sediment to settle.

In the 1-d exposure experiments, a single organism was placed in a system containing "clean" AC-free sediment, and left there for 24 h, after which the organism was transferred to an MFB test chamber and its behavior was recorded over a 24-h period (control). The same individual organism was then placed in a system containing AC-enriched sediment for 24-h exposure, after which its behavior was recorded in the same MFB chamber for 24 h. The experiment was replicated at n=20, using 20 individuals in 20 MFB chambers simultaneously.

A slightly different procedure was followed for 5-d exposure. First, one individual organism was placed in a system with AC-free sediment for 5 d, after which the organism was transferred to an MFB test chamber and its behavior was recorded for 24 h. The organism was then transferred to a clean aerated system with food consisting of autumn-shed poplar leaves. After a 24-h recovery period, the organism was placed in a system containing AC-enriched sediment, and after 5 d of exposure its behavior was recorded in the same MFB chamber for 24 h. This procedure was replicated using 20 individuals in 20 chambers simultaneously. For positive controls for this methodology we refer to our previous work *(15, 18)*.

Sediment avoidance. The sediment avoidance experiment followed procedures previously published by our laboratory *(19)*. Plastic boxes (20x10x10 cm) were divided into two compartments using a plastic barrier. One compartment was filled with 2 cm of Veenkampen sediment with 0% AC, the other with AC-enriched Veenkampen sediment. The control contained sediment with 0% AC in both compartments. Afterwards, copper-free water was carefully added to a level of 2 cm and the systems were left in a climate-controlled room (18°C and 12:12 h light:dark cycle) for 24 h to allow the sediment to settle. Subsequently, the plastic barrier was carefully removed and 20 individuals were gently added to the water, so that they were free to inhabit their preferred sediment. After 72 h the temporary barrier was replaced, and the number of individuals in each compartment was recorded.

Survival and growth. Survival of *G. pulex* and *A. aquaticus* exposed to AC-enriched clean Veenkampen sediment was tested by adding 10 individuals with a length in the range of 4-7 mm to beakers with 50 mL wet sediment and 200 mL copper-free water. The beakers were aerated and organisms were fed on dry poplar leaves over a 28 d period. The experiment was performed in quadruplicate in a climate-controlled room (18°C and 12:12 h light:dark cycle). Survival was determined by gently transferring the beaker content to a tray and counting living organisms. The length of the survivors was determined using a binocular microscope (magnification 10x).

The same procedure was followed for the contaminated PH sediment, except that the test duration for this supposedly toxic sediment was not fixed a priori, and that a representative portion of this sediment was used to determine aqueous PAH exposure concentrations, as described below. Test duration was designed at 28 d, or earlier in case of 100% mortality in the acutely toxic controls. Since this situation already arose after 7 d, the assay was terminated after 7 d of exposure. To enable comparison with the 28-d whole-sediment assay with clean sediment, the quadruplicate assay was repeated for the most relevant treatments with 0 and 3% AC.

Assessment of PAH exposure concentration in the PH sediment bioassay. PAH aqueous concentrations were measured using POM passive samplers. To this end, representative subsamples of 0.5 g (d.w.) of the AC-treated sediments (range 0, 1, 3, 6, 15, and 30% AC) were added to 50 mL bottles. The bottles were filled with the water overlying the original AC-treated sediment, now supplemented with 25 mg/L sodium azide (biocide), 0.01 M calcium chloride and one POM sampler, leaving approximately 10 mL of headspace. Bottles were shaken horizontally (100 rpm) at 18°C for 28 d. POM strips in the 50-80 µm range have been shown to reach equilibrium within this time period *(20)*. After equilibration, POM strips were dried with a tissue and Soxhlet-extracted. Aqueous PAH concentrations were calculated from concentrations in POM and POM-water equilibrium partition coefficients (K_{POM}). K_{POM} values for PAH sorption to 76 µm POM are not known yet, so we measured them for the PAHs dominating the mixture (PHE, ANT, FLU, and PYR), using a previously published co-solvent method *(21)*. For details, the reader is referred to the Supporting Information (Table S3, Figure S1).

Factors that might interfere with AC or PAH toxicity could be eliminated as follows. Oxygen, pH, and ammonia were monitored on a weekly basis. Oxygen was always higher than 90%, due to the aeration of the water in the beakers, and thus could not explain the effects in the assays. Average pH was 7.7 ± 0.5. The pH fluctuations are unlikely to have caused effects either, because the fluctuations were limited and because *G. pulex* and *A. aquaticus* have been found to tolerate alkaline environments very well *(22)*. Levels of unionized ammonia were 0.33 ± 0.51 mg/L regardless of AC dose, whereas 24-h LC_{50} values reported for *G. pulex* and *A. aquaticus* are 4.3 and 9.5 mg/L NH_3-N, respectively *(23, 24)*. The AC (as received and washed) was analyzed for total (*aqua regia* extractable) concentrations of heavy metals *(25, 26)*. Concentrations of Cr, Cu, Ni, Zn, Pb, As in AC were such that even at 30% AC, the contribution of AC bound metals was less than 5% of the total concentration (Supporting Information, Table S2). This implies that metals did not interfere with treatment effects. A contribution to control mortality can also be considered negligible for two reasons. First, sulfide levels on a molar basis (169 mmol/kg) by far exceeded total metal levels on a molar basis (12 mmol/kg), thus keeping metals fully precipitated as metal sulfides *(27)*. Consequently, they were unavailable for uptake by invertebrates. Second, any remaining exposure to sediment-bound metals would be limited because both *G. pulex* and *A. aquaticus* primarily relate to sediment surface and overlying water. ΣPCB concentrations (170 µg/kg) were a factor four lower than probable effect concentrations of 670 µg/kg as reported by MacDonald et al. *(28)*.

Chemical analysis

Representative subsamples of the sediment (1 g d.w.) were extracted with Accelerated Solvent Extraction (ASE 350, Dionex, USA) using 60 mL cyclohexane/acetone (1:1). Extracts were concentrated to 1 mL, exchanged to cyclohexane, and cleaned up over Al_2O_3 columns. The eluates were reduced to 1 mL, exchanged to acetonitrile and rereduced to 1 mL, after which 2-methylchrysene was added as an internal standard. POM samplers were Soxhlet-extracted with 70 mL of methanol for 3 h *(16)*. Clean-up and analysis were identical to that of the sediment samples. Extracted PAHs were quantified using a Hewlett-Packard model 1100 HPLC. After injection of 20 µl of sample, compounds were separated on a 4.6 mm Vydac guard and analytical reverse phase C_{18} column (201GD54T and 201TP54, respectively) which were thermostatically controlled at 22 °C. The mobile phase consisted of methanol/water. Detection was done using an HP 1100 MFD detector operating in the multi-emission wavelength mode. Numerous experimental and analytical blanks were used. Average clean-up recoveries ranged from 71 ± 5.3% (PHE) to 95 ± 6.3% (InP) (n=3). All data were corrected for the resulting values.

Total organic carbon and native black carbon contents of sediments were determined in triplicate using the chemothermal oxidation method described by Gustafsson et al. *(29)*. Organic carbon was removed by thermal oxidation at 375 °C, inorganic carbon by *in situ* acidification. The samples were analyzed using an EA 1110 CHN elemental analyzer (CE Instruments, Milan, Italy). Quality assurance included several procedure blanks and reference samples, following previously published procedures *(30, 31)*.

Data analysis

The significance of differences between sediment black carbon contents was tested using unpaired t-tests. In the MFB experiments, mean locomotion and ventilation were calculated for each individual. Because data were not normally distributed (Kolmogorov-Smirnov test, $p < 0.05$), Kruskal-Wallis H tests were applied to test for significant differences between observed behavioral patterns and AC concentrations. The null hypothesis (no difference between groups) was rejected when significance was lower than 0.05. Results of the survival, growth, and habitat choice experiments were analyzed using one-way ANOVA. All analyses were performed with PASW Statistics 17.0 (SPSS, Chicago, IL, USA). Dose-response data were modeled using the (best fitting) four-parameter logistic model available in SigmaPlot 8.0 (Systac Software Inc, San Jose, California, USA), which was also used to calculate LC_{50} and EC_{50}.

Results and discussion

Sediment and AC characteristics

Relative errors in replicated PAH concentration measurements were small (1.2 – 4.4% and 2.1 – 8.6% for PH and Veenkampen sediment, respectively, Table S1), confirming the quality of the analytical methods used. Total PAH concentration (ΣPAH) in the PH sediment was 1107 mg/kg, which classifies this sediment as heavily polluted according to Dutch standards *(32, 33)*. PAH concentration ratios ANT/178, FLU/(FLU + PYR), BaA/228 and InP/ (InP + BghiP) were 0.55, 0.42, 0.21, and 0.56, respectively, which would identify the PAH contamination as of pyrogenic origin *(34)*. Total PAH concentration in the 'clean' Veenkampen sediment was 4.7 mg/kg, which is about a factor 8 below toxicity thresholds (Table S1). PAH concentration ratios ANT/178, FLU/(FLU + PYR), BaA/228 and InP/ (InP + BghiP) were 0.0015, 0.48, 0.0004, and 0.42, respectively, which would identify the background PAHs as of petrogenic / pyrogenic origin. Both clean and contaminated sediments had a native black carbon (BC) content of about 2% (Table S1). These BC levels were not statistically different from each other (unpaired t-test, $t_4 = -2.12$, $p = 0.548$).

Toxicity tests

Motility patterns measured with the Multispecies Freshwater Biomonitor (MFB). These experiments tested whether the locomotion and ventilation of the species were affected by sediment AC levels. The validity of these tests was assessed in our earlier work, showing negative effects of pharmaceuticals on locomotion and ventilation of *G. pulex (35)*. The current study used the MFB to characterize two types of behavior of *G. pulex*. Lower frequencies (0-2.5 Hz) corresponded to locomotion of the species, i.e. walking and swimming. After 1 d of exposure to AC containing sediment, the median time spent on locomotion behavior by individuals in all treatment conditions proved variable, ranging from 6 to 45% (Figure S2a). This variation in locomotion has been observed before and might be explained by individual variability in terms of factors such as specimen characteristics (gender and body size), feeding state, and presence of contaminants *(15, 36)*. The variation in locomotion was, however, independent of the AC concentration in the sediment (Kruskal-Wallis, $\chi_2(5) = 7.488$, $p = 0.187$). Similarly, no difference between AC treatments was observed at the higher frequencies of 2.5-8 Hz, corresponding to ventilation in amphipods (Kruskal-Wallis, $\chi_2(5) = 7.862$, p = 0.164). *A. aquaticus* demonstrated similar behavioral patterns (Figure S2b), although the time it spent on locomotion was lower than for *G. pulex;* only 3-4% AC amendment did not affect the activity of *A. aquaticus* (Kruskal-Wallis, $\chi_2(5) = 4.844$, $p = 0.435$ for locomotion, $\chi_2(5) = 3.572$, $p = 0.613$ for ventilation). Even after an extended (semi-chronic) exposure of 5 d, there was no difference in locomotion or ventilation between AC treatments, neither for *G. pulex* (Kruskal-Wallis, $\chi_2(5) = 7.382$, $p = 0.194$ for locomotion, $\chi_2(5) = 7.827$, $p = 0.166$ for ventilation) nor for *A. aquaticus (*Kruskal-Wallis, $\chi_2(5) = 2.720$, $p = 0.743$ for locomotion, $\chi_2(5) = 2.821$, $p = 0.728$ for ventilation) (Figure 1).

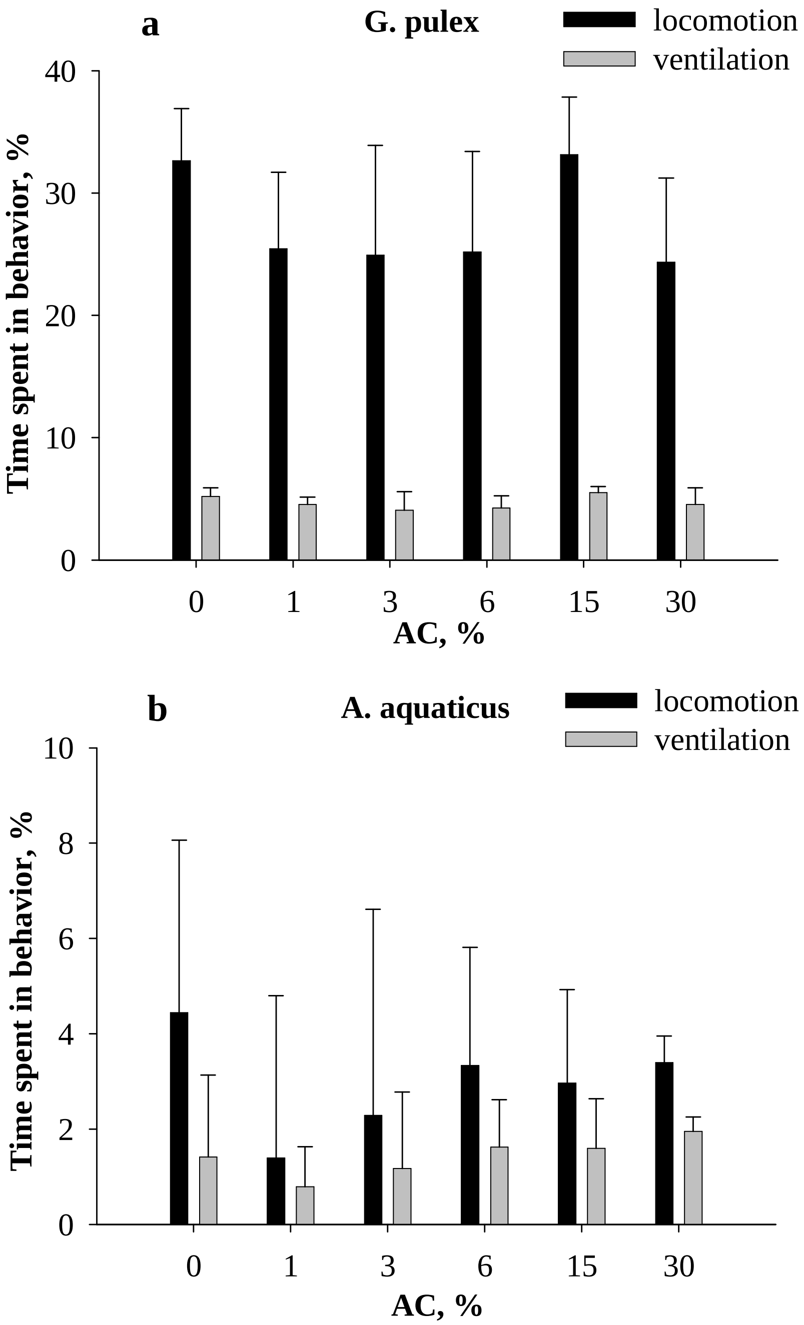

Figure 1. Percentage of time spent on locomotion and ventilation activity (median, 75th percentile, n=20) after 5-d exposure of (a) *G. pulex* and (b) *A. aquaticus* to non-contaminated sediment enriched with AC.

Sediment avoidance. Our whole-sediment avoidance experiments aimed to test whether invertebrate species would avoid or prefer control/non-contaminated sediments containing AC, as a function of AC dose. The validity of the test setup was assessed in our earlier work *(19)*.

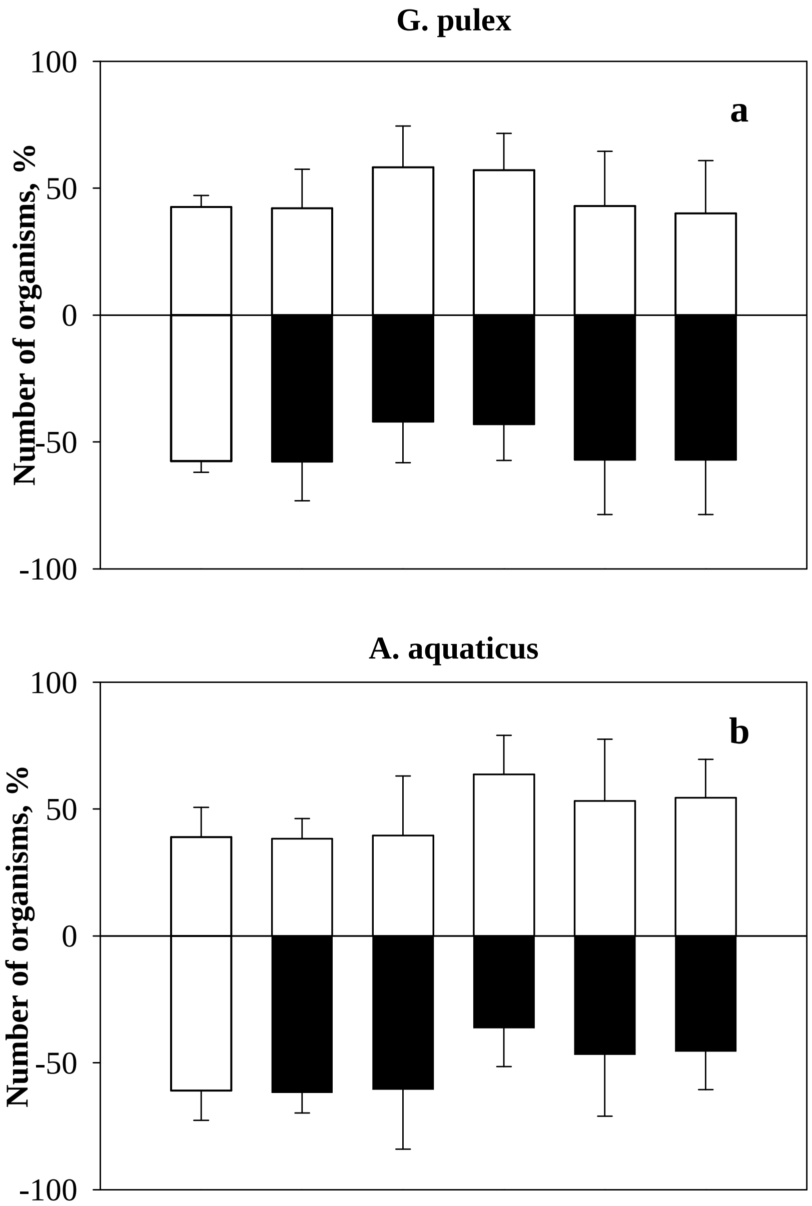

Figure 2. Number (SD, n=4) of *G. pulex* (a) and *A. aquaticus* (b) retrieved from each AC treatment after 3 d of exposure to non-contaminated sediment. Upper bars represent individuals recovered from sediment containing 0% d.w. AC; lower bars (black) represent individuals from AC-containing sediment (from left to right 0, 1, 3, 6, 15, and 30% d.w. AC).

In the current study, *G. pulex* and *A. aquaticus* individuals distributed themselves randomly over the aquaria containing AC-free sediment in both compartments, i.e. the control systems, (open bars in Figure 2), as well as in the aquaria with AC. Consequently, they did not demonstrate any preference for, or avoidance of, AC-enriched sediment up to AC levels as high as 30% (one-way ANOVA, F (5, 18) = 0.984, p = 0.454 for *G. pulex* and F (5, 18) = 1.504, p = 0.238 for *A. aquaticus*). The results of this experiment are in general agreement with those obtained by Jonker et al. *(12)* who did not observe clear avoidance of AC sediment by *Asellus aquaticus* or *Corophium volutator* either, as indicated by inconsistent dose–response relationships.

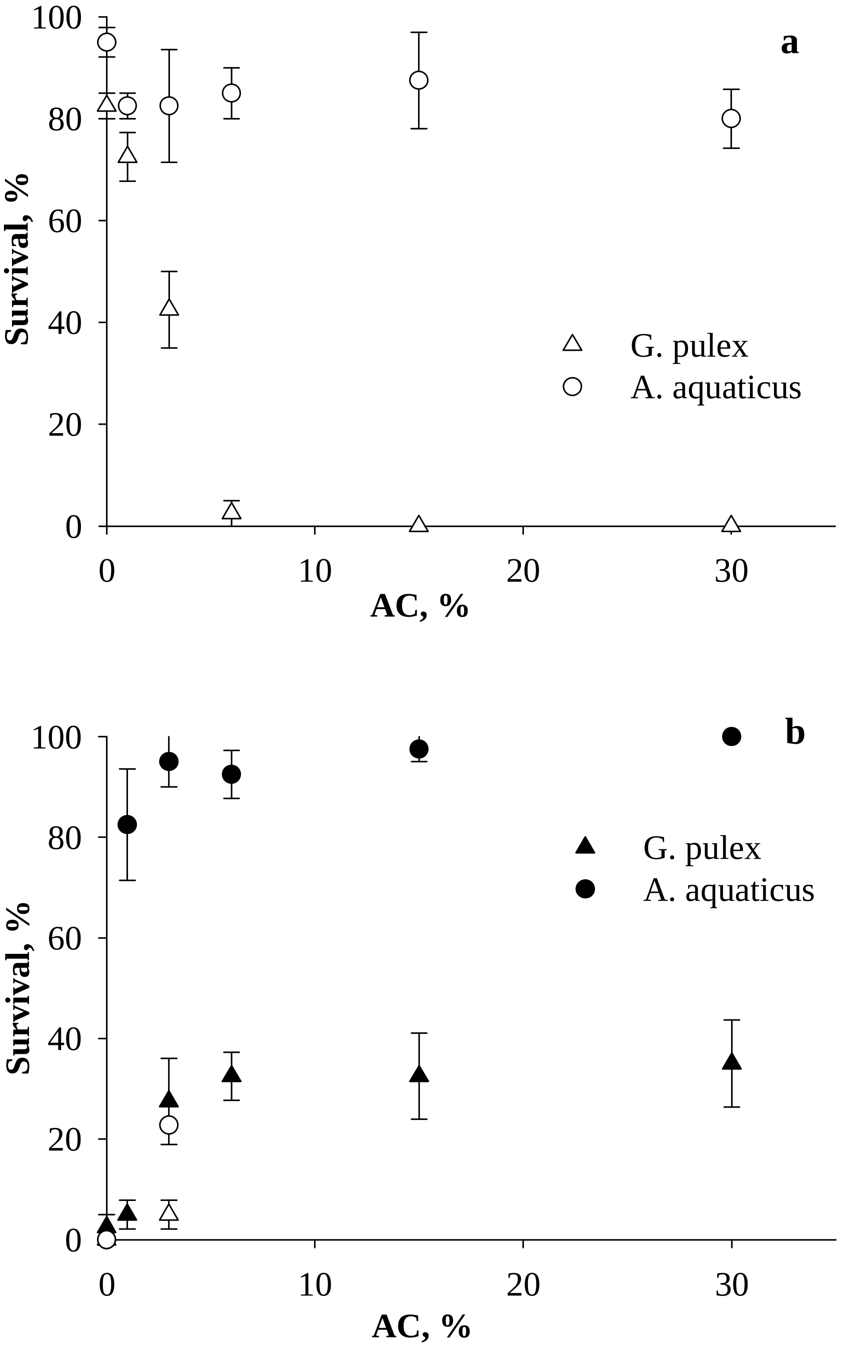

Figure 3. Survival (SE, n=4) of *G. pulex* (triangles) and *A. aquaticus* (circles) after (a) 28-d exposure to non-contaminated Veenkampen sediment and (b) 8-d (black symbols) and 28-d (open symbols) exposure to contaminated sediment, as a function of AC level.

Survival and growth. The whole-sediment 28-d toxicity tests with *G. pulex* in uncontaminated Veenkampen sediment revealed decreased survival at higher AC levels (Figure 3a). No survivors were found in systems with sediment enriched with 6, 15, and 30% AC. The lethal concentration for 50% of the test population (LC_{50}) was determined to be 3.07% (SD 0.64). Possible explanations for these AC effects include dilution of the nutritional quality of sediments, or possible adsorption of essential nutrients *(6, 12)*. In contrast to *G. pulex*, *A. aquaticus* survived at all AC concentrations, in numbers which were not statistically different from the control group (one-way ANOVA, F (5, 18) = 0.600, p = 0.701) (Figure 3a).

The whole-sediment toxicity tests with highly contaminated PH sediment showed no survivors of either species in the controls, after only 7 d of exposure (Figure 3b). This confirms the acute toxicity of this sediment and is also why the experiment was terminated on the eighth day of exposure. In contrast to the clean sediment, AC amendments now appeared to cause increased survival, leading to maximum survival of 30-35% and 100% for *G. pulex* and *A. aquaticus*, respectively, at 3% AC or higher (Figure 3b). Remarkably, the increase in survival was already highly significant at the lowest level of AC addition, i.e. 1% (Figure 3b). In the 28-d sediment test with 3% AC added to the same contaminated sediment, AC also caused increased survival of *A. aquaticus*, but less than in the 8-d test (Figure 3b). Again, no survivors were found in the sediment without AC.

As for *G. pulex* on the uncontaminated Veenkampen sediment, there were no significant size differences between individuals exposed to sediments enriched with 0, 1, and 3% AC (one-way ANOVA, F (2, 9) = 0.221, p = 0.806) (Figure S3). The size of *A. aquaticus*, however, decreased with increasing AC levels, and although the difference was small, it was statistically significant. The effect concentration for 50% of the test population (EC_{50}) was determined to be 5.30% (SD 1.59).

Linking observed mortality in contaminated sediment to PAH exposure concentrations

To test the hypothesis that the observed advantageous effect of AC amendment to the heavily contaminated PH sediment was due to a decrease in bioavailable concentrations of PAHs, PAH exposure was determined using POM passive samplers. These could not be employed directly in the test systems because PAH transport in the bed sediments would have been too slow to reach chemical equilibrium with the sampler. Instead, the samplers were equilibrated in parallel systems, in which the AC-amended sediments were suspended. The resulting exposure concentrations can be assumed to approach those in the actual bioassay systems, because (a) both sediment-water-AC systems were already at equilibrium prior to exposure so that differences in turbulence would not cause differences in aqueous PAH concentrations, and (b) organisms as well as POM samplers extracted negligible amounts of PAHs from the AC-enriched sediment (less than 2.5 ± 0.3% for the 0% AC treatment and less than 0.05 ± 0.005 % for the 30% AC treatment). Addition of 1, 3, 6, 15, and 30% d.w. AC resulted in reductions of aqueous ΣPAH concentrations by factors of 10, 150, 400, 230, 3500 and more than 5000, respectively (Figure S4). The observed differences in mortality between different

AC levels can be qualitatively explained by comparing the PAH concentrations with PAH toxicity data for the test organisms. PHE, ANT, FLU, and PYR constituted more than 95% of the aqueous ΣPAH concentration. Because the relative potencies of these four PAHs differ, the additivity of their response was addressed using the toxic unit (TU) approach, i.e., the total toxicity of the dominant PAH was expressed as a sum of the ratios of the aqueous exposure concentrations and threshold effect concentrations (LC_{50}) for each of the individual PAHs in the mixture *(37, 38)*. To our knowledge, no LC_{50} values for *G. pulex* and *A. aquaticus* have been published for these PAHs. Therefore, the PAH exposure levels were compared with LC_{50} values for two closely related Gammarids, *Gammarus aequicauda* and *Gammarus locusta*. In 48-h toxicity tests with *G. aequicauda* and *G. locusta*, LC_{50} values for PYR were determined to be 74 and 61 µg/L, those for FLU 50 and 43, and those for PHE 170 and 150, respectively *(39)*. For ANT, the LC_{50} was assumed to be equal to that for PHE, given the similarity between these chemicals ($\text{Log}K_{OW}$, molecular weight and shape). Assuming that the PAH LC_{50} values for *G. pulex* can be approximated by the average values for *G. aequicauda* and *G. locusta*, allows the calculation of TU values for the different AC treatment conditions (Table S4). The decrease in TU values to almost zero at higher AC levels is consistent with the increased survival of both species (Figure S5). At TU=1 (LogTU=0), survival is approximately 2%, instead of the theoretically expected 50% (Figure S5). We hypothesize that the lower survival was caused by the longer exposure time in the current toxicity test, i.e. 8 d as compared to 2 d for the cited literature data. Assuming a first-order mortality model $N(t)=N_0e^{-kt}$ where N and N_0 are the numbers of individuals at times t and zero, respectively, and k is the mortality rate (d^{-1}) *(40)*, 50% survival after 48 h yields a mortality rate constant k of 0.35 d^{-1} for the literature data on Gammarids (see SI for calculation). Using the same model, 2.5 % survival after 8 d (Figure S5) yields a mortality rate constant k of 0.46 d^{-1} for the current experiments. Although associated with considerable uncertainty, this analysis shows that the current TU-based dose response curves are consistent with those reported in the literature *(39)*, and thus that the observed advantageous effect of AC amendment on the test species can be explained from the reduced combined toxicity of the PAH mixture.

Implications

Given the complexity of ecosystems, complete certainty regarding the absence of ecological side effects of AC amendments cannot be given. Effects may be different for other types of AC, other organisms and other environmental conditions. Still, given the existing literature, the current work has narrowed down the uncertainty with respect to safe ranges of AC application by including behavioral endpoints and further extending the range of species tested.

The current study used uncontaminated sediments that may represent the most vulnerable ecological settings. Using test results from this sediment to answer the question of safety would follow the precautionary principle, because AC effects may be more pronounced in the absence of other stressors. The series of whole-sediment behavioral toxicity tests with clean sediment demonstrated the absence of behavioral responses like locomotion, ventilation or avoidance. Our tests with *A. aquaticus* identified no negative effects for up to 28 d, whereas the application level of 2-4% would affect populations of *G. pulex* to some extent. It is not likely, however, that this would lead to extinction of this species. After all, in actual AC applications, AC levels will be subjected to some spatial variation, leaving sufficient refuge for sensitive species such as *G. pulex*. In addition, AC can be applied to top layers only, so that subsequent deposition of fresh organic matter and dispersion will lead to lower levels.

It must be noted that AC will never be applied to clean sediments, only to contaminated sediments. Our study used a highly contaminated sediment representing a 'hot spot' contaminated site. In such a case, addition of 1-4 % AC yielded a striking improvement of sediment quality in 28-d chronic whole-sediment bioassays with *A. aquaticus* as well as *G. pulex*, where the latter species again proved to be the most sensitive. Assuming that AC removes the toxic chemicals from the water phase, the question remains why AC addition eventually caused 100% mortality of *G. pulex* in clean sediment, whereas it did not lead to complete extinction in the contaminated sediment. At present, we have no conclusive explanation for this, although these results are not necessarily contradictory. After all, it cannot be ruled out that the habitat quality of the sediments was partly affected by other factors than PAH and AC levels, such as organic matter quality, macrochemistry or substrate geometry *(41)*.

Most earlier studies support the current observation of insensitivity to AC dosages of 2 to 4%. Many organisms exposed to sediments amended with CM, up to an unrealistically high level of 25%, still showed high survival *(8, 9, 12-14)*. As for growth, no studies demonstrated significant effects of AC addition on either marine or freshwater species *(7, 14)*. The greatest effects seem to occur in worms, but they never lead to extinction at the 2-4% CM levels used in this remediation scenario. Moreover, effects of AC observed in short-term laboratory studies might not occur in the field. Community effects probably are less severe in field settings, where recolonization and fresh input of organic matter will continuously form new habitats on top of treated sediments.

In conclusion, application of 2-4% activated carbon to remediate contaminated sediments can be considered beneficial and favorable for benthic species, especially those linked to the water column.

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Supporting Information

Calculation of mortality rates

Following Traas et al. *(40)* exponential mortality with a constant death rate is assumed to occur in toxicity experiments:

$N(t)=N_0e^{-kt}$ (1)

where N biomass density or number of individuals at time t, N_0 the number of animal at t=0, k the mortality rate (d^{-1}) and t the duration of the experiment (d^{-1}).

For the 48 h LC_{50} we have: $\mathrm{Ln}\ (N/N_0) = -kt$

$\mathrm{Ln}\ (50/100) = -2k$

$k = 0.35\ (d^{-1})$

For the 8 d $LC_{97.5}$ (because 2.5% survives):

$\mathrm{Ln}\ (2.5/100) = -8k$

$k = 0.46\ (d^{-1})$

Determination of polyoxymethylene-water partition coefficients for phenanthrene, anthracene, fluoranthene, and pyrene

POM-water distribution coefficients (K_{POM}) were determined with a co-solvent method *(21, 42)*. This method extrapolates K_{POM} values measured at a range of methanol-water mixtures, to 0% methanol. In short, 76 µm POM strips (250-550 mg, CS Hyde Company, Lake Villa, IL, USA) were added to 250 mL bottles, each filled with a mixture of methanol and nanopure water (0, 10, 15, 20, 30, 40, and 50 volume % methanol), supplemented with 25 mg/L sodium azide (biocide) and 0.01 M calciumchloride. Each methanol-water-POM system was duplicated. Methanol-water mixtures were carefully spiked with 100 µL PAH stock solution, such that PAH solubilities were not exceeded. Bottles were closed and shaken horizontally (100 rpm) at 18°C for 6 weeks. After equilibration, the POM-strips were extracted and analysed for PAHs as described in the Materials and Methods section. The aqueous phase was extracted twice with 20 mL hexane and analysed for PAHs as described in the Materials and Methods section.

POM-methanol/water (LogK_{PM}) partitioning coefficients were calculated as C_{POM}/C_M, where C_{POM} is the PAH concentration in POM and C_M is the PAH concentration in the methanol/water mixture. POM-water coefficients (K_{POM}) were estimated by extrapolation the LogK_{PM} values to 0% methanol using linear regression (Figure S1, Table S3). Following ref *(21)*, two extrapolations were compared: regression of LogK_{PM} versus the volume fraction methanol using the range of $0<f_{MeOH}<0.5$, and regression only using the range of $0<f_{MeOH}<0.3$. Results are presented in (Table S3). The regression using the widest range of $0<f_{MeOH}<0.5$ was considered most robust. These values were used for the exposure and toxicity evaluation in the sediment bioassays. The overall average standard errors in these LogK_{POM} values were 0.08-0.11 Log unit (Table S3). Comparison of the LogK_{POM} values with literature data (Table S3), shows that they agree well to those obtained from the LogK_{POM} - LogK_{OW} relationship that was previously published for partitioning of PCBs to the same 76 µm POM material *(20)*. This confirms an earlier observation by Jonker and Koelmans *(16)* that LogK_{POM}-LogK_{OW} relationships for PAH and PCB partitioning to POM agree very well.

Table S1. PAH and PCB concentrations of Petroleum Harbor (PH) and Veenkampen sediment.

PAHs, mg/kg	**Petroleum Harbor**	**Veenkampen**	**PCBs, µg/kg**	**Petroleum Harbor**	**Veenkampen**
PYR	277 (3.1)	1.5 (0.05)	CB-18	8.4 (0.3)	<LOD
FLU	195 (5.1)	1.4 (0.03)	CB-20	7.3 (0.4)	<LOD
PHE	150 (3.4)	0.81 (0.07)	CB-28	4.3 (0.2)	<LOD
AEN	124 (1.9)	<LOD	CB-29	15 (0.7)	<LOD
ANT	98 (1.3)	0.28 (0.01)	CB-44	15 (0.6)	<LOD
CHR	57 (4.6)	0.25 (0.01)	CB-52	7.6 (0.2)	1.4 (0.05)
BeP	53 (1.9)	0.12 (0.01)	CB-101	11 (0.1)	1.6 (0.01)
BaA	49 (3.5)	0.09 (0.003)	CB-105	14 (0.6)	<LOD
BaP	27 (4.2)	0.05 (0.002)	CB-118	4.1 (0.1)	1.2 (0.06)
BbF	25 (4.0)	0.08 (0.003)	CB-138	11 (0.1)	2.5 (0.09)
InP	14 (2.9)	0.03 (0.001)	CB-149	18 (0.7)	<LOD
NAP	12 (0.41)	<LOD	CB-153	15 (0.4)	1.7 (0.07)
BghiP	9.6 (2.3)	0.04 (0.001)	CB-155	21 (0.8)	<LOD
BkF	8.3 (7.2)	<LOD	CB-180	6.1 (0.1)	0.91 (0.08)
AYL	4.8 (0.32)	<LOD	CB-194	12 (0.5)	<LOD
DBA	2.6 (0.67)	0.04 (0.001)	CB-204	1.3 (0.1)	<LOD
			CB-209	0.60 (0.02)	<LOD
∑PAH	**1107 (43)**	**4.7 (0.32)**	**∑PCBs**	**170 (7.7)**	**9.3 (0.42)**
Threshold concentration	**40**		**Threshold concentration**	**676** *(28)*	
TOC, %	6.2 (0.06)	9.8 (0.41)	**BC**, %	2.1 (0.15)	1.8 (0.25)

Values are given as means (n= 3)
LOD = 0.01-0.13 µg/L

Table S2. Concentration of metals in Petroleum Harbor sediment and AC.

	As	Cu	Pb	Zn	Ni	Cr	**∑Metals**
Background concentration of metals in PH sediment, mmol/kg d.w.	0,24	0,88	6,8	4,2	0,11	0,11	**12**
Concentration of metals in AC, mmol/kg$_{AC}$	0,059	0,11	0,018	0,11	0,57	0,54	**1,4**

Table S3. POM-76 – water partitioning coefficients (n=12) for phenanthrene, anthracene, fluoranthene, and pyrene

	PHE	**ANT**	**FLU**	**PYR**	**PHE**	**ANT**	**FLU**	**PYR**
	$0.1<f_{MeOH}<0.5$				$0.1<f_{MeOH}<0.3$			
Intercept (LogK_{POM})	4.56	4.29	5.11	5.13	4.43	4.03	4.98	4.97
SE	0.08	0.11	0.09	0.09	0.07	0.11	0.08	0.08
CI Lower 95%	4.37	4.03	4.92	4.93	4.25	3.75	4.77	4.78
CI Upper 95%	4.74	4.54	5.31	5.33	4.60	4.30	5.18	5.17
Slope	-4.67	-3.89	-5.16	-5.09	-3.95	-2.39	-4.36	-4.17
SE	0.27	0.37	0.28	0.29	0.35	0.56	0.41	0.40
CI Lower 95%	-5.27	-4.71	-5.79	-5.74	-4.82	-3.76	-5.38	-5.14
CI Upper 95%	-4.08	-3.07	-4.53	-4.44	-3.08	-1.03	-3.35	-3.19
R^2	0.97	0.92	0.97	0.97	0.95	0.75	0.95	0.95
LogK_{POM} *	4.66	4.66	5.13	5.13				

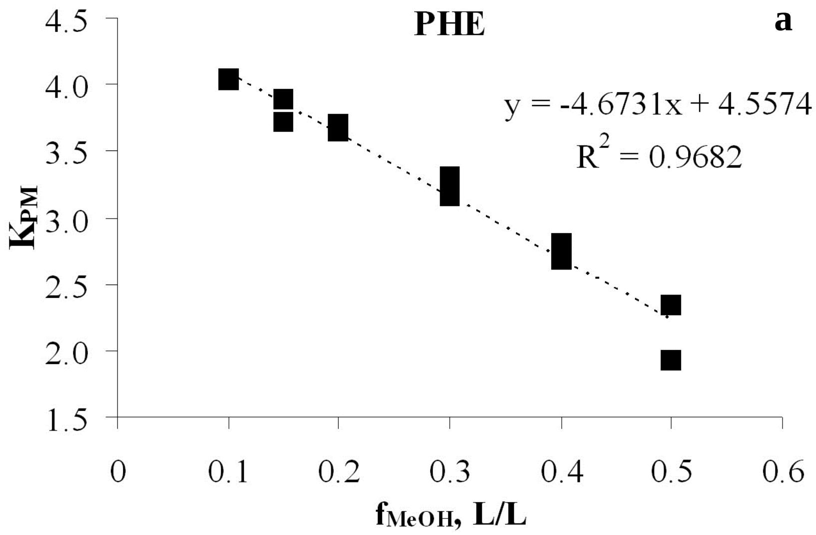
* LogK_{POM} values derived from the LogK_{POM} – LogK_{OW} relationship LogK_{POM} = 0.791 LogK_{OW} + 1.018 for PCBs based on data reported in SI Ref *(20).*

Table S4. Exposure concentration and Toxic Units of PAHs as a function of AC level in Petroleum Harbor sediment

	PHE	**ANT**	**FLU**	**PYR**	
LC_{50} (μg/L) for Gammaridae	148-174 *(39)*	148**	43-45 *(39)*	61-74 *(39)*	
AC level in sediment, %	**C_W (μg/L)**				**TU***
0	37	9.27	9.28	5.37	**0.618**
1	3.00	1.20	1.10	0.50	**0.062**
3	0.30	0.10	0.01	0.04	**0.004**
6	0.15	0.03	0.04	0.01	**0.002**
15	0.03	0.02	0.02	0.00	**0.001**
30	0.01	0.01	0.01	0.00	**0.000**

* TU of 1 would imply 50% mortality in a 48 h toxicity test assuming concentration additivity. TU calculated as TU = C_w^{PHE}/LC_{50}^{PHE} + C_w^{ANT}/LC_{50}^{ANT} +C_w^{FLU}/LC_{50}^{FLU} + C_w^{PYR}/LC_{50}^{PYR}. PAHs with negligible concentration were omitted from TU calculations.

** Assumed to be equal to the LC_{50} for PHE.



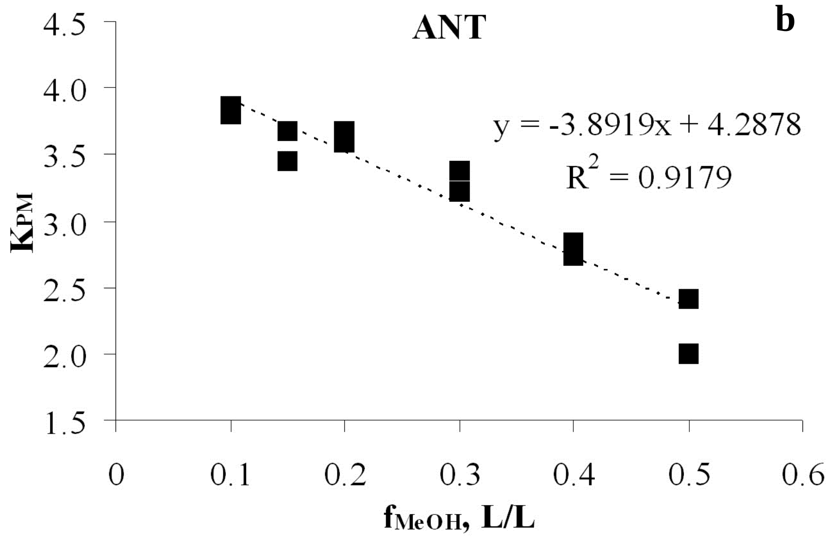
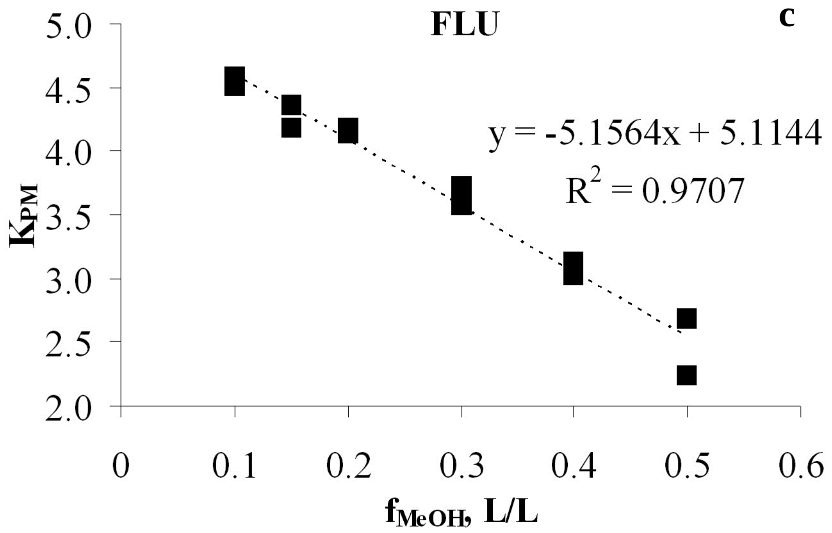


Figure S1. POM-water / methanol (LogK_{PM}) as a function of the volume fraction of methanol for phenanthrene (a), anthracene (b), fluoranthene (c), and pyrene (d).



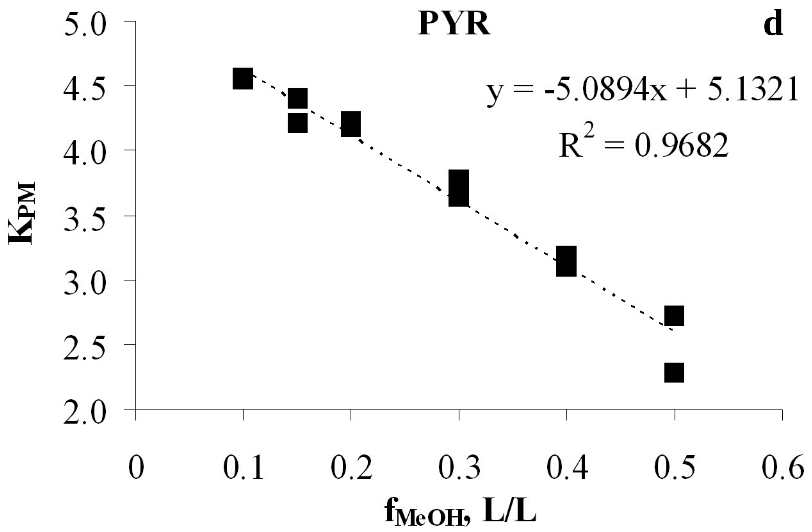


Figure S1. (continued) POM-water / methanol (LogK_{PM}) as a function of the volume fraction of methanol for phenanthrene (a), anthracene (b), fluoranthene (c), and pyrene (d).

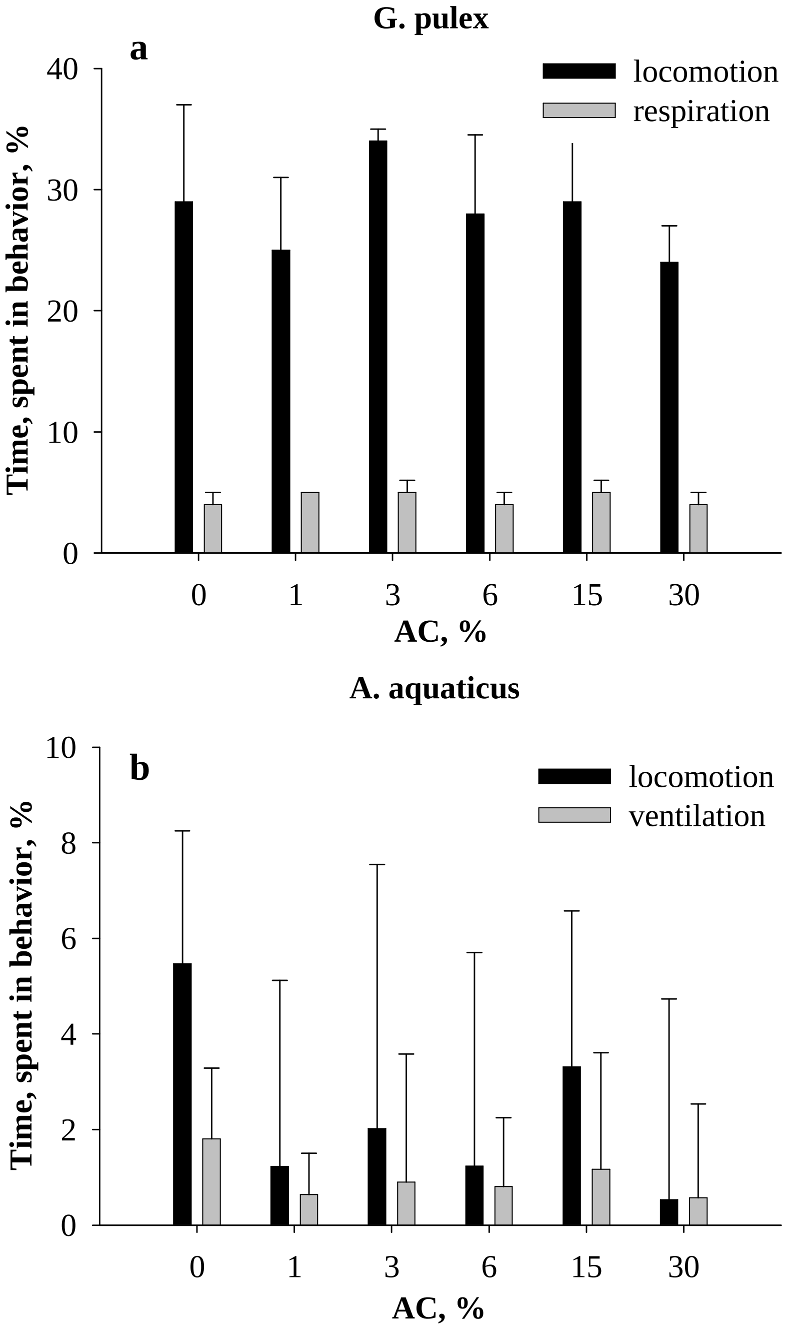


Figure S2. Percentage time spent on locomotion and ventilation activity (median, 75th percentile, n=20) by (a) *G. pulex* and (b) *A. aquaticus* after 1-day exposure to Veenkampen sediment enriched with AC.

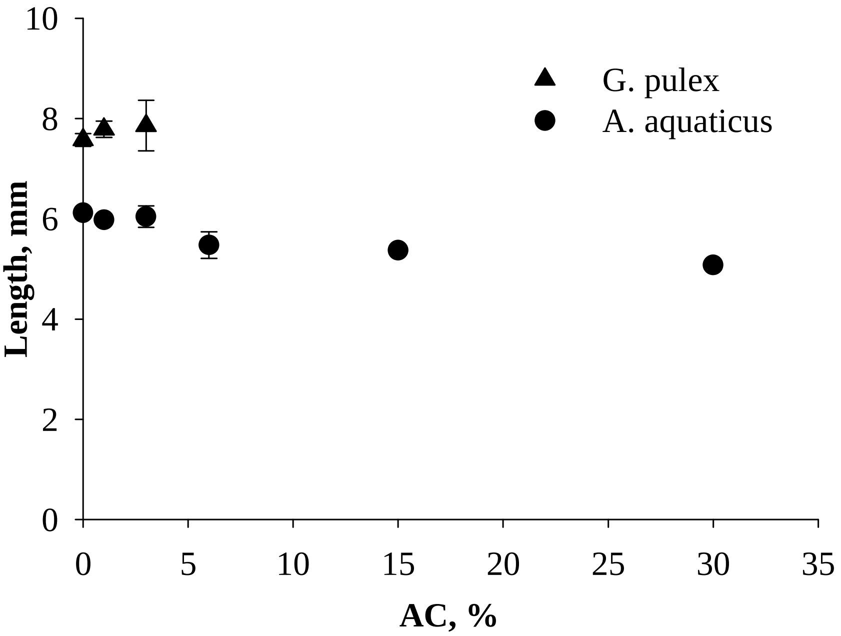


Figure S3. Size (SE, n=4) of *G. pulex* (triangles) and *A. aquaticus* (circles) individuals recovered after 28-d exposure to non-contaminated Veenkampen sediment as a function of AC levels in the sediment.

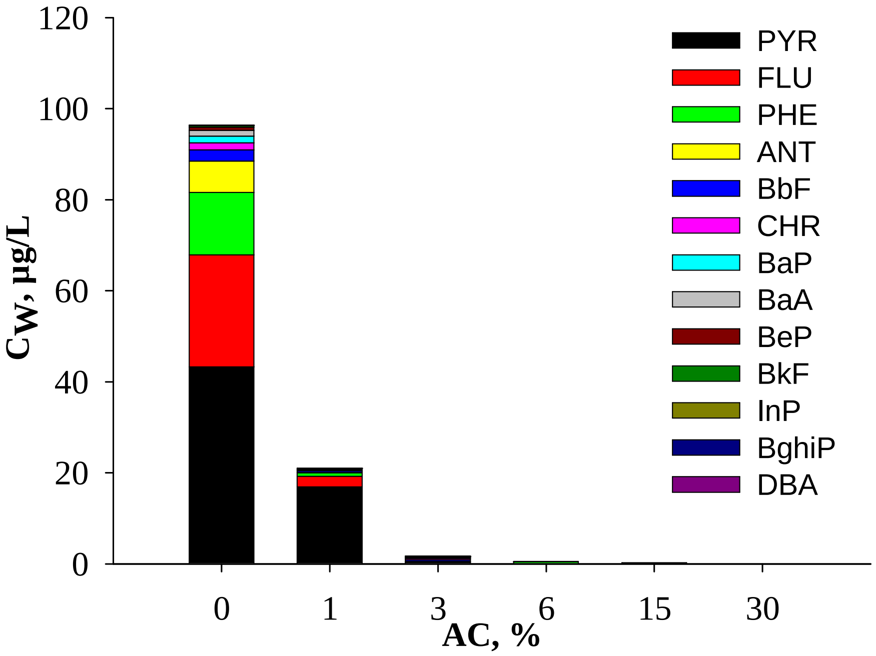


Figure S4. Equilibrium aqueous exposure concentration of PAHs as a function of AC levels in Petroleum Harbor sediment.

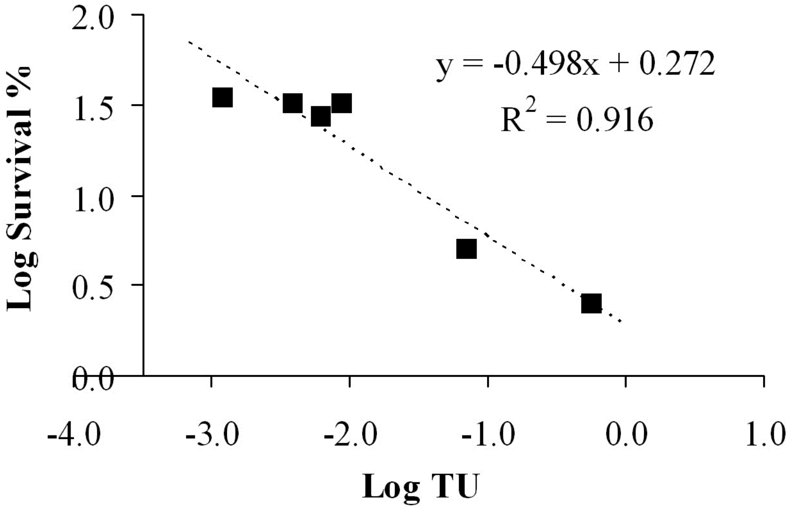


Figure S5. Log Survival (%) of *G. pulex* in Petroleum Harbor sediment enriched with AC as a function of Log TU estimated for two marine Gammarids, *Gammarus aequicauda* and *Gammarus locusta*. For calculation of TU values see Table S4.

CHAPTER 6

MODELING TRADE-OFF BETWEEN PAH TOXICITY REDUCTION AND NEGATIVE EFFECTS OF SORBENT AMENDMENTS TO CONTAMINATED SEDIMENTS

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Abstract

Adding activated carbon (AC) to contaminated sediment has been suggested as an effective method for sediment remediation. AC binds chemicals such as polycyclic aromatic hydrocarbons (PAHs), thus reducing the toxicity of the sediment. Negative effects of AC on benthic organisms have also been reported. Here we present a conceptual model to quantify the trade-off, in terms of biomass changes, between the advantageous PAH toxicity reduction and the negative effects of AC on populations of benthic species. The model describes population growth, incorporates concentration-effect relationships for PAHs in the pore water and for AC, and uses an equilibrium sorption model to estimate PAH pore water concentrations as a function of AC dosage. We calibrated the model using bioassay data and analyzed it by calculating isoclines of zero population growth for two species. For the sediment evaluated here the results show that AC may safely protect the benthic habitat against considerable sediment PAH concentrations as long as the AC dosage remains below 4%.

Introduction

Sediment contamination by hydrophobic organic compounds (HOCs) has been recognized as an environmental problem for decades *(1)*. Sediment-dwelling and pelagic organisms may be exposed to these compounds, either directly through their diet or through uptake from the water column or interstitial water, or indirectly through HOC release after resuspension or bioturbation. Dredging with subsequent disposal of the dredged material in sediment depot is the most common technique to remediate contaminated sediments. Dredging, however, is expensive, laborious, and can lead to resuspension of sediment material, increasing concentrations of HOCs in the overlying water. Moreover, dredging is also very invasive, which may be a problem in vulnerable ecosystems. Recently, amendment of contaminated sediments with activated carbon (AC) has been proposed as a less disruptive, less expensive, and more efficient remediation technique *(2)*. Several *in situ* and *ex situ* studies have demonstrated the advantageous effects of AC application, such as the reduction of bioavailable HOC pore water concentrations *(3-6)*, reduced HOC bioaccumulation *(3, 5, 7-9)* and reduced toxicity of sediment-bound HOCs *(4, 10-13)*. Despite these advantageous effects, it has also been hypothesized that AC itself may have negative impacts on the habitat quality for benthic organisms. It is important that these possible side-effects are properly addressed before AC amendments can be implemented as a safe and accepted method for sediment remediation. For several aquatic species, a variety of adverse effects of AC have been observed in laboratory settings, such as mortality *(4, 7)*, growth inhibition *(4, 9)*, and a decrease in lipid content *(3, 14)*.

A major question is under what conditions the improvement of habitat quality due to HOC immobilization would compensate for the possible negative effects of AC itself on the habitat quality for benthic aquatic organisms. Additionally, there is a need for a framework allowing these counteracting effects to be generalized. Such a framework could be calibrated for different chemicals, ecosystems, and activated carbon types and then used for decision support in the management of contaminated sediments.

Here we present a general approach to the conceptual modeling of the development of a population of benthic invertebrates in contaminated sediments amended with AC. The model calculates the direct effects of AC addition on the population, the secondary effects of AC on the reduction of pore water PAH concentrations, and the effects of these reduced PAH exposure concentrations on the population. As such, the model is also capable of quantifying the trade-off between the advantageous HOC toxicity reduction and the negative effects of AC addition on macroinvertebrate populations. The scope of the model is to describe effects for the first weeks after AC amendment. We are not aware of earlier studies modeling the combined effects of AC amendment and HOCs on benthic population development.

The general model is implemented for a specific case, using sediment- and species-specific toxicity data derived from our previously published 8- and 28-day whole sediment laboratory bioassays *(4)*. We briefly summarize the characteristics of these bioassays and introduce the modeling approach. The bioassays were used to test the effects of AC addition (0, 3, 6, 15, and 30% d.w.) to uncontaminated sediment and to sediment natively contaminated with PAHs, for two species: *Gammarus pulex* and *Asellus aquaticus*. The experimental results showed that AC addition (a) leads to lower survival and to growth inhibition of these species in uncontaminated sediment, and at the same time (b) facilitates survival of both species in the PAH-contaminated sediment *(4)*. *G. pulex* and *A. aquaticus* were selected as test organisms because they are common invertebrates in freshwater habitats and have been widely used in ecotoxicological studies *(15, 16)*. They differ in their sensitivity to AC *(4)*, and have different species-specific properties, such as behavior, feeding strategies, and routes of HOC uptake *(17)*, and thus provide a good representation of benthic communities. Moreover, these are the two species that have been most frequently studied in Europe in regards to how they are affected by AC. The sediment was a highly contaminated ‘hot spot’ sample from Petroleum Harbor (PH, Amsterdam, The Netherlands), with a total PAH concentration of 1,100 mg/kg. Yield responses to the interrelated effects of PAH toxicity and activated carbon addition on *G. pulex* and *A. aquaticus* were analyzed using a general population growth model *(18)*. The effect of AC addition on PAH aqueous exposure concentrations was quantified using an AC-inclusive equilibrium sorption submodel *(19, 20)*. The model was parameterized using literature data and the concentration-effect relationships and mortality rates derived from the laboratory experiments *(4)*.

Methods

Model description

Population dynamics in sediment amended with AC. One of the most basic models of population growth is the logistic growth model *(18, 21)*. A population with sufficient food and space to grow tends to grow at a rate that is proportional to the population size and is commonly described as:

$$\frac{dB}{dt} = kB\left(1 - \frac{B}{K}\right) \tag{1}$$

where B is biomass (mg), k is a growth rate constant (d^{-1}), and population growth is limited by the carrying capacity K (i.e. an upper limit of population size) (mg). We assume that in the first relatively short period, as in the 28-d toxicity tests from which the majority of the input parameters for the model were derived *(4)*, the population is unconstrained by resource limitations, that is, B is small relative to K, and the population growth follows an exponential pattern *(18)*:

$$\frac{dB}{dt} = kB \tag{2}$$

Whereas population growth occurs through production or assimilation, growth failure may occur through respiration, natural mortality, and mortality caused by toxic chemicals. These are the factors we included in the growth model. Respiration was described as a gross loss term and was not subdivided into costs for maintenance, growth, and reproduction. Population growth due to reproduction and recolonization is not relevant for our toxicity test systems and is therefore omitted. Similarly, the model does not consider biomass losses due to inter- and intra-specific competitions or predation. The resulting population growth equation follows previously published approaches *(18, 22, 23)*, and details the rate constant k in eq 2 as follows:

$$\frac{dB}{dt} = (k_a - k_r - k_{inh} - \mu_{nat} - \mu_{AC} - \sum_{i=1}^{m} \mu_{PAH_i})B \tag{3}$$

where k_a is an assimilation rate constant (d^{-1}), k_r is the respiration rate (d^{-1}), k_{inh} is a growth inhibition rate (d^{-1}), and μ_{nat}, μ_{AC}, and μ_{PAHi} are rates constants for natural mortality, mortality due to AC and mortality due to individual PAH i, respectively, (d^{-1}). The summation term adds up the mortality rates due to all m individual PAH_i to obtain one overall mortality rate ($\sum\mu_{PAHi}$) for the PAH mixture present in the sediment pore water. The use of these mortality rate constants implies that mortality is assumed to be a first-order process, proportional to population size. Following Traas et al. *(24)*, the mortality rate μ (d^{-1}) due to the stressors, i.e. either an individual PAH (or mixture of PAHs) or AC, is modeled to depend on their concentration C (µg/L) in the water, according to:

$$\mu = \frac{1}{D}\ln\left[1 + \left(\frac{C}{LC_{50}}\right)^{b}\right] \tag{4}$$

where LC_{50} is the concentration at which 50% mortality is observed in a single species toxicity test (µg/L), b (> 0) is a slope parameter of the concentration-response curve on a linear scale, and D is the duration of the single species toxicity test (d^{-1}). Parameterization and calibration of the model eqs 3 and 4 is detailed below.

Trade-off between toxicity reduction and negative effects of activated carbon. The trade-off between the advantageous effect of PAH toxicity reduction and the direct negative effects of AC addition on the test species was addressed using the parameterized and calibrated model to calculate population equilibria. The population equilibrium for a species is the combination of model variables that results in a stable population with zero growth. In our case, these model variables are % AC and total PAH concentration. The equilibria can be visualized graphically by plotting the line of zero growth for each of the species. The lines of zero growth are called isoclines, and separate the regions in the state space where the population increases from the regions where the population decreases.

Since the population equilibrium occurs when the population density is not changing, we can calculate the isoclines by equating dB/dt in eq 3 to zero, or:

$$B(k_a - k_r - k_{inh} - \mu_{nat} - \mu_{AC} - \sum_{i=1}^{m} \mu_{PAH_i}) = 0 \tag{5}$$

Eq 5 has two solutions. The first solution, $B = 0$, is called a trivial equilibrium and effectively represents the absence of the species, which therefore is not relevant from an ecological point of view. The second solution balances the assimilation rate constant, k_a, to all loss rate constants in the model, that is, the rate constants for respiration, growth inhibition, and mortality:

$$\mu_{AC} = k_a - k_r - k_{inh} - \mu_{nat} - \sum_{i=1}^{m} \mu_{PAH_i} \tag{6}$$

Eq 6 shows that if k_a, k_r, k_{inh}, and μ_{nat}, are known, the mortality rate constant due to AC (μ_{AC}) can be calculated for any value of the mortality rate due to PAH ($\sum\mu_{PAHi}$), and vice versa. It is more convenient, however, to express eq 6 in terms of the control variables C_{AC} (as % AC) and the aqueous concentration for PAH$_i$: C_W^i, or even better, the total concentration of PAH in the solid phase. This can be achieved by substituting eq 4 parameterized for AC into μ_{AC}, and substituting eq 4 parameterized for PAH toxicity into $\mu_{PAH,i}$, which yields:

$$\frac{1}{D_{AC}} \ln\left[1 + \left(\frac{C_{AC}}{LC_{50}^{AC}}\right)^{b_{AC}}\right] = k_a - k_r - \mu_{nat} - \sum_{i=1}^{m} \frac{1}{D_{PAH_i}} \ln\left[1 + \left(\frac{C_W^i}{LC_{50}^i}\right)^{b_i}\right] \tag{7}$$

Eq 7 determines the isocline, linking C_{AC} values (% AC) to those values of C_W^i in the mixture of PAHs that result in zero growth of the population, so a $\sum\mu_{PAHi}$ can be calculated for each AC concentration. Note that numerous combinations of concentrations C_W^i in the pore water mixture of PAHs may result in the same value for $\sum\mu_{PAHi}$ (the right-hand summation term in eq 7). However, the actual composition of the PAH mixture in the sediment pore water is fixed and sediment-specific, and under equilibrium conditions has to relate to a fixed ratio of solid phase PAH concentrations in the sediment. Therefore, we first calculated the isocline-$\sum\mu_{PAHi}$ from eq 7 and then fitted the pore water concentrations C_W^i of the four dominant PAHs, constituting more than 95% of the aqueous ∑PAH concentration (phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), and pyrene (PYR)) *(4)*, to fulfill two criteria: (a) the $\sum\mu_{PAHi}$ value calculated from the four fitted C_W^i values equates to this required isocline-

$\sum\mu_{PAHi}$, and (b) the solid phase PAH concentrations C_{sed}^{i} for the four dominant PAHs as calculated from the fitted values for C_{W}^{i} by equilibrium sorption modeling are in agreement with the corresponding PAH C_{sed}^{i} ratios in the PH sediment (Table S1). For this conversion of pore water concentrations of individual PAHs (C_{W}^{i}) to solid phase concentrations (C_{sed}^{i}) single or multiple domain sorption models may be selected, that may or may not account for sorption non-linearity to 'hard carbon' phases *(10, 20, 25-28)* depended on the case considered. Here, we decided to keep the model general and to follow the approach that seems to be accepted most frequently in the recent literature, which is a multiple domain Freundlich sorption model *(10, 19, 20)*. The model accounts for the distribution of PAHs over the organic matter domains of organic carbon (OC) and black carbon (BC) and added AC:

$$\sum_{i=1}^{m} C_{sed}^{i} = f_{OC}\sum_{i=1}^{m} K_{OC}^{i} C_{W}^{i} + f_{BC}\sum_{i=1}^{m} K_{BC}^{i}\left(C_{W}^{i}\right)^{n_{F,BC}} + f_{AC}\sum_{i=1}^{m} K_{AC}^{i}\left(C_{W}^{i}\right)^{n_{F,BC}} \qquad (8)$$

where $\sum C_{sed}$ (μg/kg) is the sum concentration of *m* PAHs sorbed to the total sediment, which is assumed to remain unchanged after AC addition, and f_{OC}, f_{BC}, and f_{AC} are the fractions of OC, BC, and AC, respectively (kg/kg$_{\text{sed}}$), K_{OC} is the organic carbon normalized sorption coefficient for OC (L/kg$_{\text{OC}}$), K_{BC} and K_{AC} are the Freundlich adsorption coefficients for BC and AC, respectively, (μg/kg)/(μg/L)^{nF} and $n_{F,BC}$ and $n_{F,AC}$ are the Freundlich exponents for BC and AC, respectively. The conversion of the PAH mortality rate ($\sum\mu_{PAHi}$) to pore water concentrations and then to PAH concentrations in the sediment solid phase that correspond to the actual composition of the sediment can be performed for any sediment using this procedure. For a given PAH mortality rate ($\sum\mu_{PAHi}$), however, sediments with a different PAH profile will yield a different $\sum C_{sed}$ based on eq 8. In summary, for a given level of PAH $\sum C_{sed}$, this model procedure provides the value of % AC for which a stable population of zero growth can be expected, or vice versa. It is convenient to have the isocline expressed in terms of $\sum C_{sed}$ (solid phase) rather than pore water concentration, since total contaminant concentrations are the common descriptors in sediment quality management. With respect to the application of eq 8 we formulate three disclaimers. First, non-equilibrium may cause pore water concentrations to be higher than predicted by this equilibrium model. Second, eq 8 may yield theoretical values for $\sum C_{sed}$ that are beyond the range of PAH concentrations for which the BC and AC sorption parameters were calibrated. Third, at high C_{W}^{i}, sorption behavior may not comply with the Freundlich model because of saturation of the AC and BC surfaces. To better address saturation of the surface of hard carbon materials such as BC and AC, Langmuir or Polanyi-Dubinin-Manes models have been suggested before *(29)*. Because of better data availability and the lesser number of parameters needed, we evaluated a Langmuir model scenario as an alternative to eq 8:

$$\sum_{i=1}^{m} C_{sed}^{i} = f_{OC}\sum_{i=1}^{m} K_{OC}^{i} C_{W}^{i} + f_{BC}\sum_{i=1}^{m} \frac{K_{d}^{BC} C_{W}^{i}}{1+\frac{K_{d}^{BC} C_{W}^{i}}{C_{\max}^{BC}}} + f_{AC}\sum_{i=1}^{m} \frac{K_{d}^{AC} C_{W}^{i}}{1+\frac{K_{d}^{AC} C_{W}^{i}}{C_{\max}^{AC}}} \qquad (9)$$

where K_d is the initial slope of the isotherm equal to the sorbent-water distribution coefficient (L/kg) at low C_W^i, and C_{max} is the maximum adsorption capacity (µg/kg) of the sorbent. A detailed explanation of eq 9 is provided as Supporting Information.

Parameterization of the model

As explained in the introduction, the model was parameterized using data derived from 28-d and 8-d exposure experiment with uncontaminated and PAH-contaminated sediment, respectively, amended with different AC concentrations *(4)*. To our knowledge, this is the only dataset available that can be evaluated in the context of the proposed model framework.

Biomass estimation. Biomass (B) was monitored by counting the number of individuals in a series of whole-sediment toxicity tests described previously *(4)*. The observed numbers were converted to biomass using length - dry weight relationships established by Graca et al. *(35)* (Table 1). For *G. pulex*, the relationship reads: Ln DW = 3 Ln L - 5.64, where DW and L are the dry weight (mg) and length (mm) of an individual organism, respectively. For *A. aquaticus*, the relationship is: Ln DW = 2.7 Ln L - 4.58. Assimilation and respiration rates, estimated from the balanced energy equation, were taken from the literature *(36, 37)* (Table 1).

Mortality and growth inhibition rates. Natural mortality of *G. pulex* and *A. aquaticus* was estimated from the observed mortality in the experimental controls *(4)* by fitting eq 3 to the dose-response curve with parameters k_a, k_r, k_{inh}, μ_{AC}, and μ_{PAH} set to zero. LC_{50}^{AC}, b_{AC}, and D_{AC} (eq 4) for *G. pulex* were derived from a series of AC toxicity tests (Table 1) *(4)* and μ_{AC} was calculated using eq 4. For *A. aquaticus*, no concentration-effect curve could be derived to calculate LC_{50}^{AC} and b_{AC}, so μ_{AC} was estimated as total mortality observed in the sediment minus natural mortality *(4)*. For both species k_{inh} was set to zero since no growth inhibition was observed in the AC toxicity tests.

Mortality due to PAHs in AC-amended sediments was calculated in two different ways. For the purpose of modeling the population dynamics during the bioassays, mortality due to PAHs was calculated as total mortality observed in our laboratory experiments minus natural mortality and mortality due to AC. This uses the assumption that mortalities due to multiple stressors (here PAHs and AC) can be assumed additive (eq 3) *(18, 38)*. Factors that might interfere with AC and PAH toxicity in the tests like oxygen, pH, un-ionized ammonia, metals, other HOCs) were irrelevant as was shown in our previous paper *(4)*. For the purpose of modeling the isoclines, mortality due to PAHs in PH sediment was estimated using eq 4, as described above. To our knowledge, no LC_{50} and b values for *G. pulex* and *A. aquaticus* have been published for individual PAHs. However, it has been shown previously that the shape of the dose-response curve, which is determined by the median sensitivity of the exposed populations, is similar for compounds with the same mode of action *(39)*. Thus, β, the slope parameter of the log-transformed dose-response relationship (β = 1/b), was assumed to be the same for all individual PAHs, both for *G. pulex* and *A. aquaticus* (Table 1) *(39)*.

As for LC_{50}, the values for two closely related gammarids, *Gammarus aequicauda* and *Gammarus locusta* were taken to feed the model (Table 1) *(40)* since species with similar traits have similar sensitivity to stressors *(17)*. Using the previously published approach *(4)*, the LC_{50} for ANT was assumed to be equal to that for PHE, given the similarity between these chemicals (LogK_{OW}, molecular weight, and shape) and between their final chronic values *(41)*.

Sediment characteristics. The total concentrations of PAHs in the system ($\sum C_{sed}$), f_{OC}, f_{BC} , and f_{AC} were determined experimentally and are given in Table S1 *(4)*. The K_{OC} values for amorphous carbon were calculated from compound class specific quantitative structure property relationships (QSPRs) taken from van Noort *(42)*. The QSPR for PAHs, is: LogK_{OC} = 1.11 LogK_{OW} – 1.14. LogK_{OW} values for PAHs were taken from Booij et al. *(43)*. Following *(19)*, BC and AC Freundlich sorption affinity constants for all individual chemicals (K_{BC} and K_{AC}) and their Freundlich exponents were estimated using previously published data *(10, 25, 28, 44-47)*. Values for K_d for BC and AC were taken from Jonker and Koelmans *(30)* and corrected for one order of magnitude organic matter fouling, as reported previously *(29, 31)*. Adsorption capacities C_{max} were taken from van Noort *(32-34)*.

Uncertainty analysis. A robust uncertainty analysis was performed for the isocline calculations by varying the values of the input parameters within a range of plus or minus one SD (Table 1). If no SD was available, the input parameter value was varied within 20% of the values (Table 1). The resulting lowest and highest isocline estimates were plotted together with the isocline at the default parameter values.

Table 1. Default model parameters (SD)

<table>
<tr><td></td><td></td><td colspan="20"><i>G. pulex</i></td><td colspan="20"><i>A. aquaticus</i></td></tr>
<tr><td></td><td></td><td colspan="40">Biological parameters</td></tr>
<tr><td>Assimilation rate</td><td>k_a[b], d^{-1}</td><td colspan="20">0.052 <i>(36)</i></td><td colspan="20">0.051[d] <i>(37)</i></td></tr>
<tr><td>Respiration rate</td><td>k_r[b], d^{-1}</td><td colspan="20">0.034 <i>(36)</i></td><td colspan="20">0.008 [d] <i>(37)</i></td></tr>
<tr><td>Natural mortality</td><td>μ_{nat}[a,c], d^{-1}</td><td colspan="20">0.0069 (0.0021)</td><td colspan="20">0.0019 (0.0022)</td></tr>
<tr><td></td><td></td><td colspan="40">Activated Carbon</td></tr>
<tr><td></td><td></td><td colspan="4">1</td><td colspan="4">3</td><td colspan="4">6</td><td colspan="4">15</td><td colspan="4">30</td><td colspan="4">1</td><td colspan="4">3</td><td colspan="4">6</td><td colspan="4">15</td><td colspan="4">30</td></tr>
<tr><td></td><td></td><td colspan="4"></td><td colspan="4">0.0260
(0.0165)</td><td colspan="4">0.1987
(0.0823)</td><td colspan="4">0.2398
(0.0021)</td><td colspan="4">0.2398
(0.0021)</td><td colspan="4">0.0050
(0.0030)</td><td colspan="4">0.0062
(0.0115)</td><td colspan="4">0.0041
(0.0045)</td><td colspan="4">0.0036
(0.0089)</td><td colspan="4">0.0064
(0.0056)</td></tr>
<tr><td>AC toxicity</td><td>28-d LC_{50}[a,c], %</td><td colspan="20">3.1 (0.64)</td><td colspan="20">-</td></tr>
<tr><td></td><td>b[b,c], -</td><td colspan="20">4.5</td><td colspan="20">-</td></tr>
<tr><td></td><td>D_{AC}[c], d</td><td colspan="20">28</td><td colspan="20">28</td></tr>
<tr><td></td><td></td><td colspan="40">Polyaromatic hydrocarbons</td></tr>
<tr><td>PAH toxicity</td><td>2-d LC_{50}[b], µg/L <i>(40)</i></td><td colspan="5">PHE</td><td colspan="5">ANT</td><td colspan="5">FLU</td><td colspan="5">PYR</td><td colspan="5">PHE</td><td colspan="5">ANT</td><td colspan="5">FLU</td><td colspan="5">PYR</td></tr>
<tr><td></td><td></td><td colspan="5">150</td><td colspan="5">150</td><td colspan="5">50</td><td colspan="5">60</td><td colspan="5">150</td><td colspan="5">150</td><td colspan="5">50</td><td colspan="5">60</td></tr>
<tr><td></td><td>b[b,f], -</td><td colspan="20">2.36</td><td colspan="20">2.36</td></tr>
<tr><td></td><td>D_{PAH}[c], d</td><td colspan="20">2</td><td colspan="20">2</td></tr>
<tr><td>Sorption affinity parameters</td><td>$LogK_{BC}$[a,e], (µg/kg$_{\mathrm{BC}}$)/(µg/L)$^{\mathrm{nF,BC}}$</td><td colspan="5">7.5 (0.2)</td><td colspan="5">7.5 (0.2)</td><td colspan="5">7.7 (0.3)</td><td colspan="5">7.7 (0.3)</td><td colspan="5">7.5 (0.2)</td><td colspan="5">7.5 (0.2)</td><td colspan="5">7.7 (0.3)</td><td colspan="5">7.7 (0.3)</td></tr>
<tr><td></td><td>$LogK_{AC}$[a,e], (µg/kg$_{\mathrm{AC}}$)/(µg/L)$^{\mathrm{nF,AC}}$</td><td colspan="5">7.7 (0.3)</td><td colspan="5">7.7 (0.3)</td><td colspan="5">8.6 (0.3)</td><td colspan="5">8.6 (0.3)</td><td colspan="5">7.7 (0.3)</td><td colspan="5">7.7 (0.3)</td><td colspan="5">8.6 (0.3)</td><td colspan="5">8.6 (0.3)</td></tr>
<tr><td></td><td>Log $C_{\max}^{BC}$[g], µg/kg</td><td colspan="5">6.91</td><td colspan="5">6.91</td><td colspan="5">6.73</td><td colspan="5">6.73</td><td colspan="5">6.91</td><td colspan="5">6.91</td><td colspan="5">6.73</td><td colspan="5">6.73</td></tr>
<tr><td></td><td>Log $C_{\max}^{AC}$[g], µg/kg</td><td colspan="5">7.45</td><td colspan="5">7.45</td><td colspan="5">6.97</td><td colspan="5">6.97</td><td colspan="5">7.45</td><td colspan="5">7.45</td><td colspan="5">6.97</td><td colspan="5">6.97</td></tr>
<tr><td></td><td>Log K_d^{BC}[h], L/kg</td><td colspan="5">5.56</td><td colspan="5">5.76</td><td colspan="5">6.04</td><td colspan="5">6.04</td><td colspan="5">5.56</td><td colspan="5">5.76</td><td colspan="5">6.04</td><td colspan="5">6.04</td></tr>
<tr><td></td><td>Log K_d^{AC}[h], L/kg</td><td colspan="5">7.76</td><td colspan="5">7.96</td><td colspan="5">8.06</td><td colspan="5">8.06</td><td colspan="5">7.76</td><td colspan="5">7.96</td><td colspan="5">8.06</td><td colspan="5">8.06</td></tr>
<tr><td></td><td>$n_{F,BC}$[b,e], -</td><td colspan="20">0.7</td><td colspan="20">0.7</td></tr>
<tr><td></td><td>$n_{F,AC}$[b,e], -</td><td colspan="20">0.7</td><td colspan="20">0.7</td></tr>
</table>

[a] Uncertainty analysis used value ±SD. [b] Uncertainty analysis used value ±10%. [c] Calculated using data from *(4)*. [d] 1 mg = 20.7 kJ *(36)*. [e] Estimated using data from *(10, 25, 28, 44-47)* as summarized in *(19)*. [f] b (=1/β) estimated using data from *(39)*. [g] Estimated using data from *(32-34)*. [h] Estimated using data from *(30)*.

Results and discussion

Modeling population dynamics in AC-amended sediment

Mortality rates due to AC and PAHs. The results of the whole-sediment 28-d toxicity tests with *G. pulex* and *A. aquaticus* in uncontaminated sediment *(4)* were used to calculate the mortality rates due to AC. For *G. pulex*, the mortality rate due to AC gradually increases with increasing AC concentration and appears to level off at higher AC concentrations, i.e. > 15% (Figure S1a). This may suggest that addition of AC at these very high concentrations will probably cause 100% mortality of the population. In contrast to *G. pulex*, *A. aquaticus* survived at all AC concentration and its mortality rates due to different AC concentrations were very low and not statistically different from one another (one-way ANOVA, *F*(5, 18) = 0.514, *p* = 0.763) (Figure S1). Therefore, the average value of 0.005 d^{-1} for all AC concentrations was used to calculate the isoclines (as described in the next section).

The results of the whole-sediment 8-d toxicity tests with *G. pulex* and *A. aquaticus* in heavily contaminated sediment were used to calculate the mortality rates due to PAHs. An increase in AC concentration in PAH-contaminated sediment leads to an exponential decrease in mortality rates for both species (Figure S1b) suggesting that 1 - 3% AC efficiently removes PAHs from the sediment pore water and thus reduces risks associated with these chemicals.

General model results. Whereas Kupryianchyk et al. *(4)* evaluated the results of the bioassay using statistical tests, we here evaluate the modeling of the population dynamics in these laboratory tests. The agreement between modeled and measured values for the biomass increase in the bioassays is good for *G. pulex* and *A. aquaticus* in uncontaminated and heavily contaminated sediment (Figure 1).

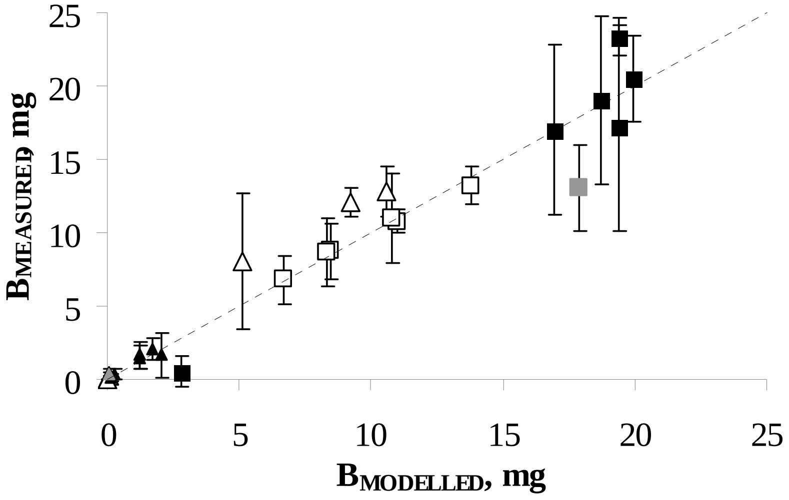

Figure 1. Modeled vs. measured biomass (±SD) of *G. pulex* (triangles) and *A. aquaticus* (squares). Open symbols relate to 28-d toxicity tests in uncontaminated sediment, closed black and closed gray symbols relate to 8- and 28-d toxicity test in PAH-contaminated Petroleum Harbor sediment amended with AC, respectively. Dashed line is the 1:1 line.

The agreement between modeled and measured data includes values for two different test durations, i.e. 8 and 28 days (Figure 1). Although the latter agreement does not demonstrate a full validation of the model, it provides some support for the assumed validity of the first-order approach as condensed in eqs 2 and 3.

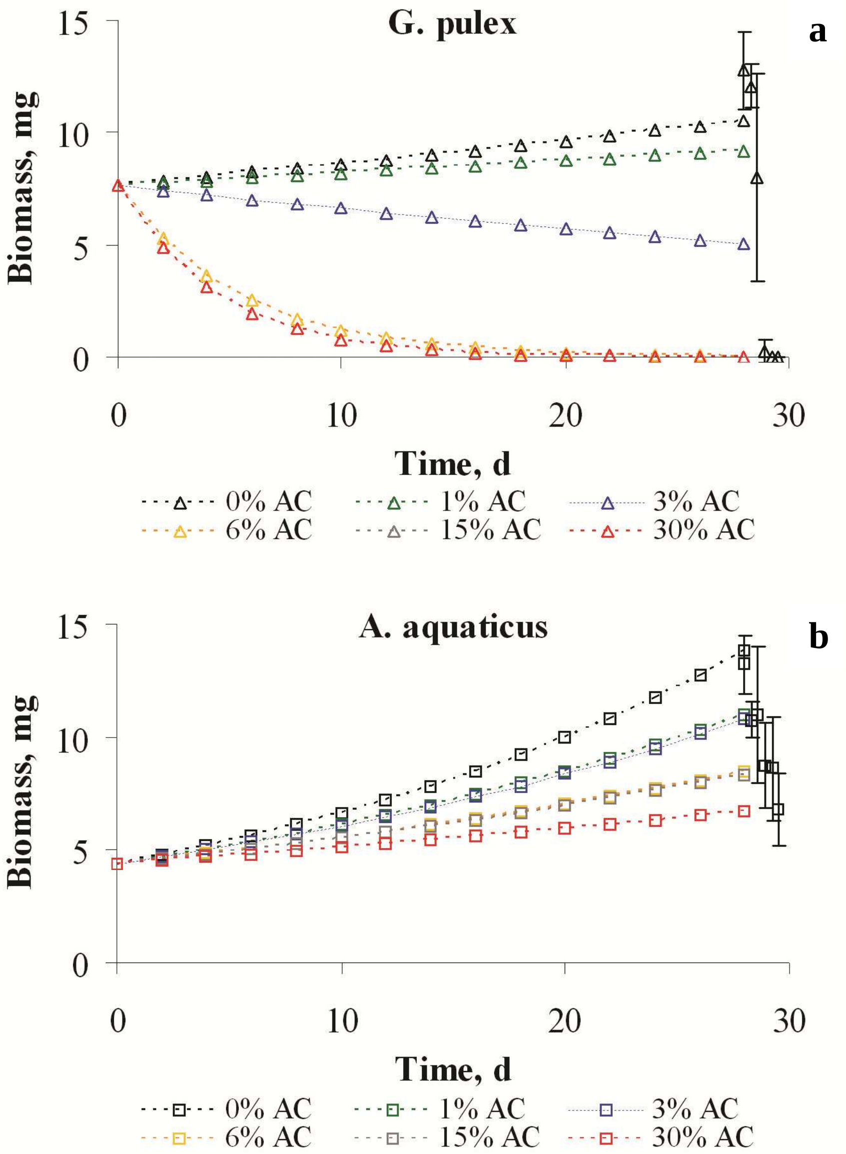

Figure 2. Population dynamics of *G. pulex* (a) and *A. aquaticus* (b) in uncontaminated sediment amended with 0, 1, 3, 6, 15, and 30% AC d.w. The markers correspond to a biomass (SD) measured in the 28-d toxicity test. The markers were deliberately set apart by ±1 d to avoid overlap of error bars (±SD).

Population dynamics in uncontaminated AC-amended sediment. The calculated mortality rates were used as input to model the population development of *G. pulex* and *A. aquaticus* in uncontaminated and heavily contaminated (PH) sediment. It appeared that amendment of uncontaminated sediment with 1% AC has no or only very mild effects on the modeled population dynamics of *G. pulex* (Figure 2a). Addition of 3% AC leads to an approximately 50% inhibition of biomass development, compared to the control group. Amendment of sediment with AC > 3% has a significant effect on *G. pulex* and eventually leads to extinction of the population. As for *A. aquaticus*, addition of AC to clean sediment also affects the modeled biomass development of the species. However, the predicted decrease in biomass can largely be explained by growth inhibition of *A. aquaticus* rather than mortality caused by AC addition (Figure 2b). After all, the fitted growth inhibition constant is about three times higher than the mortality rate constant at sediment AC concentrations exceeding 3% (Table 1).

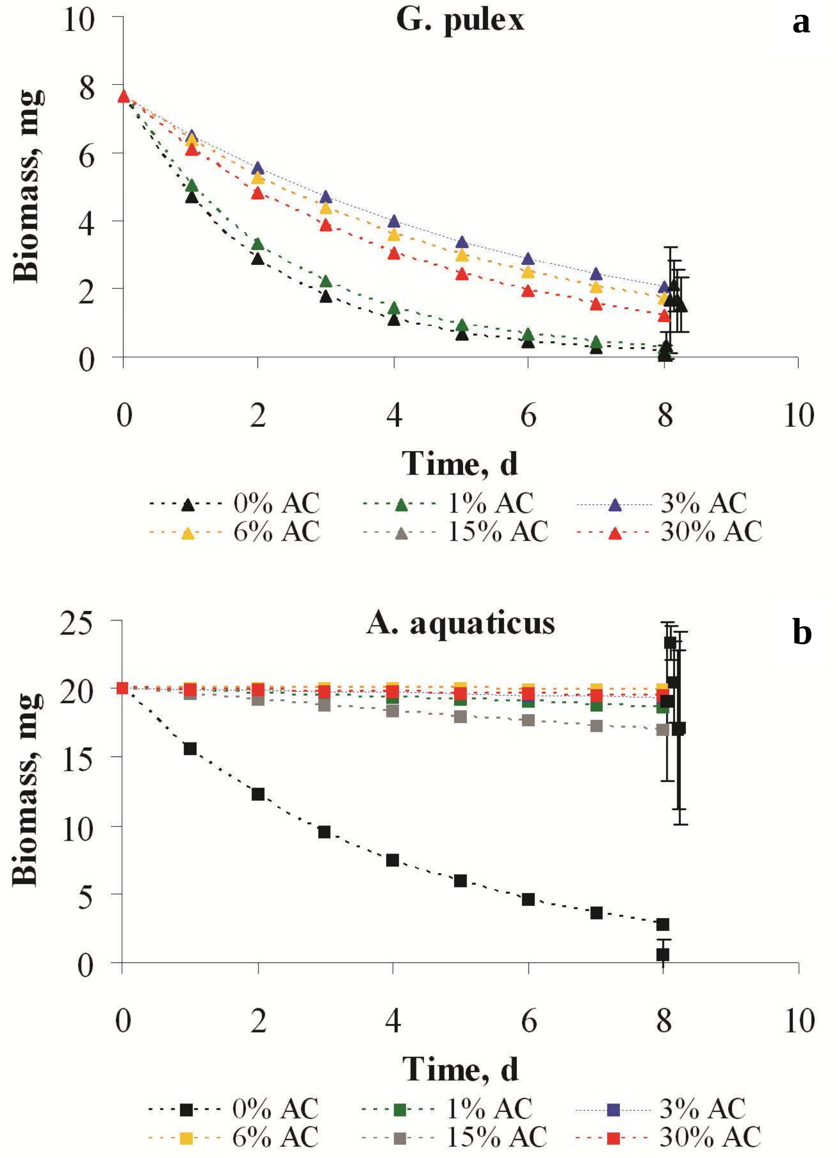

Figure 3. Population dynamics of *G. pulex* (a) and *A. aquaticus* (b) in PAH-contaminated sediment amended with 0, 1, 3, 6, 15, and 30% AC d.w. The markers correspond to biomass (±SD) measured in the 8-d toxicity test. The markers were deliberately set apart by ± 0.5 d to avoid overlap of error bars (SD).

Population dynamics in PAH-contaminated sediment amended with AC. In contaminated PH sediment without AC, the modeled effect of PAHs on the *G. pulex* population is severe and leads to a rapid decline of the population density within several days (Figure 3a). AC addition is able to improve survival of the species. Even the highest doses of AC, however, do not completely 'mask' the high levels of PAHs in the PH sediment, which results in a predicted extinction of the population of *G. pulex* (Figure 3a). Note that the 30% AC curve, which represents the condition with the highest reduction of PAH pore water concentrations, does not provide the best overall growth condition for *G. pulex.* This can be explained by the fact that at these high AC levels, the negative effects of AC are bigger than the positive effects of the reduction of pore water concentrations and associated toxicity of the PAHs. Instead, the curve for 3% AC appears to provide a better compromise for this species. Similarly, exposure of *A. aquaticus* to contaminated PH sediment without AC also leads to extinction within several days. Addition of AC to PH sediment again leads to survival, which for this AC-tolerant species requires only 1% AC, and does not show any decline at higher AC concentrations (Figure 3b).

The assimilation, growth, respiration, growth inhibition, and AC- and PAH-related mortality rate constants as specified in Table 1 and Figure S1 may be lumped into one overall value per AC concentration in the PH sediment, from which a population half-life can be calculated. If we define the time of extinction as four times the half-life, the calibrated model predicts that 3% AC extends the time to extinction from approximately 8 to 16 days for *G. pulex* and from 12 days to infinity for *A. aquaticus.*

Modeling the trade-off between toxicity reduction and negative activated carbon effects on macroinvertebrate populations

The previous section evaluated model simulations for the conditions of our previously published bioassays. Here we address the main aim of the paper, i.e. the exact trade-off between PAH toxicity reduction and negative AC effects on *G. pulex* and *A. aquaticus*, by simulating population equilibria for PH sediment. The equilibria are plotted as isoclines defining all combinations of AC dosage (% AC) and total PAH concentration in sediment (ΣC_{sed}) that yield zero growth of the population, and where the PAH ratios of the individual PAHs that make up ΣC_{sed}, agree with the ratios in the PH sediment (Figure 4). The PAH concentration matching that of PH sediment is marked in Figure 4. Lower concentrations can be regarded as dilutions of PH sediment, whereas higher concentrations resemble hypothetical sediments with a higher loading of PAHs. For *G. pulex*, the population equilibrium in untreated sediment is observed at $\mathrm{Log}\sum C_{sed} = 3.23$ (1,700 mg/kg) (Figure 4a, intersect of isocline with 0% AC line). This means that the population grows if the PAH concentration in untreated PH sediment is lower than this value. An increase in $\sum C_{sed}$ increases the toxicant-related mortality and therefore requires an increased concentration of AC to keep the population at equilibrium.

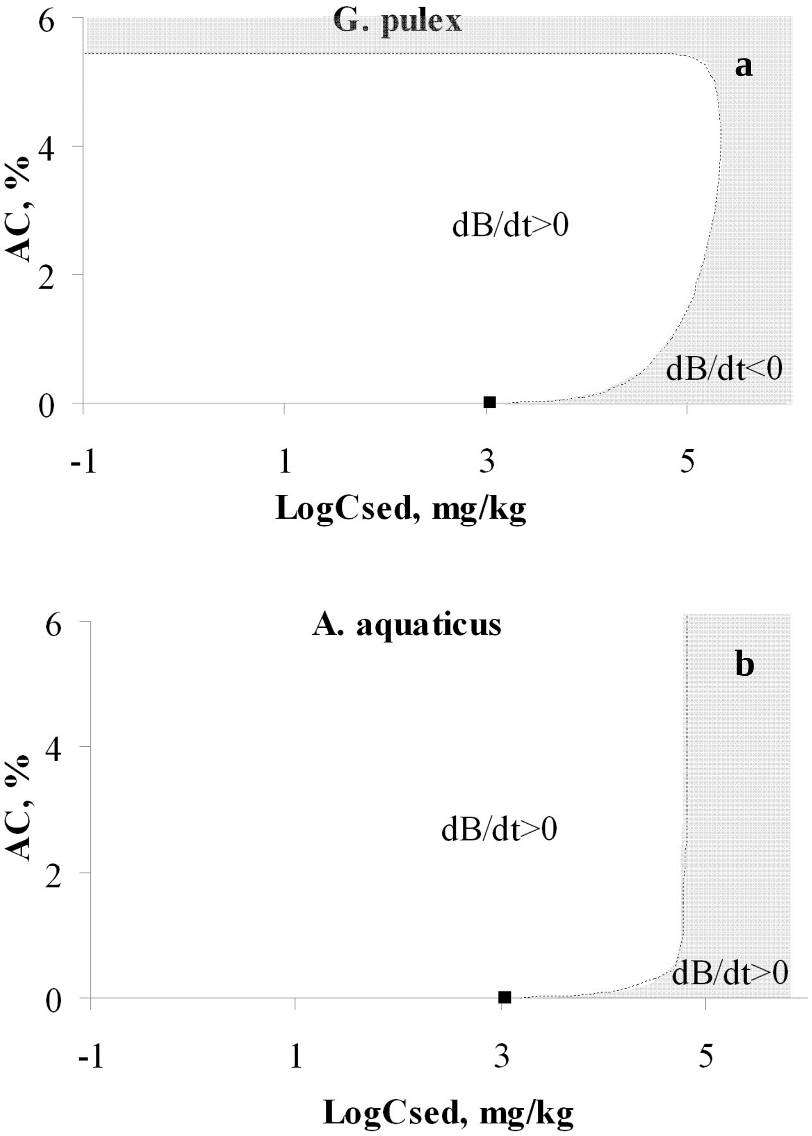

Figure 4. Isoclines, i.e. lines of zero growth, for *G. pulex* (a) and *A. aquaticus* (b). An isocline separates the part of the state space where the populations decrease (dashed area) from the state space where the populations increase (blank area). The black marker corresponds to the position of Petroleum Harbor sediment in the state space. To convert aqueous PAH exposure to sediment PAH concentrations, a Freundlich sorption model (eq 8) was used.

Increasing Log$\sum C_{sed}$ from 3.23 to a theoretical value of 5.34 (i.e., 220,000 mg/kg) requires an AC dose of 0% increasing to 4%, that is, about 1% AC per 70,000 mg/kg of extra $\sum C_{sed}$. This agrees to an unrealistically high AC binding capacity of 7 g PAH per g of AC, which illustrates the limitation of the Freundlich model to correctly describe sorption behavior at the highest concentration levels in Figure 4. A further increase in the PAH concentration becomes lethal and causes growth inhibition of the population. Besides the limit in $\sum C_{sed}$ there is a similar upper limit in the AC dose, which is indicated by the higher bound of the isocline.

When Log$\sum C_{sed}$ gradually varies from -1.00 to 5.34 (i.e. from 0 to 220,000 mg/kg), the tolerance to AC gradually varies from 4.0 to 5.5 %AC (Figure 4a). The maximum tolerance for PAHs is reached at an AC dose of about 4% and as indicated, is unrealistically high (220 g/kg PAH). This is explained by the Freundlich sorption model used (eq 8), which assumes equilibrium sorption to high affinity materials such as black carbon and activated carbon without a sorption maximum.

For *A. aquaticus*, the population equilibrium for untreated sediment is observed at Log$\sum C_{sed}$ = 3.02 (1,600 mg/kg) (Figure 4b, intersect of isocline with 0% AC line). Since the mortality of *A. aquaticus* due to AC is constant in the range of 1 - 30% AC (i.e. 0.005 d^{-1} on average), the isocline is constrained mainly by the toxicity of the PAHs in the sediment pore water. This implies a limit to the tolerance to PAHs, which in this case is calculated as Log$\sum C_{sed} \approx 4.82$ (65,000 mg/kg), and no limit to the tolerance (no upper bound) for AC (Figure 4b).

Once the isocline of zero growth has been estimated, one can predict what range of AC additions may be considered safe for a species, if 'safe' is defined as sustaining a habitat quality sufficient for population growth. For instance, for a sediment with Log$\sum C_{sed}$ = 4.30 (20,000 mg/kg), population growth is expected to occur between AC concentrations of 0.5 and 5.5 % (Figure 4). We emphasize that this result is conditional, i.e. it depends on the model formulations, the species used, the conditions in the test and the specific sediment employed in the tests. However, individual PAH profiles in aquatic sediments may show limited variation. For instance, the PAH contamination in the PH sediment we studied was identified to be of pyrogenic origin *(4)*. Consequently, we assume that the isoclines for *G. pulex* and *A. aquaticus* may look very similar for other sediments of pyrogenic origin, since PAH concentration ratios for this type of sediments show a narrow range *(48)*.

The results of the uncertainty analysis show that the uncertainties in model parameters at both ends of their uncertainty ranges (either ± SD or ± 10%) yield considerable uncertainty in the exact position of the isoclines (Figure S2). It is still possible, however, to define safe ranges of AC application, albeit by taking the conservative estimates of the isoclines that define the state space in which populations of *G. pulex* and *A. aquaticus* increase over time (Figure S2).

Using the same approach, isoclines were also calculated using a Langmuir sorption approach (eq 9). In this scenario the isoclines show the same general shape as the ones calculated with the Freundlich model, with almost identical values for AC% (Figure S3). However, the isocline values for Log$\sum C_{sed}$ are 1.3 to 1.8 unit lower than calculated using the Freundlich model (Figure 4 vs. Figure S3). This is explained by the fact that at equal values of C_W, the Langmuir model (eq 9) calculates lower values for $\sum C_{sed}$ than the Freundlich model (eq 8) does, due to inclusion of sorption saturation. At equal values of $\sum C_{sed}$ the Langmuir model thus calculates higher aqueous phase concentrations resulting in higher toxicity and to a smaller area in the state space where biomass development is positive ($dB/dt > 0$). In untreated sediment (AC % = 0), the population equilibrium is calculated at Log$\sum C_{sed} \approx 2.72$ (530 mg/kg) for both species (Figure S3), which is three times lower than predicted with the

Freundlich isotherms (Figure 4). This result agrees better to the experimental observation that both species did not survive in bioassays with untreated PH sediment, but did survive when an AC dose of 1% was added *(4)*. Increasing Log$\sum C_{sed}$ from 2.72 to a theoretical value of 3.34 (i.e., 2,200 mg/kg) now requires an AC dose of 0% increasing to 4%, that is, about 1% AC per 900 mg/kg of extra $\sum C_{sed}$ (Figure S3). This agrees to an AC binding capacity of 0.090 g PAH per 1 g of AC, which complies to the maximum adsorption capacities ($\sum C_{max}$) provided by van Noort *(32)*, which were used as input in the model. Based on the Langmuir scenario (Figure S3), a maximum of about 1 g/kg PAH with AC lower than 4% would be a conservative estimate of the limits for population growth.

In conclusion, a Langmuir modeling approach showed better agreement with experimental observations than a Freundlich approach. Although higher AC concentrations might have an effect on the biomass development of sensitive species such as *G. pulex*, the overall effects of AC addition to PAH contaminated sites are expected to be advantageous as long as AC is added at optimum concentrations (1 - 4%). At these AC concentrations, the positive effects of AC in terms of reducing PAH toxicity outweigh direct negative effects of AC.

Implications

The previous sections have shown how concepts from population ecology, environmental chemistry, and ecotoxicology may be unified in a simple framework to evaluate the interaction between multiple stressors, where one of the stressors has an advantageous (antagonistic) effect on the other. Once sufficient geochemical characteristics of sediments are known, like in a typical site-specific risk assessment, the state space where these characteristics support population growth of benthic communities can be simulated, taking into account the uncertainty in input parameters. If necessary, equations for population growth (eq 3), dose-response (eq 4), or exposure modeling (eq 8 and 9) may be adapted. This may include more detail in modeling for increased realism in higher tier assessments. For instance, better parameterization of Langmuir type sorption models (eq 9), which also may account for sorption competition, may further increase realism at the high concentration ranges for $\sum C_{sed}$, such as they may occur at ‘hot spot’ locations. Because higher realism implies increased uncertainty, one might also choose for simplification of the sorption or effect submodels (e.g., *(26, 27)*). If accurate pore water concentration data are available, it may be preferred to use eq 7 directly, thereby omitting relatively complex sorption submodels. Furthermore, the validity of current assumptions such as additivity of AC and toxicant mortality, and translatability of AC effects across sediments may be studied in more detail.

The current framework was evaluated for a specific case, but may be generally applicable to cases where sorbents are added to soils or sediments as amendments. Several recent approaches in sediment or soil treatment use the concept of sorbent addition, using, e.g., biochars, nanoparticles, or clays *(2, 49)*. As such, the conceptual modeling approach presented here may be used as a supporting tool in risk assessment or when designing sediment remediation scenarios. Obviously, for field applications more factors and processes need to be considered. For instance, the current model implementation addressed the potential effects of sorbents shortly after amendment of sediment, which is a relevant time frame for recolonization of benthic habitats. However, although this was realistic in terms of test species, environmental conditions and use of natively contaminated natural sediments, effects may be different at longer time scales and for other types of AC. Reported effects of AC from laboratory experiments may be less pronounced in ecologically realistic field settings. After all, deposition of fresh organic matter and dispersion of AC will form a new habitat for benthic species and may decrease or even eliminate effects observed in laboratory studies *(50)*. Furthermore, effects of AC could originate from reduction in the availability of trace nutrients *(3)*, which may be replenished more easily in an open system. Consequently, future work has to address the model's potential for field validation and application, including more accurate constraining of parameters where necessary and understanding their variability under natural conditions *(27, 28)*. This includes accounting for other variables that are important for biomass growth, like nutrient loads, dissolved oxygen content, presence of macrophytes or carrying capacity *(51, 52)*. Also, the use of other indicators of improved environmental quality than biomass, like biodiversity or species abundance, may be explored. Field-relevant processes such as colonization, competition and predation are available already in ecological models *(52)* and can easily be linked to the model constructs proposed and evaluated in this paper. Future work should also include validation of parameters using field data from demonstration sites.

Acknowledgments

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Supporting Information

Modeling the trade-off between toxicity reduction and negative activated carbon effects on macroinvertebrate populations using a Langmuir sorption approach

At low concentrations, monolayer adsorption onto BC and AC can be described with a Langmuir model:

$$C_{sed} = \frac{bC_{\max}C_W}{1+bC_W} \tag{1}$$

where C_{max} (µg/kg) is the maximum adsorption capacity of the sorbent and b (L/µg) is the sorption affinity. At low concentrations, when $bC_W << 1$, eq 1 reduces to:

$$K_d = \frac{C_{sed}}{C_W} = bC_{\max} \tag{2}$$

where K_d is the sorbent-water distribution coefficient (L/kg). Combining eqs 1 and 2 yields:

$$C_{sed} = \frac{K_d C_W}{1+\frac{K_d C_W}{C_{\max}}} \tag{3}$$

Now the pore water concentrations of individual PAHs (C_W^i) can be converted to solid phase concentrations (C_{sed}^i) by adding a Langmuir term as in eq 3 for BC as well as for AC to a linear partitioning term for amorphous organic matter (OC). This yields eq 9 in the manuscript:

$$\sum_{i=1}^{m} C_{sed}^i = f_{OC}\sum_{i=1}^{m} K_{OC}^i C_W^i + f_{BC}\sum_{i=1}^{m} \frac{K_d^{BC} C_W^i}{1+\frac{K_d^{BC} C_W^i}{C_{\max}^{BC}}} + f_{AC}\sum_{i=1}^{m} \frac{K_d^{AC} C_W^i}{1+\frac{K_d^{AC} C_W^i}{C_{\max}^{AC}}} \tag{4}$$

Table S1. Concentrations of four dominant PAHs, organic and black carbon content in Petroleum Harbor sediment

	Concentration
C_{PHE}, mg/kg	150 (3.4)
C_{ANT}, mg/kg	98 (1.3)
C_{FLU}, mg/kg	195 (5.1)
C_{PYR}, mg/kg	277 (3.1)
$\sum C_{sed}$, mg/kg	1100 (43)
f_{OC}, %	6.2 (0.06)
f_{BC}, %	2.1 (0.15)

Values are given as means (SD, n = 3).

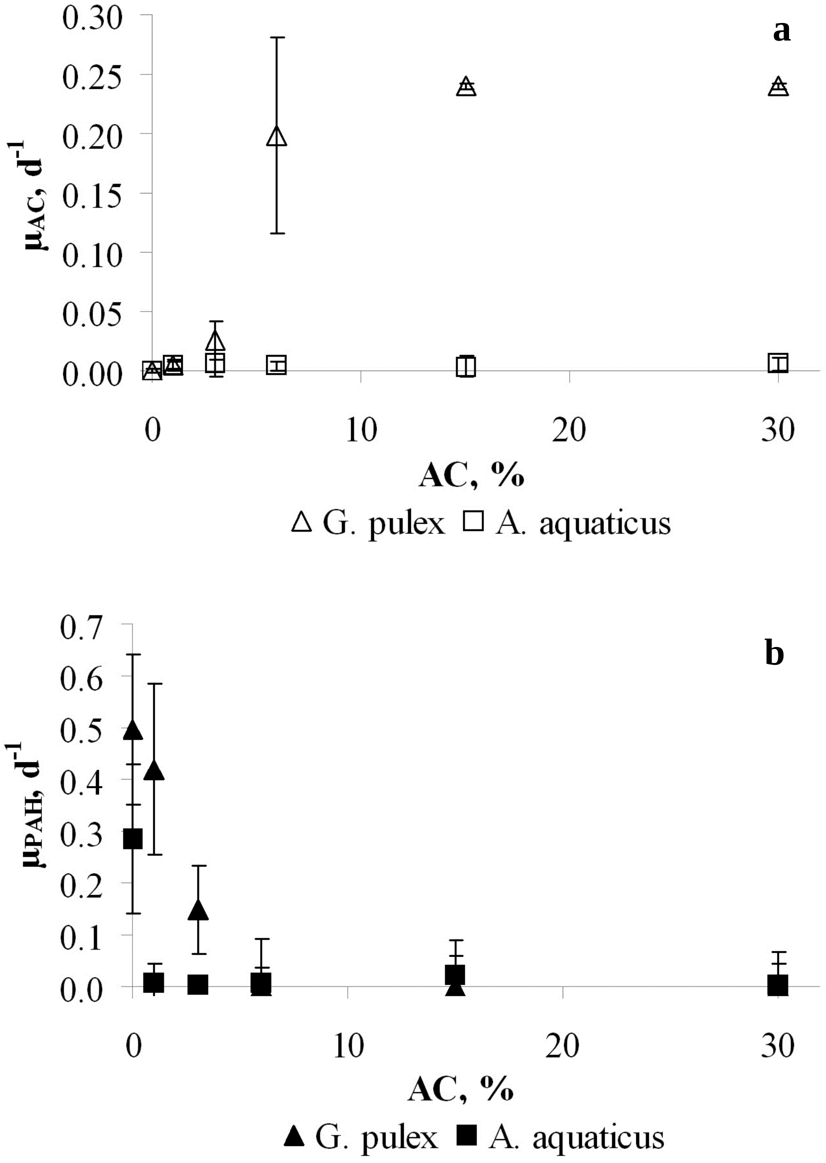
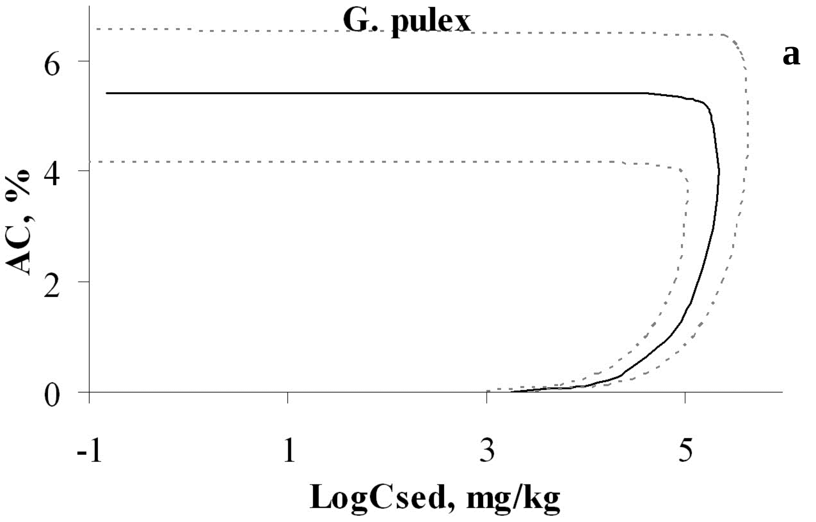


Figure S1. Mortality (SD) of *G. pulex* (triangles) and *A. aquaticus* (squares) due to AC (a) and PAHs (b) as a function of AC concentration.



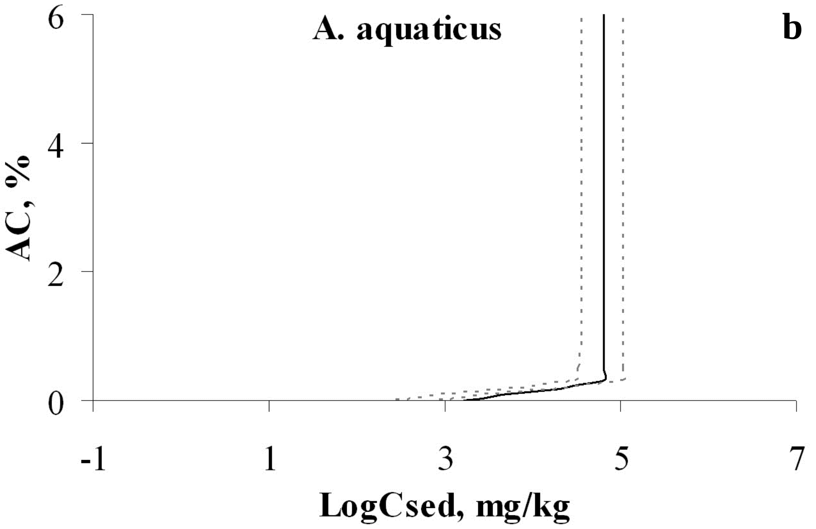
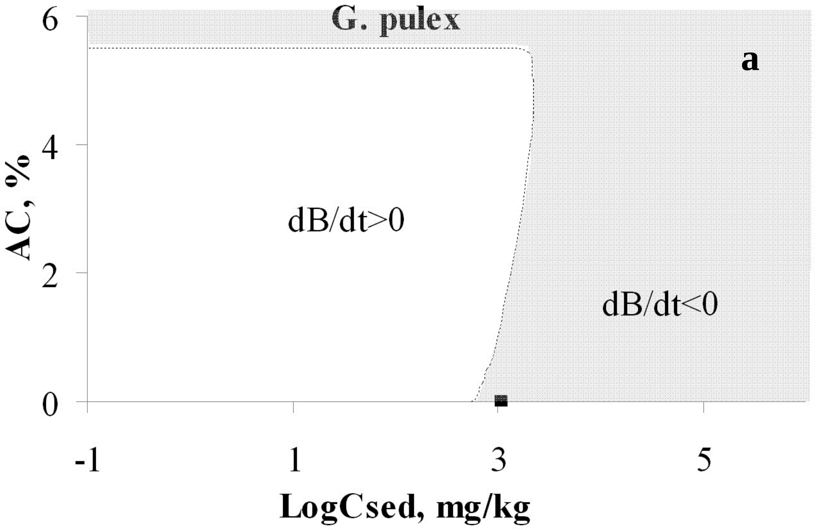


Figure S2. Uncertainty in the isoclines, i.e. lines of zero growth, for *G. pulex* (a) and *A. aquaticus* (b). Uncertainty ranges have been estimated using initial model parameters plus and minus SD or 10% of their values (Table 1). C_{sed} was calculated numerically using eqs 7 and 8.



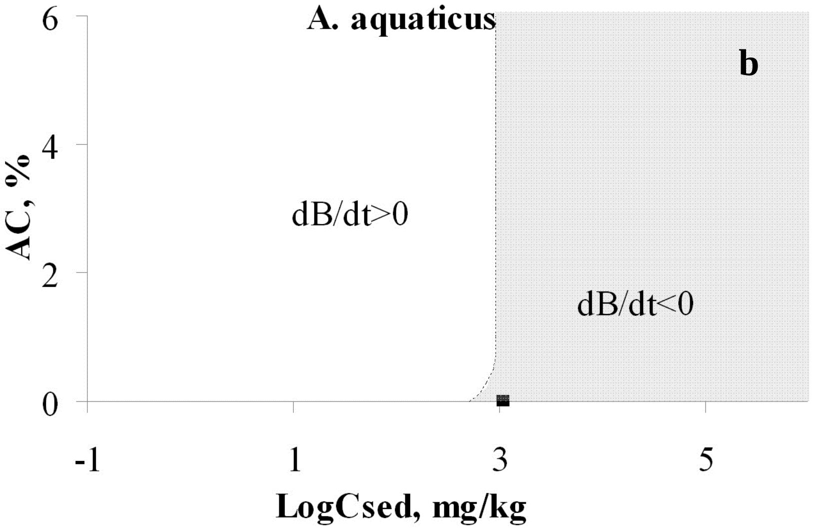


Figure S3. Isoclines, i.e. lines of zero growth, for *G. pulex* (a) and *A. aquaticus* (b). An isocline separates the part of the state space where the populations decrease (dashed area) from the state space where the populations increase (blank area). The red marker corresponds to the position of Petroleum Harbor sediment in the state space. To convert aqueous PAH exposure to sediment PAH concentrations, a Langmuir sorption model (eq 9) was used.

CHAPTER 7

LONG-TERM RECOVERY OF BENTHIC COMMUNITIES IN SEDIMENTS AMENDED WITH ACTIVATED CARBON

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Abstract

Using activated carbon (AC) for sediment remediation may have negative effects on benthic communities. To date, most AC effect studies were short-term and limited to single species laboratory tests. Here, we studied the effects of AC on the recolonization of benthic communities. Sediment from an unpolluted site was amended with increasing levels of AC, placed in trays and randomly embedded in the original site, which acted as a donor system for recolonization of benthic species. After 3 and 15 months, the trays were retrieved and benthic organisms identified. A positive trend with AC was detected for species abundance after 3 months, whereas after 15 months a negative trend with AC was detected for Lumbriculidae and Pisidiidae. On the community level, statistical analyses showed a considerable recovery in terms of species diversity and abundance in 3 months, and full recovery of the community after 15 months. This was explained from migration of individuals from the donor system, followed by further migration and reproduction of the species in the next year. AC treatments explained 3% of the variance in the community data. This work suggests that AC community effects are mild as long as AC levels are not too high (1-4%).

Introduction

Contaminated sediments pose a risk to aquatic environments by inducing changes in benthic communities *(1-4)*. Methods to remediate contaminated sediments aim at reducing sediment toxicity and traditionally rely on dredging. However, dredging is costly, laborious, may result in incomplete removal of the contaminated sediment or in resuspension of large amounts of contaminated particles, or may fail to reduce pore water concentrations of contaminants *(5)*. Moreover, sediment remediation by dredging leads to the total physical deterioration of benthic habitats and benthic communities. Sediment amendment with strong sorbents like activated carbon (AC) has been proposed as an alternative to dredging *(6, 7)*. It has been shown that AC efficiently reduces aqueous concentrations of hydrophobic organic compounds (HOCs) in aquatic sediments *(6-8)*, bioaccumulation of HOCs from contaminated sediments *(9, 10)*, and thus decreases the toxicity of sediments to different benthic species, e.g. *Ampelisca abdita*, *Gammarus pulex*, *Americamysis bahia*, *Asellus aquaticus*, *Lumbriculus variegatus*, *(11-14)*. At the same time, sediment amendment with AC may have negative effects on aquatic organisms. Reported negative effects include mortality to *Gammarus pulex* and *Corbicula fluminea*, growth inhibition in *Corbicula fluminea*, *Mytilus edulis* and *Neanthes arenaceodentata*, and decreased egestion rates and lipid content in *Lumbriculus variegatus (13-18)*. However, these observations relate to closed laboratory experiments with single species. We hypothesise that actual community effects are less severe in open field settings, where recolonisation occurs and where dispersion of AC and fresh input of organic matter will continuously form new habitats on top of treated sediments. Species in field settings may have a higher tolerance to stressors as a result of competition and selection *(19, 20)*. If effects of AC originated from a reduction in the availability of trace nutrients *(15, 21)*, this would be less serious in an open system where nutrients would be replenished more easily. Macrophytes will contribute to diversity in habitat by providing refugee and local differences in sediment structure, thus stimulating biodiversity of benthic species *(22)*. We are aware of only one study that directly compared contaminant effects in laboratory bioassays with community effects in the field *(4)*. They found that only 1.9% of *in situ* macroinvertebrate variation in the field was explained by laboratory bioassay responses, which supports the relevance of the aforementioned alleviating processes. Hence, translating observed laboratory effects at the species level to the community level in the field can be problematic. Apart from the translation issue, the mixing of AC into sediments on a large scale may partially disturb benthic habitats and benthic communities. Consequently, studies at the community and ecosystem level are essential to assess the ecological consequences of AC applications. To date, only three studies address AC effects on the community level. Cho et al. *(23)* observed no effect of the sediment amended with 3.2% AC on diversity and abundance of benthic communities after 6 and 18 month of exposure. Cornelissen et al. *(24)*, reported that benthic macrofauna composition and diversity were affected by different AC cappings, with an AC–clay mixture having a lower impact on the community than AC only or AC capped with sand. Näslund et al. *(25)* reported a considerable negative effect of a 1-2 mm AC capping treatment on macrofauna richness. These three studies show that the information on community level effects still is limited and contradictory. Mixing AC into the sediment typically will be associated with a severe physical disturbance of the sediment and relatively strong initial effects to the community due to initially high AC concentrations in the sediment top layers. Consequently, it makes sense to consider community effects in terms of recovery potential, i.e. by investigating recolonization of the amended sediments after an initial removal of benthic species. To our knowledge, the effects of AC amendments on the recolonization by benthic invertebrates have not been addressed before.

The aim of the present study was to determine the effects of AC concentration on the recovery of benthic communities in treated sediments over time. Community composition was characterized in terms of species diversity and abundance prior to treatment, after short-term recolonization (3 months) and after longer-term recolonization and community development (15 months). Five AC concentrations (0-10%) were tested in a controlled and replicated yet ecologically realistic field experiment, including interaction with macrophytes. To better isolate ecological effects of AC only, a non-polluted site was used. The key questions are: (1) what are the effects of sediment treatment with AC on the benthic community; (2) how does the subsequent recovery of benthic communities depend on time; and (3) which environmental variables play a role during the recovery process. Measurement of AC was included in all treatments to be able to address the long term fate of AC after sediment treatment.

Materials and methods

The study site

The colonization experiment was conducted in an uncontaminated natural ditch in "de Veenkampen" (VK), an experimental field site of Wageningen University, The Netherlands (51°58'52"N, 5°37'25"E). The ditch (3 m width, 1 m depth) is surrounded by extensive low-productive grasslands and fed by deep groundwater. Prior to the experiment, the benthic community composition was assessed, showing the presence of Insecta, Gastropoda, Malacostraca, Bivalvia, and Oligochaeta. Prior to the experiment, a sediment sample was taken for analysis of organic matter content. The sediment had a native black carbon (BC) and total organic carbon (TOC) content of 1.8 and 9.8 %, respectively (Table S1, Supporting Information). Although there was no direct source of contamination for the ditch, the presence of hydrophobic contaminants such as polychlorobiphenyl (PCB) and polycyclic aromatic hydrocarbons (PAHs) was tested and reported previously *(14)*. Total PAH and PCB were 4.7 mg/kg and 9.3 µg/kg, respectively, which is far below published toxicity thresholds, (Table S1).

Community colonization experiment

In short, colonization was studied by first removing sediment from the site, cleaning it from invertebrates, treating the sediment with AC, putting the treated sediment back in the ditch in trays, and monitoring the recolonization in these trays, where the surrounding community acts as a continuous donor system (Figure S1).

Sediment was collected from the site using 0.5 mm mesh size net in May 2009, sieved on a 2 mm mesh sieve, homogenized on a rollerbank for 24 h, and stored for two weeks in 26 L polyethylene buckets without headspace at 20°C to create anoxic conditions. These conditions eliminated all macroinvertebrates in order to prevent false colonization during the experiments. After anaerobic treatment, powdered AC (D50 = 15 µm , SAE Super, Norit, The Netherlands) was added to get final concentrations 0, 2, 4, 6, and 10 % d.w. Prior to use, AC was wetted to remove air pockets. After mixing with AC, sediment was homogenized on a rollerbank for 1 week. Open polypropylene trays (25 x 16 x 15 cm) were filled with 2 L of the treated sediment resulting in a sediment thickness of 5 cm and embedded in the unpolluted donor sediment at a distance of 0.5 to 1 m from each other. The randomly embedded trays included 20 trays (five AC treatments, 4 replicates) for community assessment after 3 months and an identical set of 20 trays for community assessment after 15 months. Trays were connected to wires spanning the width of the ditch in order to prevent the trays from sinking too deep in the sediment. The experiment was executed in the period from June 2009 till October 2010. After 3 and 15 months of exposure the trays were carefully retrieved. First, macrophytes present in the trays were removed and collected for dry weight determination. Second, a representative mixed sediment subsample was taken from each individual tray to determine TOC, BC and added AC (see below). Finally, for collecting the macroinvertebrates present in a tray, the sample material was sieved on 200 µm mesh size to reduce the sample volume, preserved in 96% ethanol and stored at 4 ºC. In the laboratory, benthic animals were sorted out from the remaining material under a binocular (magnification 10x), counted, and identified to the lowest possible taxonomic levels using available keys. This was done by certified biologists specialized in benthic invertebrate identification. Additionally, three macroinvertebrate samples from the donor system were taken with a standard dipnet (mesh size 0.5 mm) from a surface area of approximately 0.3 m^2. To eliminate any possible influence of cross-contamination with AC, these samples were taken at a distance of 10 m from the AC-treated trays, one upstream and two downstream. Three sediment samples for TOC, BC and AC determination were taken outside the trays (VK samples) at the centre of the test site, 10 cm from the trays with the highest AC concentration (i.e. 6-10%).

TOC and BC were determined in quadruplicate using chemothermal oxidation *(26)*. In short, organic carbon was removed by thermal oxidation at 375ºC (CTO375) and then inorganic carbon by *in situ* acidification with 2M HCl. The samples were analyzed using an EA 1110 CHN elemental analyzer (CE Instruments, Milan, Italy). AC was determined in quadruplicate using a wet chemical oxidation method developed and validated for this purpose *(27, 28)*. Briefly, sediment samples oxidized by 0.1M potassium dichromate in concentrated sulfuric acid solution were analyzed using the CHN elemental analyzer. Quality assurance included many blanks and reference samples. Note that these methods for BC and AC are operationally defined and not fully selective: CTO375 will also detect part of the AC, whereas the wet oxidation method is expected to detect residual carbon (RC), composed of a constant background level of natural BC plus added AC (RC=BC+AC).

Statistical analyses

Univariate analysis. AC treatment effects on the benthic community were studied using univariate community measures: number of taxa, species abundance, and the Shannon diversity index (*H*), describing the species diversity of the benthic community:

$$H = -\sum_{i=1}^{n} \left(p_i \ln p_i \right) \qquad (1)$$

where p_i is the relative abundance of a taxon *i*, calculated as the proportion of individuals of a given taxon to the total number of individuals in the community, and *n* is the number of taxa in the community.

The univariate community measures were normally distributed (Kolmogorov-Smirnov test $p = 0.05$) and therefore one-way ANOVA followed by Tukey's post-hoc test were applied to test for treatment effects. A two-tailed t-test was used to test for differences in the absolute abundance of species in each of AC treatments after 3- and 15-month exposure periods. The relationship between the tested variables was studied with Pearson's correlation. The null hypothesis (no difference between treatments) was rejected when $p<0.05$. Results were reported as a trend if $0.05<p<0.10$. All analyses were performed with PASW Statistics 17.0 (SPSS, Chicago, IL, USA). Linear regression analysis was performed in Microsoft Excel 2010 (Microsoft Corporation, Redmond, WA, USA).

Multivariate analysis. Redundancy Analysis (RDA) with partitioning of the variance was used to detect patterns and origins of variation in the macroinvertebrate data *(3, 4)*. Prior to the multivariate analysis, the data were Log(abundance+1) transformed. First, RDA was performed to quantify the variance explained by the explanatory variables (treatment, duration of exposure, macrophyte biomass) together. Then, the explanatory power and significance of each variable were determined through a series of single constrained RDAs, followed by Monte Carlo permutation tests with 499 permutations. The multivariate analyses were performed with CANOCO 4.5 for Windows *(29)*.

Results and discussion

Total organic carbon, black carbon and activated carbon after three and fifteen months

Mean (± SD) TOC after 3 and 15 months of exposure in the AC-treatments varied from 8.1 (± 1.1) to 12.2 (± 1.9) and from 5.2 (± 1.6) to 11.3 (± 0.6) % d.w., respectively (Figure S2a), thus showing some variability between the treatments as well as between time points. The analysis of AC content with the wet oxidation method showed a good proportionality with nominal AC concentrations up to 10% AC in the samples taken after 3 months (RC = 0.57 (±0.04)· (nominal AC) + 2.39 (±0.25), $R^2 = 0.94$; Figure S2b). The intercept of the regression line agrees well to the apparent 2 % RC in the control (Figure S2b), which relates to the background of natural BC in the Veenkampen sediment. The slope of the regression line (0.57±0.04) indicated that the wet oxidation method captured approximately 57 % of initial AC, which is approximately 10-30 % lower than the recoveries of powdered AC reported earlier *(27, 28)*. This could be explained from dilution of AC that may have occurred due to deposition of fresh organic material as was also observed in a long-term field experiment at Hunters Point, in San Francisco Bay, USA *(23)*. Analysis of the sediment adjacent to the trays with 6 and 10 % AC (samples VK1, VK2, and VK3 in Figure S2b) showed some higher RC contents compared to the controls (0% AC) and to the initial AC content in the ditch. We have no conclusive explanation for these differences. It cannot be ruled out that besides dilution, some transfer of AC from the trays to the near surroundings may have occurred during the long term exposure period. However, the differences in RC between tray and VK samples can also be explained from heterogeneity in the natural VK sediment, or from the difference in sampling method and pre-treatment of tray sediment samples versus VK sediment samples. The AC content in the treatments with 6 and 10 % AC, was lower than nominal AC concentration in the samples taken after 15 months (Figure 1). Other than local dilution with fresh OM, we have no conclusive explanation for this observation.

The comparison of results from the wet oxidation method with those obtained with CTO375 reveals the superiority of the former method in quantifying AC (Figure S3). The results of the BC analysis with CTO375 also show an increase with nominal AC concentration, but the method sensitivity is about 4-6 times lower than that of the wet oxidation method. Apparently, the CTO375 method is able of detecting about 15% of the AC type applied in this study. This agrees to earlier observations of carbon losses during the oxidation process of AC at 375º C *(28, 30, 31)*. The results of this study imply that the wet oxidation method can be suitable for analysis of AC in environmental samples.

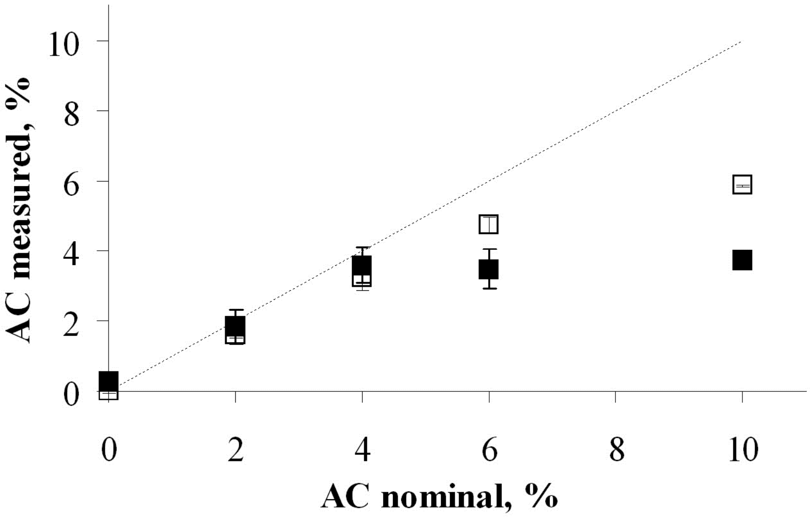

Figure 1. Measured activated carbon (AC) concentration (SD, n=4) with the wet oxidation method, vs. initial, nominal AC concentration in the Veenkampen sediment after 3 (open symbols) and 15 (closed symbols) months of exposure. AC is calculated as the difference between total residual carbon (RC) and natural black carbon (BC). The dashed line is the 1:1 line.

Community effects after three months of recolonization

After 3 months of exposure, a total of 26 taxa was identified in the treated sediments, most of them belonging to taxonomic classes of Insecta, Bivalvia, Gastropoda, Hirudinea, and Oligochaeta. Taxa that occurred in large numbers in all treatments were Pisidiidae, Lumbriculidae, Tanyponidae, and Erpobdella octoculata. The number of taxa in the trays varied from 4 to 11 (Figure S4a) and was not significantly different between treatments (one-way ANOVA, F (4, 16) = 1.148, p = 0.370). The number of individuals ranged from 180 to 1100 individuals/m^2 (Figure S5a). Remarkably, the absolute abundance of species in the controls without AC was lower than in treatments with AC (Figure S5a). The difference was not statistically significant (one-way ANOVA, F (4, 16) = 2.939, p = 0.053), but still may be interpreted as a trend. AC has been shown to alter bacterial communities and to cause an increase in bacterial production *(25)*. This may have an effect on nutrient cycles and consequently might relate to the observed differences in macrofauna abundances.

In the donor system a total of 11 different taxa was identified, dominated by other taxa than in the AC-treatments, e.g. Planorbidae, Pisidiidae, Asellidae, and Cloeon. The number of taxa ranged from 8 to 11 and the number of individuals was 720 - 910 individuals/m^2 (Figure S4a, Figure S5a). Comparison of the numbers of taxa and individuals in the control trays to those for the donor system shows that 65 % of the taxa from the donor system were present in the trays, and that taxa density in the control trays is almost 60 % lower compared to the donor system (Table 1). Interestingly, the benthic community recolonized the AC-treatments to a greater extent, viz. 72-94 % of the taxa and 63-99 % of the individuals.

The mean Shannon index (± SD), ranged from 1.40 (± 0.11) to 1.74 (± 0.18) for the AC treatments (Table 1, Figure S6a) and the observed differences were too small to be significant (one-way ANOVA, F (4, 16) = 0.938, p = 0.467), suggesting that sediment amendment with AC did not have an effect on biodiversity and abundance of the benthic taxa. The slightly higher Shannon index in the donor system was not significantly different either.

Macrophytes found in the trays belonged to the taxonomic groups *Chara sp*, *Elodea nuttallii, Potamogeton obtusifolius, Glyceria sp* and *Alisma plantago-aquatica.* The most abundant species found in all treatments was *Chara sp.* Analysis of macrophyte density showed a significant difference amongst treatments (one-way ANOVA with post-hoc, F (4, 16) = 5.767, p = 0.005), (Figure S7a). However, no relationship between macrophyte composition and densities and benthic composition or abundance was found after 3-m exposure (Pearson’s correlation, r (21) = 0.228, p = 0.320).

Community effects after fifteen months of recolonization

After long term exposure of 15 months, the treatments were still dominated by taxonomic classes of Insecta, Bivalvia, Gastropoda, Hirudinea, and Oligochaeta. A total of 25 taxa (vs. 26 after 3-month exposure) was identified in the treatments. Numerically abundant were Lumbriculidae, Tanypodinae, Erpobdella octoculata, Cloeon, and Pisidiidae. The number of taxa in the trays varied from 5 to 14 (Figure S4b), did not differ significantly between treatments (one-way ANOVA, F (4, 16) = 1.603, p = 0.222) and was comparable to the situation after 3 months post-treatment. The number of individuals ranged from 930 to 5200 individuals/m^2. The abundance of species slightly decreased with increasing AC (Figure S5b), however, this was not significant (one-way ANOVA, F (4, 16) = 0.496, p = 0.739). The donor system community now was dominated by the same taxa observed in the treatments, e.g. Chironomini, Lumbriculidae, Tanypodinae, Erpobdella octoculata, Cloeon, and Pisidiidae. The number of taxa in the donor system ranged from 8 to 12 and the number of individuals from 1040 to 1410 individuals/m^2 (Figure S4b and Figure S5b). Comparing the number of taxa and individuals in the control trays to the data for the donor system 15 months after treatment, it appears that 94 % of the taxa from the donor system were observed in the trays and density was almost twice as high as in the donor system (Table 1). We have no conclusive explanation for the higher density. To some extent this may be explained from missing individuals from the donor system with body size <0.5 mm, as was mentioned in the method section. However, natural spatial heterogeneity may provide a more plausible explanation. As trays and donor systems were ~10 m apart, some natural difference in habitat quality may have developed in 15 months. As for the AC-treatments, 75-103 % of the taxa from the donor system were present, whereas species density was 125-190 % of that in the donor system (Table 1). This indicates that after 15 months the benthic community completely recolonized the sediment treated with up to 10 % AC. This also shows that the trays did not act as barriers for recolonization for any of the species.

Mean (± SD) Shannon index ranged from 1.25 (± 0.29) to 1.54 (± 0.44) for the treated sediments (Table 1, Figure S6b), and was not different between AC-treatments (one-way ANOVA, F(4, 16) = 0.582, *p* = 0.680). Again the value for the donor system was slightly higher compared to AC treatments (1.89 ± 0.06) but not significant.

Macrophytes present in the trays were *Chara sp*, *Elodea nuttallii*, *Potamogeton obtusifolius*, *Fontinalis sp*, and *Alisma plantago-aquatica.* The variation in macrophyte densities between AC-treatments was not significant (one-way ANOVA, F(4, 16) = 1.998, *p* = 0.143) (Figure S7b) and quite comparable to the macrophytes densities after 3-month exposure period.

Time dependence of community recovery

The previous sections showed that there were no significant AC treatment effects on the recovery of the benthic community. However, the occurrence of progressive recolonization was clear and statistically significant. After 3 month exposure over summer (June to October 2009), some of the taxa were already present in high numbers, often equal to those found in the donor system. At that time, the total numbers of individuals of all species were already similar in the trays and in the donor system. A year later, i.e. 15 months post-treatment (June 2009 to October 2010), species abundance was not only higher than after 3 m of exposure but also higher than in the donor system. This suggests that recolonization during the first three months occurred mainly through active or passive migration of individuals from the donor system to the treatments, whereas recolonization over the following year occurred through both migration of adults and juvenile recruitment *(32)*. No obvious patterns in dominant fauna, presence of tolerant versus sensitive species could be observed between treatments, with two exceptions. First, a decreased abundance of Lumbriculidae was observed in the treatments with AC-sediment after 15 months (Table S2, Figure S8a). The difference in absolute abundance was statistically significant (one-way ANOVA, F (4, 16) = 3.024, *p* = 0.049) with the 10% treatment deviating from the others (Tukey post hoc test). Negative effects of AC addition on Lumbriculidae have been reported previously *(15, 16, 21, 33)*. It has been argued that sediment amendment with AC not only changes the geochemical characteristics of the sediment but also the dietary condition of deposit feeders *(21)*. When exposed to sediment enriched with AC, which has a low nutritional value, worms may start to metabolize their own lipids in order to avoid starvation. In the short term this can lead to a decrease in lipid content, ingestion and egestion rates, as has been shown in earlier laboratory experiments *(15, 16, 21, 33)*. In the long term, however, these processes might result in a decreased abundance of the populations. Second, the abundance of Pisidiidae was shown to be significantly lower after 15 months compared to 3-month exposure period (t-test, Table S3, Figure S8b).

Table 1. Recolonization, biodiversity and macrophyte density as a function of treatment and time[a].

System or AC treatment, %	**3 months**				**15 months**			
	Recolonization[b], %		**Shannon index**	**Macrophytes, g d.w.**	**Recolonization[b], %**		**Shannon index**	**Macrophytes, g d.w.**
	Taxa	**Individuals**			**Taxa**	**Individuals**		
Donor system	-	-	1.88 (0.35)[c]	-	-	-	1.89 (0.06)[c]	-
0	64 (9.3)[d]	38 (21)[d]	1.51 (0.21)[d]	0.41 (0.24)[d]	94 (11)[d]	190 (74)[d]	1.43 (0.20)[d]	1.34 (1.07)[d]
2	94 (37)	92 (24)	1.62 (0.53)	0.71 (0.49)	75 (17)	187 (83)	1.25 (0.29)	0.39 (0.56)
4	72 (19)	63 (17)	1.40 (0.11)	1.73 (1.29)	88 (15)	125 (65)	1.41 (0.32)	0.64 (0.62)
6	89 (27)	74 (53)	1.74 (0.18)	0.16 (0.14)	85 (5.8)	169 (25)	1.31 (0.19)	1.22 (0.62)
10	86 (25)	99 (24)	1.43 (0.25)	1.68 (0.21)	103 (26)	145 (128)	1.54 (0.44)	0.31 (0.13)

[a] Values are given as means (SD, n=4, [c] n=3, [d] n=5).

[b] Calculated as number in trays divided by number in surrounding donor system *100%.

Furthermore, after 3 months a positive trend with increasing AC dose was detected for this species (one-way ANOVA, F(4, 16) = 2.713, *p* = 0.067). However, after 15 months, this trend was no longer significant (F(4, 16) = 1.630, *p* = 0.215) suggesting a decrease of AC effects over time. These AC effects can also be explained by altered dietary conditions of the clams, which may cause reduced feeding and, in turn, reduced growth and reproduction *(34)*. Additionally, exposure to AC might lead to gill-clogging by fine AC particles that affect both feeding and respiration of the animals *(35)*. Earlier studies showed ecotoxicological effects of AC on bivalve molluscs and worms *(13, 15-18, 21)*, and identified these species as sensitive to AC application. Now that our data reveal similar trends in realistic field settings, we suggest that the further investigation of the sensitivity of these species in realistic field settings is a research priority.

Multivariate analysis of the community data

RDA revealed that 49.5% of the variation in the dataset was explained by duration of the exposure, AC content (WO method), and presence of macrophytes. The remaining unexplained variation may be due to biological factors unaccounted for in this study, like predation, competition, sediment habitat characteristics, food quality and availability, pH, temperature, or oxygen content. The duration of exposure to the AC treated sediment was highly significant in the forward selection procedure, explaining 43.6 % of the total variation in the benthic community structure (*p* = 0.002) (Table 2). AC explained 3% of the variation, which also was significant (*p* = 0.020). An AC community effect based on variance partitioning has not been reported before. Interestingly, the contributions of macrophytes density was the smallest, i.e. 2.4%, and not significant (*p* = 0.108).

Table 2. Partitioning of the variance in the community data[a].

	Initial AC as explanatory variable		**Measured AC as explanatory variable**	
Source	**Variation explained, %**	***p* value**	**Variation explained, %**	***p* value**
AC content	9.00	0.008	3.10	0.020
Exposure time	44.8	0.002	43.6	0.002
Macrophytes	2.40	0.046	2.20	0.108
Unexplained	43.7	-	51.5	-

[a] % variation explained, as obtained from redundancy analysis with activated carbon (AC) concentration, exposure time and macrophytes density as explanatory variables.

Using the nominal AC concentration instead of AC measured with WO, yielded a higher impact of AC (9% variation explained and higher significance; Table 2). However, we consider the result with measured AC as more realistic and relevant because (a) it better reflects actual exposure, and (b) the other explanatory variables were also considered after exposure.

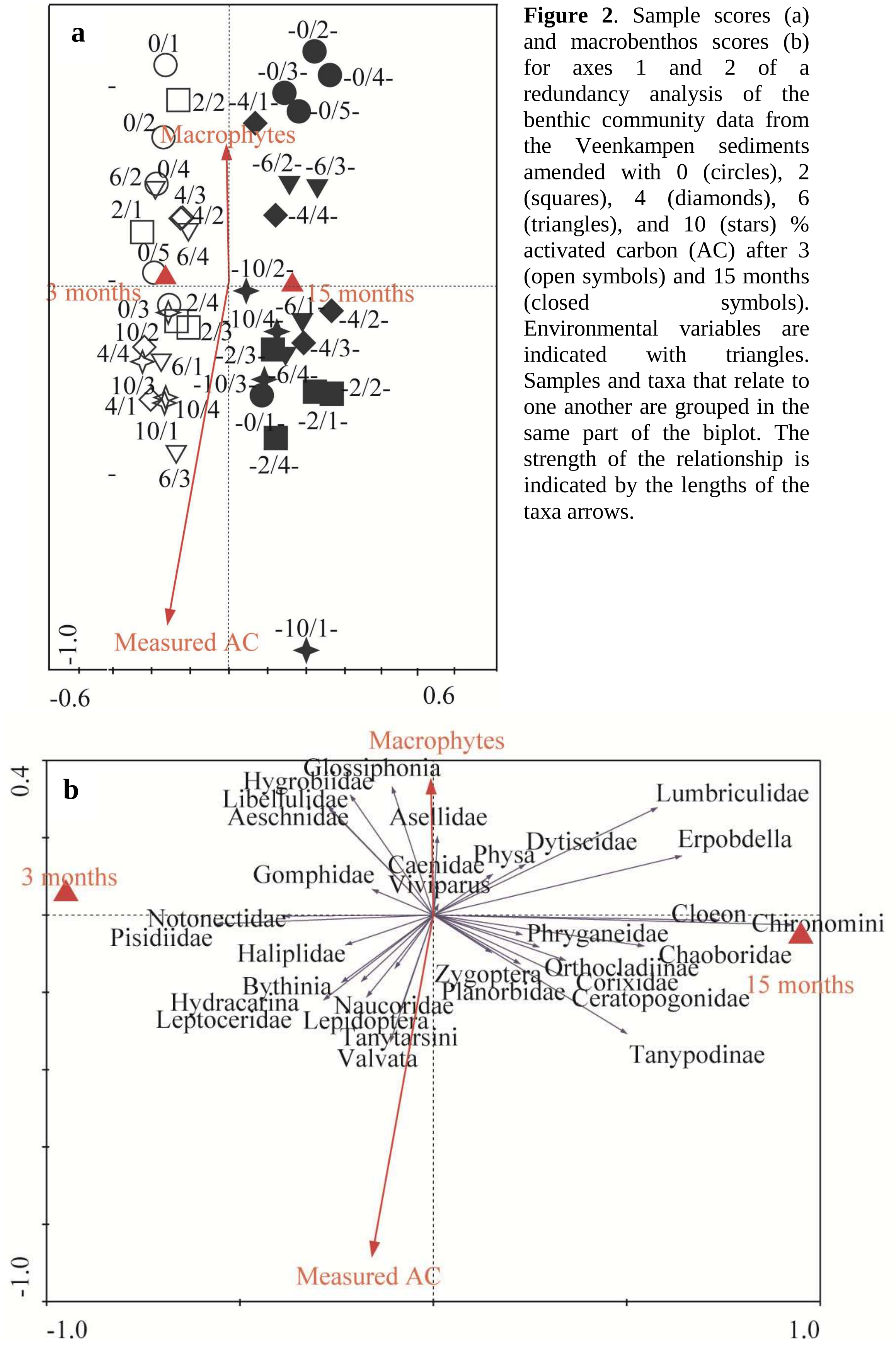

Figure 2. Sample scores (a) and macrobenthos scores (b) for axes 1 and 2 of a redundancy analysis of the benthic community data from the Veenkampen sediments amended with 0 (circles), 2 (squares), 4 (diamonds), 6 (triangles), and 10 (stars) % activated carbon (AC) after 3 (open symbols) and 15 months (closed symbols). Environmental variables are indicated with triangles. Samples and taxa that relate to one another are grouped in the same part of the biplot. The strength of the relationship is indicated by the lengths of the taxa arrows.

The first two RDA axes accounted for 44.7 and 3.1 % of variation in the samples and species data, respectively. The first RDA axis shows a clear separation of the samples based on the duration of the exposure, i.e. trays retrieved after 3- months are on the left-hand side and those retrieved after 15 months are on the right-hand side of Figure 2a. The second RDA axis relates to AC concentration with the highest level in the lower part of the graph (Figure 2a). Accordingly, taxa found in few systems regardless AC content and exposure time occupy the centre of the ordination plot and belong to Caenidae, Zygoptera, Phryganeidae, Gomphidae, Valvata, Viviparus, Bythinia, Physa, Asellidae, and Glossiphonia heteroclita (Figure 2b). Taxa in the left-hand side of the diagram, viz. Aeshnidae, Hygrobiidae, Notonectidae, Lepidoptera, and Libellulidae show a strong correlation with samples retrieved after 3 months of exposure. However, the abundance of these taxa is so low (Table S2) that absence of the aforementioned taxa in samples retrieved after 15 months should not be interpreted as an AC treatment effect. Numerically dominant species in the study, e.g. Lumbriculidae, Erpobdella octoculata, Tanypodinae, Chironomini, Cloeon, and Chaoboridae, corresponded closely to samples retrieved after 15-month exposure and indicate a role of time in recolonization process.

Although positions of samples and taxa along the second RDA axis correlate with the AC gradient (Figure 2b), treatments and taxa were not clearly separated or grouped based on AC concentration. Moreover, a higher dispersal of samples of the same AC treatment after 15 months compared to 3 month exposure, suggests that natural processes have a higher effect on community structure, richness and abundance than disturbances related to sediment treatment and/or AC effects. Thus, our data do not support a strong impact of AC on the recolonization of benthic communities.

Implications

In summary, the above analysis shows that the benthic community recovered well in a period of 15 months, despite addition of up to 10 % AC to the sediment. The detection of a statistically significant effect of AC on the community level was not considered to be alarming because it was only 3%. After recovery, the number of taxa and their abundance were comparable to that prior to treatment. Moreover, assemblage composition, taxonomic richness and abundance found in this study agreed to those reported recently for a wide range of natural and semi-natural lentic water bodies, consisting of 18 Dutch drainage ditches and small lakes *(36)*. Consequently, we argue that our recolonized systems can be considered as having a good ecological status. However, whereas a positive trend with AC was detected for species abundance after 3 months, a negative trend with AC was detected for Lumbriculidae and Pisidiidae after 15 months. This illustrates the sensitivities of these species to AC in a field community. This sensitivity was known from earlier single species laboratory tests *(13, 15-18, 21, 37)*. It can be argued that effects of AC reported in the literature, such as altered lipid content, ingestion and egestion rate, condition index, and mortality *(13, 15-18, 21, 37)* relate to species-specific life-history traits *(38)*. For instance, it has been argued before that taxa ingesting the sediment and living with their body completely or partially in the sediment are more sensitive and more affected by sediment treatment than other species that are more or partly connected to the overlying water *(33)*. Consequently, we suggest future studies should explore the sensitivity of these species in a wider variety of realistic field settings. Effects of AC additions on reproduction (the least studied end point) would be of great importance for a better understanding of AC effects on benthic communities in the long term. As for other taxa, the effect of AC in the field seems to be absent or less severe than in the laboratory experiments *(14, 16, 17)*. Despite the existence of species relatively sensitive to AC amendments, they were not extinct after long term exposure. Consequently, at the level of the entire community and for AC levels used in technical applications (<4%), we consider the effects of AC addition to unpolluted sediment to be mild.

Furthermore, it should be noted that AC will never be applied to clean sediments. Sediments that are to be remediated carry high concentrations of HOCs. For such sediments it has already been shown that at AC concentrations <4% , the positive effects of AC in terms of reducing HOC toxicity, outweigh the negative ecological effects of AC application and therefore lead to a substantial improvement of habitat quality *(14, 23, 33, 39)*.

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Supporting Information

Table S1. PAH and PCB concentration, total organic carbon (TOC) and black carbon (BC) content in Veenkampen sediment *(14)*.[a]

PAHs	C, mg/kg	PCBs	C, µg/kg
Acenaphthylene	<LOD	CB-18	<LOD
Acenaphthene	<LOD	CB-20	<LOD
Anthracene	0.28 (0.01)	CB-28	<LOD
Benzo[a]anthracene	0.09 (0.003)	CB-29	<LOD
Benzo[a]pyrene	0.05 (0.002)	CB-44	<LOD
Benzo[b]fluoranthene	0.08 (0.003)	CB-52	1.4 (0.05)
Benzo[e]pyrene	0.12 (0.01)	CB-101	1.6 (0.01)
Benzo[ghi]pyrylene	0.04 (0.001)	CB-105	<LOD
Benzo[k]fluoranthene	<LOD	CB-118	1.2 (0.06)
Chrysene	0.25 (0.01)	CB-138	2.5 (0.09)
Dibenzo[a,h]anthracene	0.04 (0.001)	CB-149	<LOD
Fluoranthene	1.4 (0.03)	CB-153	1.7 (0.07)
Indeno[1,2,3-cd]pyrene	0.03 (0.001)	CB-155	<LOD
Naphthalene	<LOD	CB-180	0.91 (0.08)
Phenanthrene	0.81 (0.07)	CB-194	<LOD
Pyrene	1.5 (0.05)	CB-204	<LOD
		CB-209	<LOD
∑PAH	**4.7 (0.32)**	**∑PCBs**	**9.3 (0.42)**
Threshold concentration for intervention	**40**[b]	**Probable effect concentration**	**676**[c]
TOC, %	9.8 (0.41)	**BC**, %	1.8 (0.25)

[a] SD between parenthesis. LOD = limit of detection.
[b] ref *(40)*.
[c] ref *(41)*.

Table S2. Taxa list of benthic macroinvertebrates.

Phylum	Class	Taxon	Average absolute abundance in the AC treatments and in the donor system											
			3 months						15 months					
			0	**2**	**4**	**6**	**10**	**Donor[a]**	**0**	**2**	**4**	**6**	**10**	**Donor[a]**
Annelida	Oligochaeta	Lumbriculidae	2.40	3.00	2.00	2.50	-	-	36.6	6.75	10.3	19.8	1.50	0.87
	Hirudinea	Glossiphonia heteroclita	1.00	1.50	0.50	0.25	1.50	0.60	2.00	-	0.75	0.25	0.50	0.53
		Erpobdella octoculata	1.20	1.50	0.50	0.75	1.25	1.60	5.60	4.75	2.75	4.00	3.75	2.18
Mollusca	Gastropoda	Viviparus	-	-	0.25	-	-	-	-	-	-	-	0.25	-
		Valvata	-	-	-	0.25	0.25	-	-	-	0.25	-	-	-
		Bythinia	-	-	0.25	0.25	-	-	-	-	-	-	-	-
		Physa	-	-	-	-	-	2.13	0.80	-	-	-	-	-
		Planorbidae	0.20	0.25	0.25	-	-	7.96	-	0.50	-	0.75	2.00	-
	Bivalvia	Pisidiidae	5.60	17.8	13.5	14.3	22.3	3.07	7.00	3.25	2.50	5.75	6.67	2.44
Anthropoda	Arachnida	Hydracarina	0.20	-	-	0.25	0.50	-	-	-	-	-	0.25	-
	Malacostraca	Asellidae	0.20	0.75	-	0.25	0.25	7.60	0.80	-	-	1.00	-	1.13
	Insecta	Cloeon	-	-	-	-	-	4.71	3.60	1.25	3.00	2.25	3.25	6.93
		Caenidae	-	0.25	-	-	-	-	-	-	0.25	-	-	-
		Aeshnidae	0.40	0.25	-	-	-	-	-	-	-	-	-	-
		Gomphidae	-	0.25	-	-	-	-	-	-	-	-	-	-
		Libellulidae	0.20	0.50	-	-	-	-	-	-	-	-	-	-
		Zygoptera	-	-	-	-	-	-	-	-	-	0.25	-	-
		Notonectidae	0.20	0.50	0.25	1.00	-	-	-	-	-	-	-	-
		Corixidae	-	-	-	-	-	2.87	0.40	0.25	0.25	-	0.75	0.93
		Naucoridae	-	0.25	-	-	0.25	-	-	-	0.25	-	-	-
		Haliplidae	0.20	0.25	0.25	0.25	1.50	1.20	0.60	-	-	-	0.25	0.73
		Dytiscidae	-	-	-	-	-	-	0.20	-	-	-	0.25	-
		Hygrobiidae	0.40	-	-	-	-	-	-	-	-	-	-	-
		Leptoceridae	-	-	0.75	0.50	0.25	0.67	-	-	0.25	-	-	-
		Phryganeidae	-	-	-	-	-	-	-	-	0.25	0.25	-	0.67
		Lepidoptera	-	-	-	0.25	-	-	-	-	-	-	-	-
		Chaoboridae	0.60	-	-	0.50	-	0.93	3.60	10.3	5.50	6.25	1.50	5.24
		Tanypodinae	-	2.00	2.00	3.00	3.50	3.33	3.00	31.5	4.50	6.25	15.8	11.7
		Tanytarsini	-	0.25	-	0.25	0.25	-	-	-	-	-	0.50	-
		Chironomini	0.20	1.25	0.75	0.75	0.75	0.80	52.4	56.3	44.5	55.5	52.0	29.6
		Ceratopogonidae	-	0.50	0.25	-	1.00	-	1.20	0.50	1.75	1.25	1.50	1.20
		Orthocladiinae	-	0.25	-	-	0.25	4.33	-	0.75	0.50	0.75	0.25	1.33

[a] The abundance in the donor system (0.3 m^2) is normalized to the surface area of that in AC treatments (0.04 m^2)

Table S3. Statistics of unpaired t-tests used to study the effect of the exposure time on absolute abundance of Pisidiidae in different AC treatments.

AC treatment	**d.f.**	***t*-value**	***p*-value**[a]
0	8	-0.487	0.639
2	6	5.090	0.002**
4	6	6.518	0.001**
6	6	1.295	0.243
10	6	2.881	0.028*

[a] * = $p < 0.05$; ** = $p < 0.01$

Figure S1. Pictures of colonization experiment: (a) test trays with AC-sediment before (to the left) and after (to the right) the exposure, (b) macrobenthos present in one of the AC-treatments.

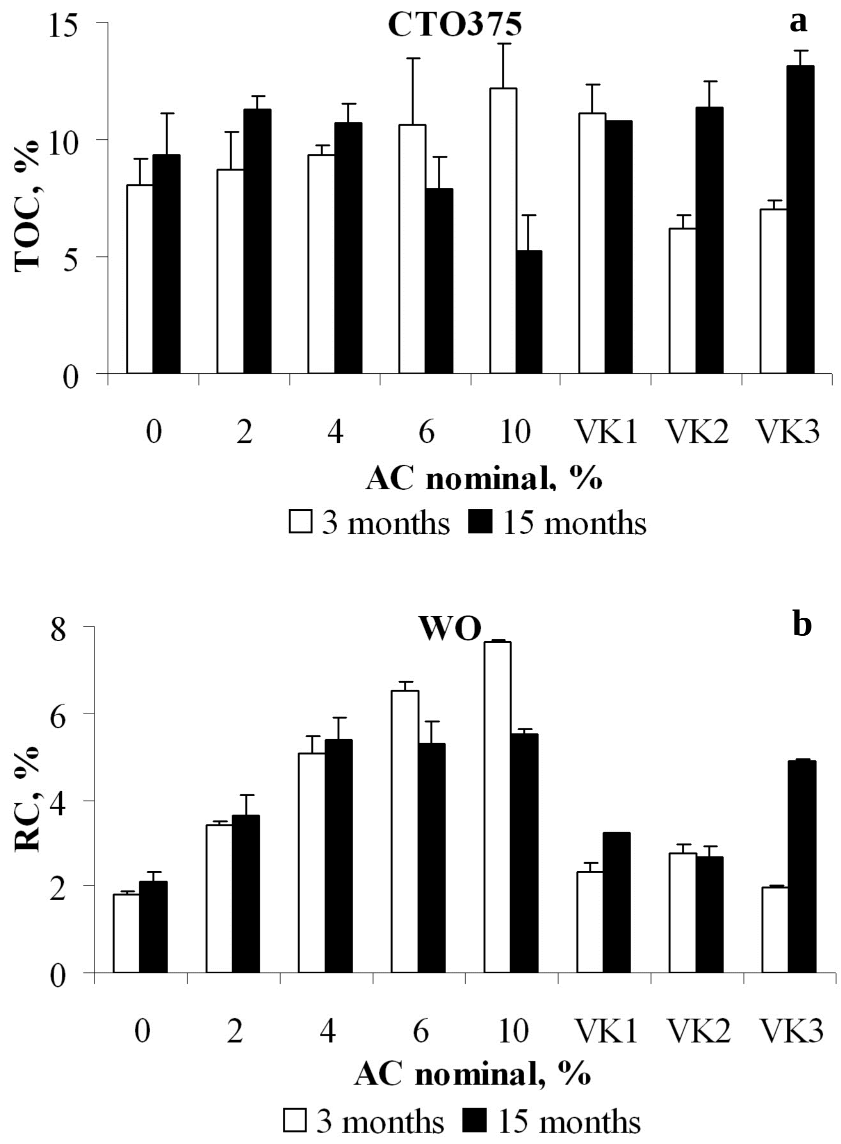


Figure S2. Total organic carbon measured with CTO375 method (SD, n=4) (a) and residual carbon measured with wet oxidation method (SD, n=4) (b) in the Veenkampen sediment after 3 (open bars) and 15 (closed bars) months of exposure. "VK" relates to sediment samples from the Veenkampen donor system. Residual carbon (RC) is the sum of natural black carbon (BC) and added activated carbon (AC) (RC=BC+AC). Linear regression of RC against nominal AC for the 3 month data: RC % = (0.57 ±0.04)·(nominal AC) + (2.39±0.25), $R^2 = 0.94$.

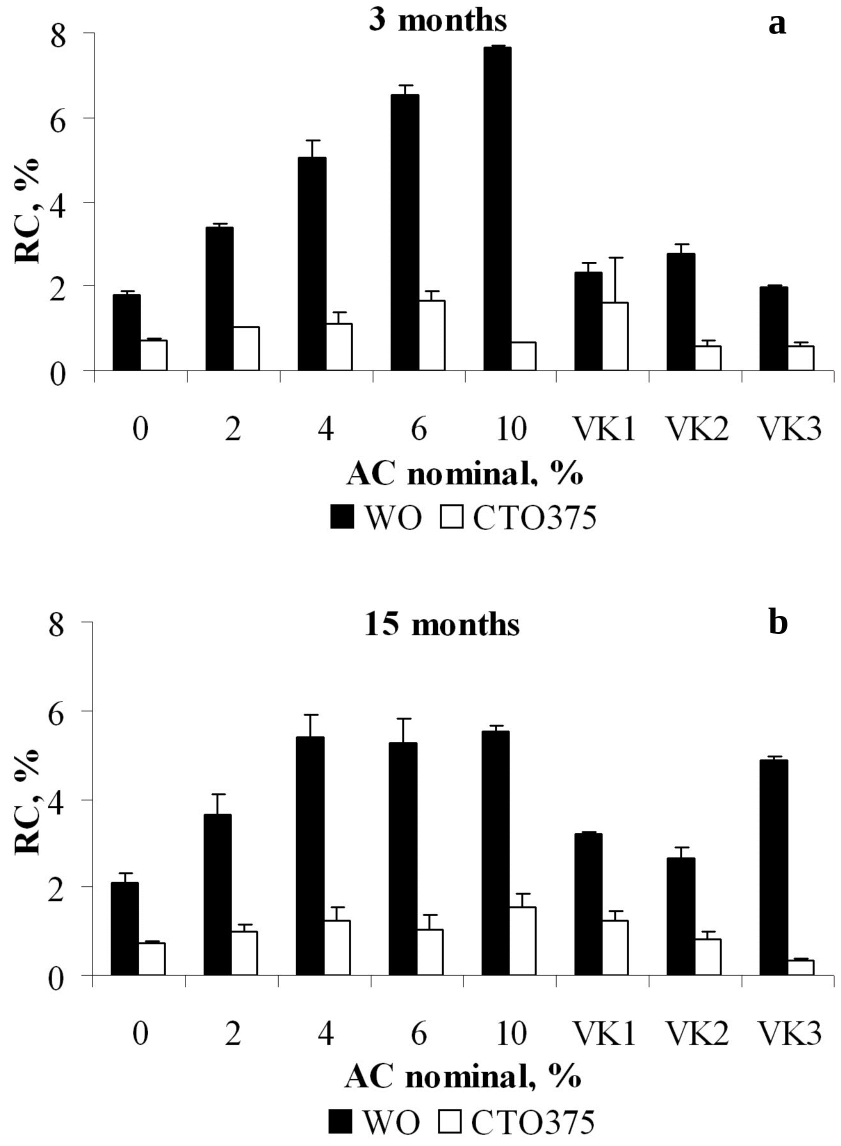
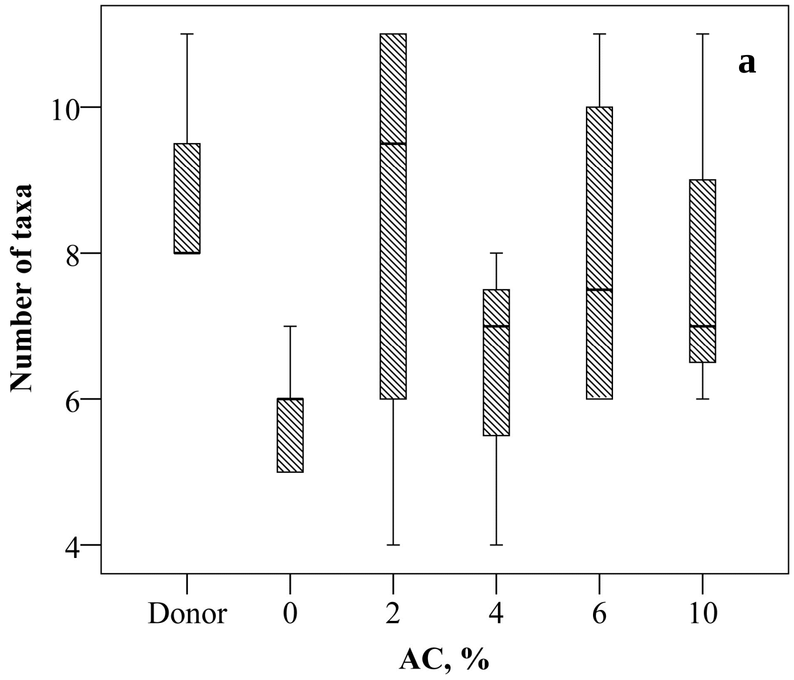


Figure S3. Residual carbon (SD, n=4) in the Veenkampen sediment after (a) 3 and (b) 15 months of exposure analyzed with wet oxidation (closed bars) and chemothemal oxidation method (open bars). "VK" relates to sediment samples from the Veenkampen donor system. Residual carbon (RC) is the sum of natural black carbon (BC) and added activated carbon (AC) (RC=BC+AC).



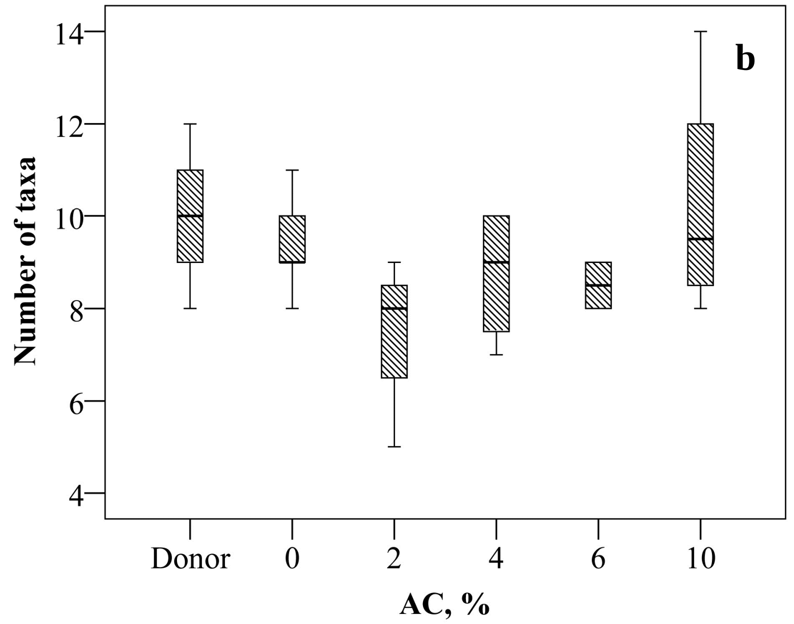
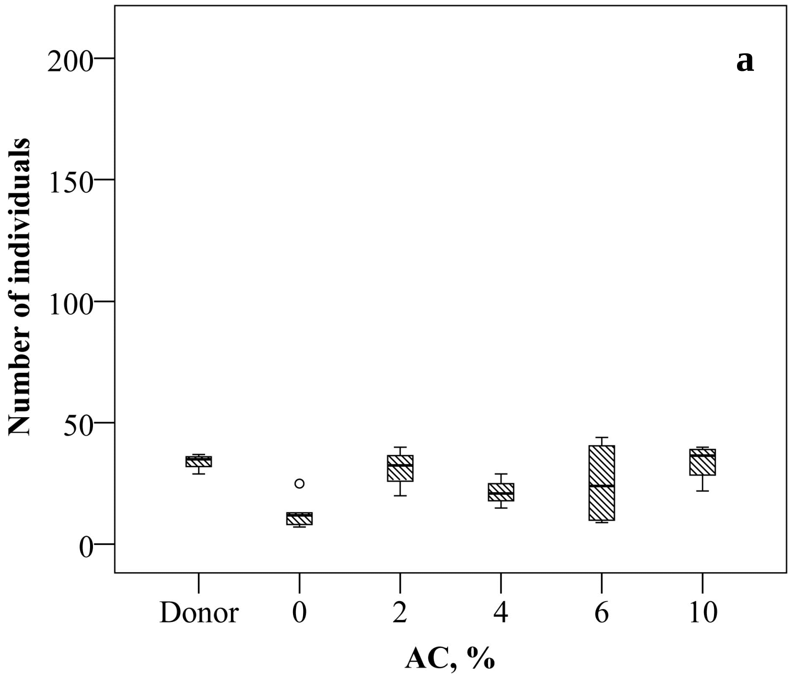


Figure S4. Number of taxa after (a) 3 and (b) 15 months of exposure to AC-sediment. Boundaries of the box plots indicate the 25th and 75th percentile. Whiskers below and above indicate the minimum and maximum of the variables. The median is indicated with the black line. 'Donor' relates to the community in the system surrounding the treated sediments.



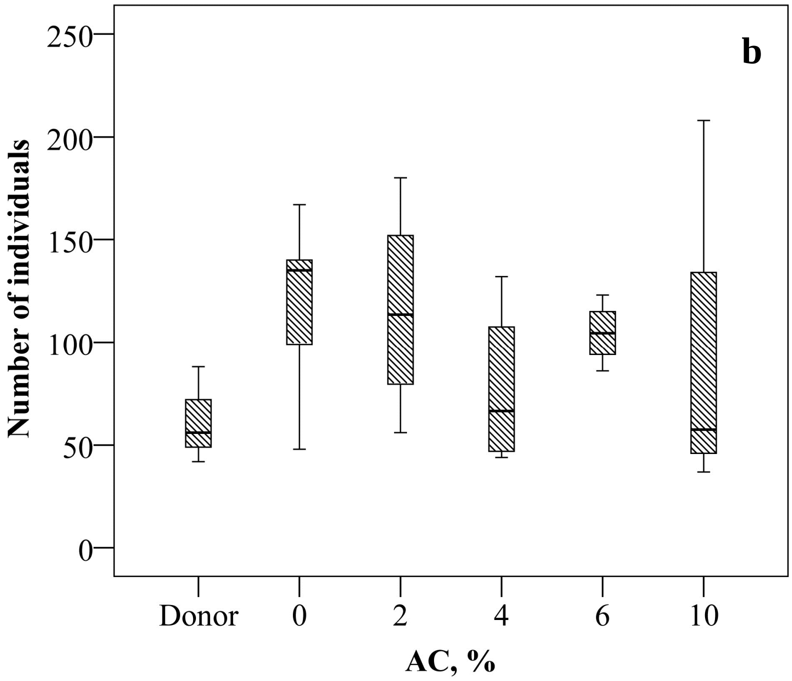


Figure S5. Macrobenthos density, individuals/m^2, after (a) 3 and (b) 15 months of exposure to AC-sediment. Boundaries of the box plots indicate the 25th and 75th percentile. Whiskers below and above indicate the minimum and maximum of the variables. The median is indicated with the black line. 'Donor' relates to the community in the system surrounding the treated sediments.

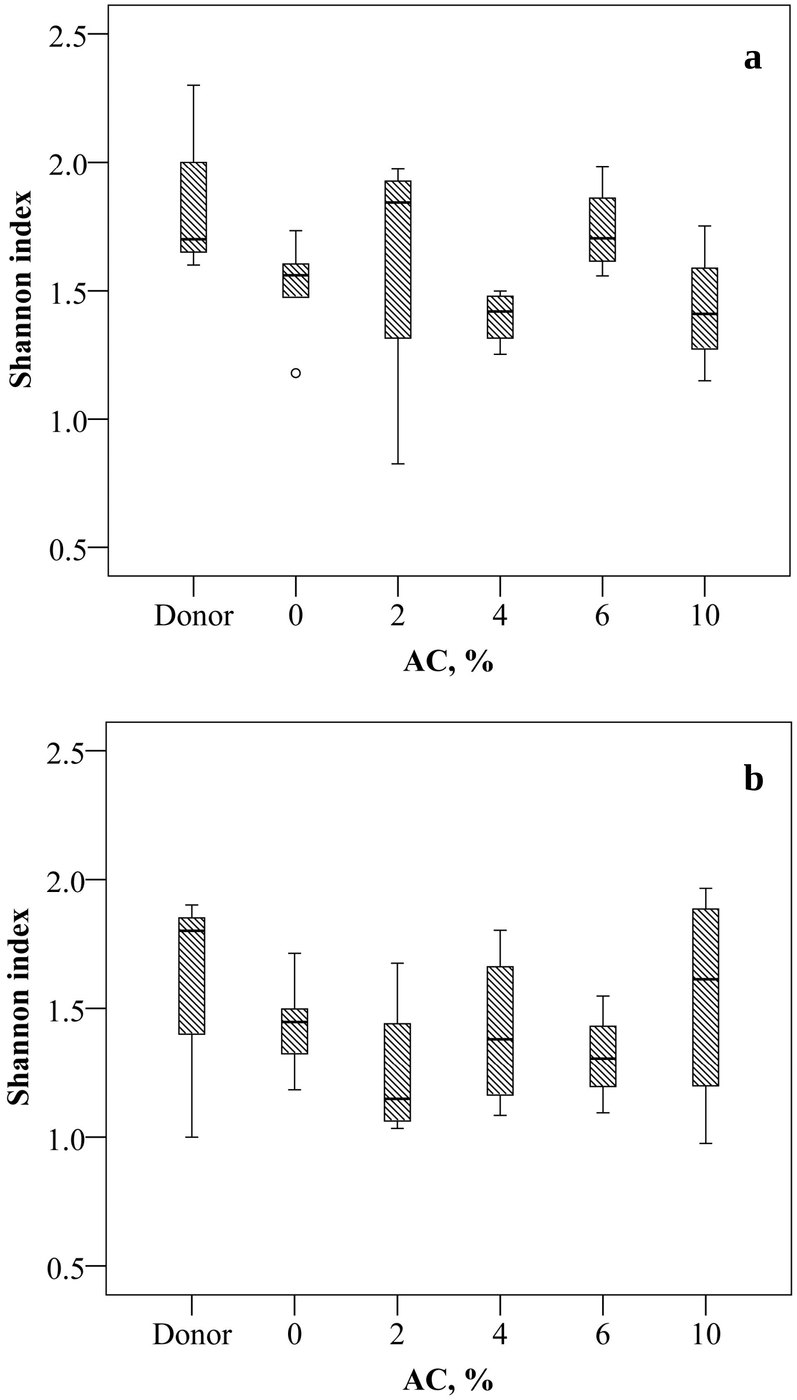


Figure S6. Shannon index after (a) 3 and (b) 15 months of exposure to AC-sediment. Boundaries of the box plots indicate the 25th and 75th percentile. Whiskers below and above indicate the minimum and maximum of the variables. The median is indicated with the black line. 'Donor' relates to the community in the system surrounding the treated sediments.

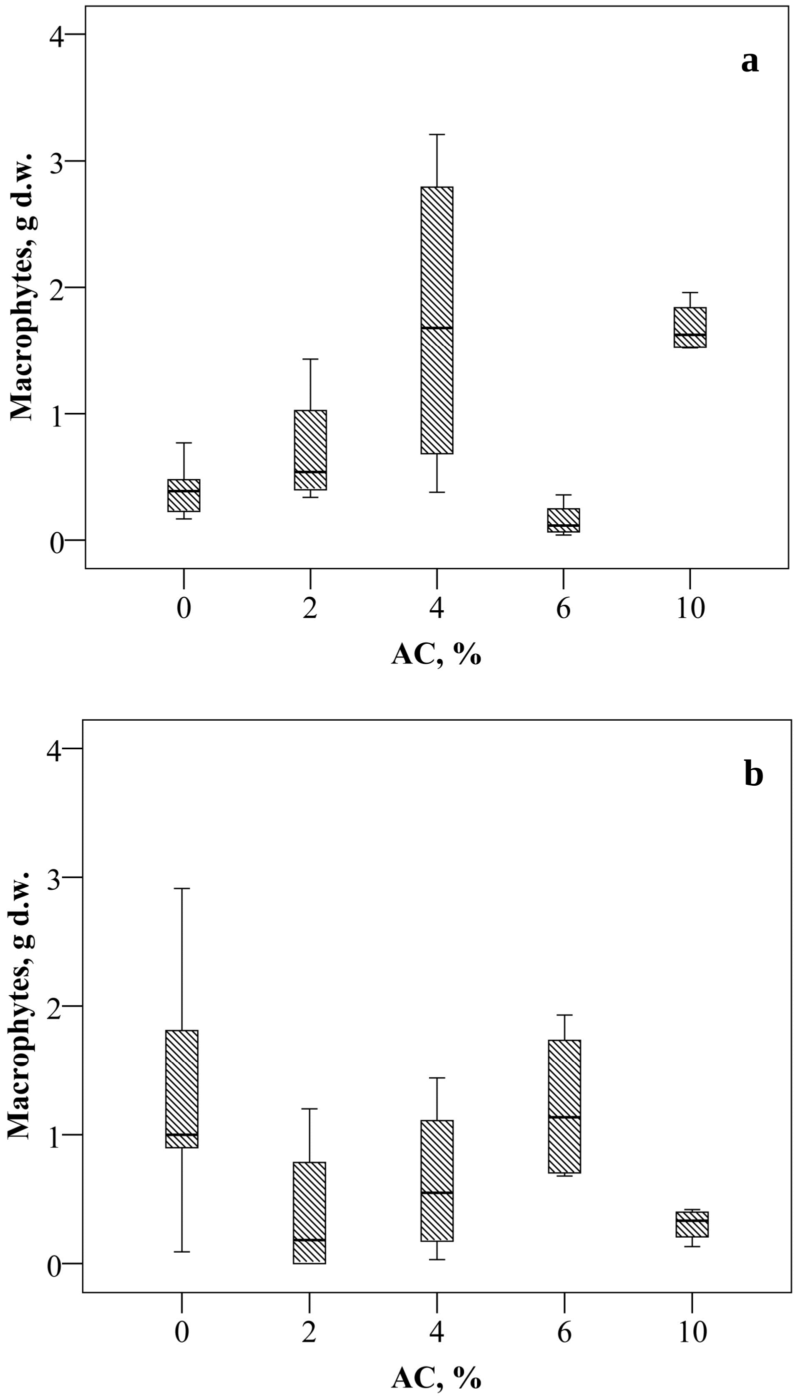


Figure S7. Macrophytes dry weight in the Veenkampen sediment amended with AC after (a) 3 and (b) 15 months of exposure. Boundaries of the box plots indicate the 25th and 75th percentile. Whiskers below and above indicate the minimum and maximum of the variables. The median is indicated with the black line.

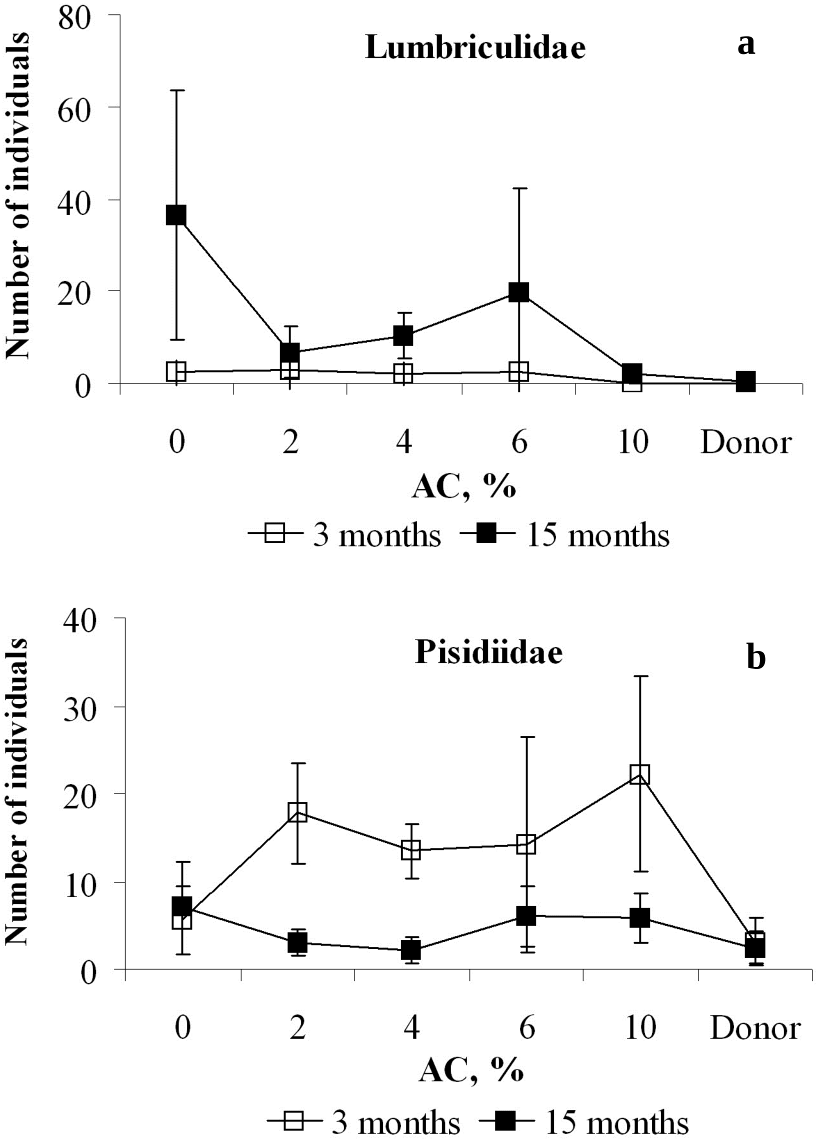


Figure S8. Absolute abundance of *Lumbriculidae (a) and Pisidiidae* (b) after 3 (open symbols) and 15-month (closed symbols) exposure to the Veenkampen sediment amended with different AC doses. 'Donor' relates to the community in the system surrounding the treated sediments. Measured activated carbon (AC) concentrations are provided in Figure S2b.

CHAPTER 8

IN SITU ACTIVATED CARBON AMENDMENT REDUCES BIOACCUMULATION IN AQUATIC FOOD CHAINS

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Abstract

In situ activated carbon (AC) amendment is a new direction in contaminated sediment remediation, 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 polycyclic aromatic hydrocarbon (PAHs) and polychlorinated biphenyl (PCBs) 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). AC sediment treatments resulted in a significant decrease in freely dissolved PCB and PAH concentrations. Sediment treated with PAC showed a reduction of accumulation of PCBs in fish by a factor of 16 bringing pollutant levels below toxic thresholds and had no significant negative effects on fish condition. Bioaccumulation in fish was governed by uptake from water and zooplankton with fish-zooplankton LogBMFs up to 1.76. Sediment amendment with GAC did not yield reductions in bioaccumulation in fish, due to limited reductions of bioaccumulation in zooplankton and invertebrates.

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) which are released into the environment as a result of natural processes and anthropogenic activities. In Europe, the Water Framework Directive requires surface waters to be chemically and ecologically healthy and safe. 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. However, these methods do not always sufficiently reduce contaminant transport. Moreover, the latter approaches are energy-intensive, expensive and disruptive.

Sediment amendment with carbonaceous materials like activated carbon has received increasing attention over the past decade *(1, 2)*. Early laboratory experiments showed that activated carbon strongly binds HOCs present in the sediment and thus reduces available concentrations of the contaminants *(3-6)*. Considerable progress has been made in understanding mechanisms of HOC binding to condensed carbon phases like AC, both through laboratory and pilot-scale field studies *(1, 2, 7, 8)*. 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 *(6)*. Three decades ago, Shea et al *(6)* tested 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 *(6)*. It is not clear however, whether such reductions are feasible in outdoor field scale aquatic systems, where highly complex processes and factors such as varying food web composition, food ingestion, omnivory or secondary effects of AC on fish health occur *(9-11)*. 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 *(2, 12-16)*. We are not aware of 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 may differ in effectiveness and ecological side effects, also different AC treatment alternatives 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 with granular AC, and mixing with granular AC with subsequent removal of granules, i.e. sediment stripping *(17)*. 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 this end, natively contaminated sediment was dredged, transported to the test site where it was homogenized, inserted in the control systems untreated or AC treated, thereby constructing outdoor ecosystems mimicking natural ditches in The Netherlands. Concentrations of PCB and PAH were monitored in sediment, pore water, zooplankton, benthic macroinvertebrates, and fish over time. Pore water concentrations were measured using POM-SPE 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. 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. 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 The Biesbosch National Park, The Netherlands, in the second half of 2011.

Study area and remediation scenarios

The field experiment was conducted from December 2011 till September 2012. In December 2011 forty four tons of sediment (d.w. 53%, bulk density 1.7 kg/L) were dredged from The Biesbosch National Park, The Netherlands, and transported to the experimental facility Sinderhoeve, Renkum, The Netherlands, where four identical ditches (15 m length, 1.5-2 m width, 1 m depth) were prepared prior 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 a nominal concentration of 4% d.w. based on 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 establishing 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 Chapter 4). 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 was transported in plastic bags (containing rearing pond water) to the experimental test site. After acclimatization for approximately 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.

Sampling

Samples were taken at six times (Figure S1). To determine total 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 from the ditch with stripped sediment after 1 month 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 matter, metals, PCB and PAH concentrations, PCB and PAH pore water concentration. Fish and invertebrate samples were analysed for PCBs and lipid contents. Zooplankton samples were analysed for PCBs and TOC.

Analytical procedures

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

PAH and PCB concentrations in pore water. PAH and PCB concentrations in sediment pore water were determined *ex situ* using the POM-SPE method *(18).* 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 *(18-20)*. Then, the pieces of POM were recovered, cleaned with wet tissue, and ASE 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}) *(19, 20).* 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 *(21)*, 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 *(21, 22)*, 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.

Biota analyses. Invertebrate and zooplankton samples were extracted with 70 ml hexane/acetone (3:1 w/w) using Accelerated Solvent Extractor (ASE 350, Dionex, USA). Extracts were concentrated to 1 mL, exchanged to hexane, and cleaned over Al_2O_3/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 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 *(23)* and 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 serie s 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 ^{63}Ni electron capture detectors. The injector and detector temperatures were 250 and 325 °C, respectively. Carrier gas was N_2 (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 respectively 290 and 230 °C. 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 *(24)*.

Data analysis

Fish condition factors (*K*) were calculated from fish weight (*W*, g), and length (*L*, cm) using Fulton's Condition Factor formula *(25)*:

$$K = 100\frac{W}{L^3} \tag{1}$$

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

$$BAF = \frac{C_{biota,lipid}}{C_W} \qquad (2)$$

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)*:

$$BMF = \frac{C_{fish,lipid}}{C_{prey,lipid}} \qquad (3)$$

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 $0.05<p<0.10$.

Result and discussion

Effect of sediment treatment with activated carbon on total and bioavailable concentrations of contaminants

$\sum_{10}$PAH and $\sum_{11}$PCB ($\sum_{7}$PCB) in the Biesbosch sediment were and 11 mg/kg and 700 (450) µg/kg, respectively (Table S1). PAH and PCB levels as well as concentrations of metals were a factor of 10, 32 and up to 40 above threshold effect levels, respectively (Table S1) *(27, 28)*. The monitored total concentrations of these groups of compounds did not change significantly over time for the untreated sediment (Figure S2), which means that no substantial chemical or biological degradation occurred for these compounds. The total concentration of PAHs in PAC, GAC, and stripped sediment decreased by 100, 48, and 43%, and the total concentration of PCBs by 100, 22, and 16%, respectively. A significant decrease in total concentrations can be attributed to HOC sequestration in the sediment or, in case of stripped sediment, HOC sequestration and removal from the sediment.

Pore water concentrations. POM-SPE based pore water concentrations of PAHs and PCBs were determined *ex situ* after equilibrating sediment for 28 d. After 1 and 4 months post-treatment, sediment treated with PAC, GAC, and GAC sediment stripping resulted in Σ_{10}PAH concentration reductions by 100, 93, and 97% (Figure 1). ΣPCB concentration in PAC, GAC, and stripped sediment decreased by 100, 70 and 83%, respectively, after 1 month and even further to 100, 84, and 90% after 4 months (Figure 1).

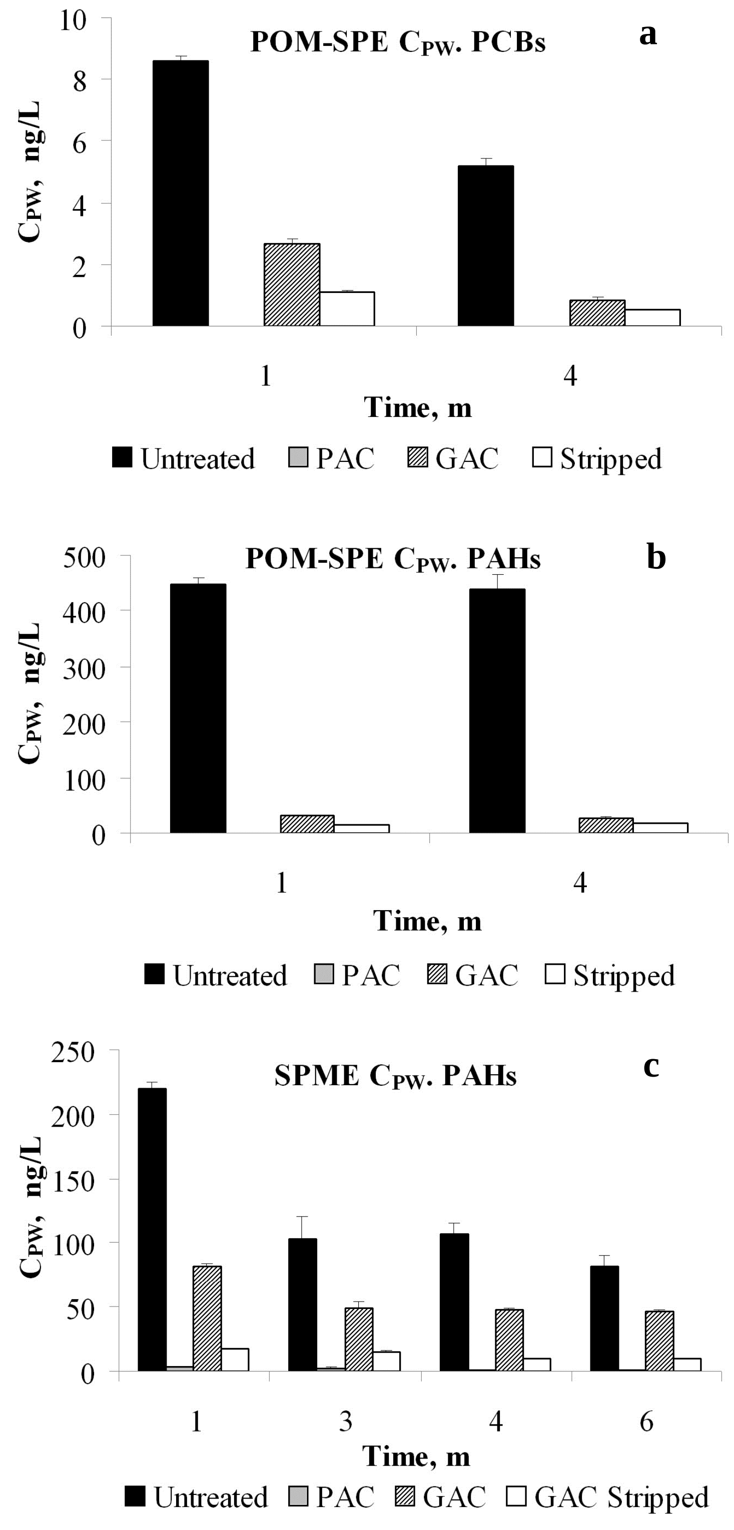

Figure 1. Σ_{13}PAH and Σ_{18}PCB equilibrium pore water concentrations measured with POM (a and b) and SPME (c) passive samplers. PCB concentrations in the PAC treatment (a and b) were below LOD, so C_{PW} for PAC was close to zero.

Treatment effectiveness was higher for PAH than for PCB (Figure 1, Figure S3 and S4), 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 nominal dosages, i.e. 4% d.w., PAC reduced the aqueous concentrations more efficiently than GAC due to the larger surface area of the AC particles and the short intra- and interparticle diffusive path lengths *(31)*. 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 4 months decreased with increasing LogK_{OW} of the compounds. We assume that the slower reduction in pore water concentration for more hydrophobic compounds is the result of their slower mass transfer from the sediment to AC. Compounds with higher LogK_{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 obtained for chemicals with lower LogK_{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* ΣPAH concentration reductions by 100, 50, and 90% (Figure 1 and S5). 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 done immediately after sediment pretreatment (homogenization and dilution). Increased sediment agitation could have led to some desorption of PAH resulting in higher pore water concentrations. At 3, 4 and 6 months post-treatment, *in situ* pore water concentrations were similar in all treatments, suggesting a state of pseudo-equilibrium (Figure 1).

Generally, *in situ* pore water concentrations measured with SPME were lower than those measured with POM-SPE (Figure S6). 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 high partition coefficient than PDMS coated fibers deployed previously *(32)*. 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 complete even after 7 weeks *(32)*. 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 sediment treatment with activated carbon on biota

Zooplankton. Zooplankton samples were dominated by cyclopoid copepods and *Chydorus sphaericus*. Zooplankton biomass showed a slight increase in time, which probably reflects natural seasonal variability (Figure S7). Zooplankton biomass was higher in GAC treated sediment, which was statistically significant 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 S11), because the availability of the phytoplankton the zooplankton feed on, depends on these nutrients. Positive trends (i.e. $0.05<p<0.10$) were indeed found between zooplankton biomass, and NO_2+NO_3 and PO_4 as independent variables (multiple regression, $p = 0.096$ and 0.096 respectively).

TOC normalized concentration of ∑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 months) (Figure 2) and significantly correlated with PCB pore water concentration ($p = 0.016$). This shows for the first time, the effectiveness of AC treatments in reducing exposure of zooplankton.

To study the net accumulation of PCBs by zooplankton due to uptake from all exposure routes, bioaccumulation factors (BAF) were calculated according to eq 2. LogBAFs increase linearly with LogK_{OW} till LogK_{OW} is approaching 7, after which the curves level off or even decline (Figure 3). LogBAF was linearly correlated to LogK_{OW} (LogBAF = (1.18±0.10)LogK_{OW} – (1.57±0.67), $p = 1.4 \cdot 10^{-4}$, $R^2=0.895$). The leveling off is sometimes explained from binding of PCBs to DOC, which increase the apparent aqueous phase concentration. 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. Remarkably, the BAF values after 1 month are identical within error limits (Figure 3) whereas the exposure concentrations vary considerably among treatments (Figure

1). 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. After three months, the differences among treatments are still limited although an order of magnitude random scatter is observed. Consequently, this may be explained by variation in zooplankton composition among ditches due to variations in macrophytes development or to random error due to sampling and analysis. From the figure a clear time effect between 1 and 3 months is observed. Again it is unlikely that this is explained by slow bioconcentration into zooplankton. However, the difference in BAF between 1 and 3 months may be explained by disequilibrium between measured sediment pore water and the overlying water where the zooplankton resides *(33)*. 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 with 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 are too high. This mechanism would imply that the difference is the least for untreated sediment, which indeed is true (Figure 3). 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 months of exposure (i.e. 6 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 months the data measured with POM more closely reflect the true pore water concentration. However, after 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 S8). This clear treatment effect could partly be explained by treatment effects on species fitness, or to treatment induced community shifts, or both. Differences in community lead to differences in sample composition and thus to a different lipid quantity and quality. After three months, only Chironomidae were found which did not show big variations in lipid content. A significant factor two lower lipid content was detected in the samples from the 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 *(15, 34)*. In order to avoid starvation, deposit feeders may start to live on their own lipids *(5, 35)*.

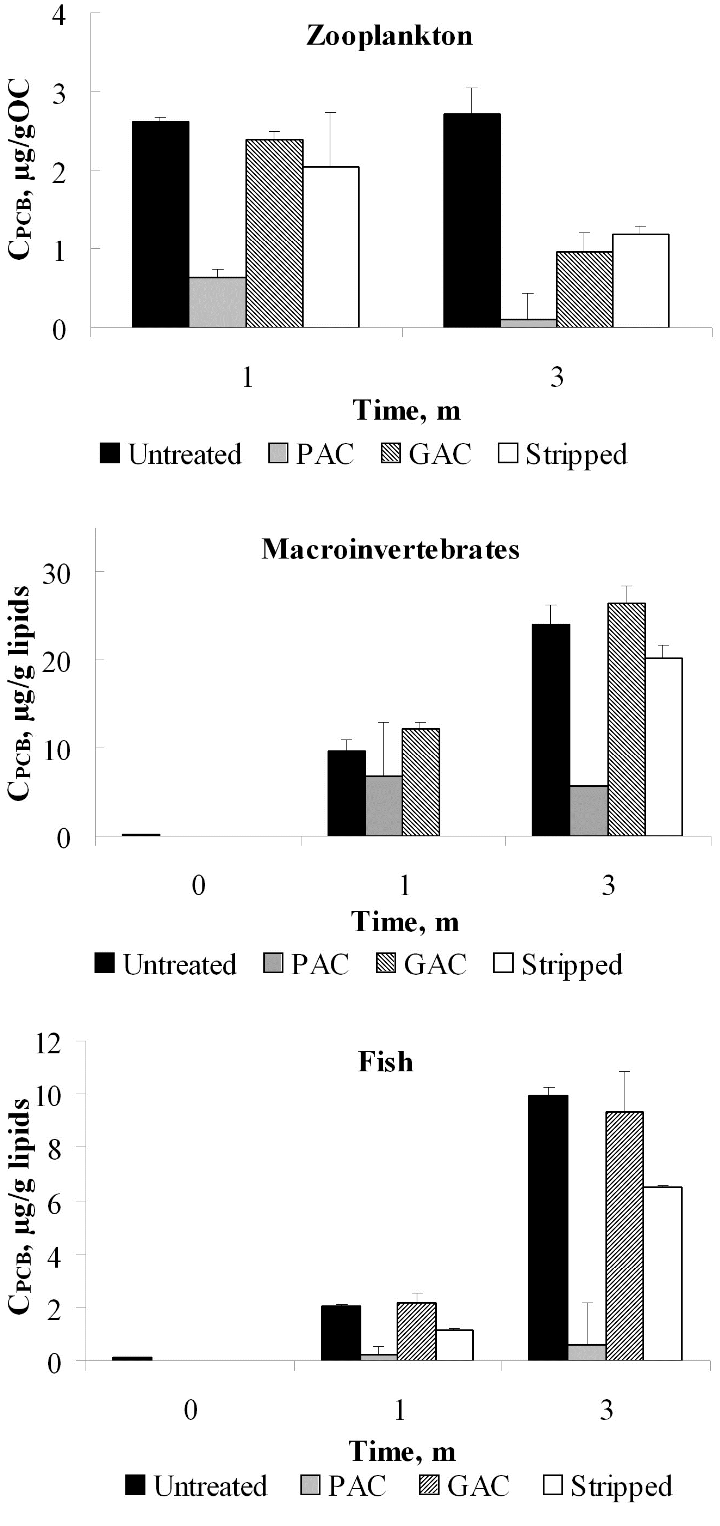

Figure 2. TOC-normalized ∑PCB concentrations in zooplankton and lipid-normalized ∑PCB concentrations in macroinvertebrates and fish from the ditches with untreated, PAC, GAC, and stripped sediment, after 0, 1 and 3 months of exposure (i.e. 3, 4 and 6 months post-treatment).

PCB analysis revealed that abundant congeners were 101, 138, 149, and 153. In general a good agreement between PCB profiles in sediment and chironomids were observed which suggest that sediment was a primary source of PCBs to chironomids. Strong correlation between PCB concentration in invertebrates and in sediment and water was observed, $p = 0.004$ and 0.003, respectively, which is in line with earlier findings *(36, 37)*. The concentration of the ∑PCBs in macroinvertebrates after 1 month of exposure was 9.5 µg/g lipids (ranging from 4.6 to 14.7 µg/g lipids) and, again remarkably, did not differ between treatments (one-way ANOVA, F (3, 6) = 1.167, p =0.373) (Figure 2). So, although POM-SPE based pore water concentrations were reduced, especially in the PAC treatment (Figure 1), 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. After 3 months of exposure (i.e. 6 months post-treatment), the ∑PCBs in macroinvertebrates increased by a factor 2 to 2.5 in all treatments, except the PAC treatment. The levels of PCBs in invertebrates from PAC sediment did not change over time and were statistically different from those found in other treatments (one-way ANOVA, F (3, 8) = 13.36, p = 0.002). The lower accumulation in PAC treated sediment now coincides with the low pore water concentrations (Figure 1), which is explained from the sediment being close to sorption equilibrium, such that the POM based measurement now provides a more accurate estimate of the *in situ* pore water concentration.

The LogBAF values calculated for invertebrates ranged from 4.4 to 8.1 and showed a linear increase with LogK_{OW}: LogBAF = (1.48 ± 0.10)LogK_{OW} – (2.72 ± 0.69), R^2=0.775, p =$1.35 \cdot 10^{-22}$) (Figure 3). No clear treatment effect on bioaccumulation was observed, which is in line with the lack of difference in ∑PCBs observed in invertebrates from untreated, GAC, and stripped sediment after 1 and 3 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 S9). 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 scales for salmon and trout. The slightly lower value compared to the fish as received was significant only for the PAC treatment after 1 month, yet the factor difference was too low to be meaningful. Most importantly, treatment effects on fish condition were not significant (1 month: one-way ANOVA, F (3, 8) = 0.748, p =0.553; 3 month: one-way ANOVA, F (3, 8) = 1.030, p = 0.430). These results for the first time show that sediment treatment with GAC or PAC has no negative effects on the condition of fish. Fish weight increased in time (Figure S9), with fish from the ditch with GAC stripped sediment having a slightly higher body weight after 1 month, and with fish from the PAC treated sediment having a lower body weight after 3 months.

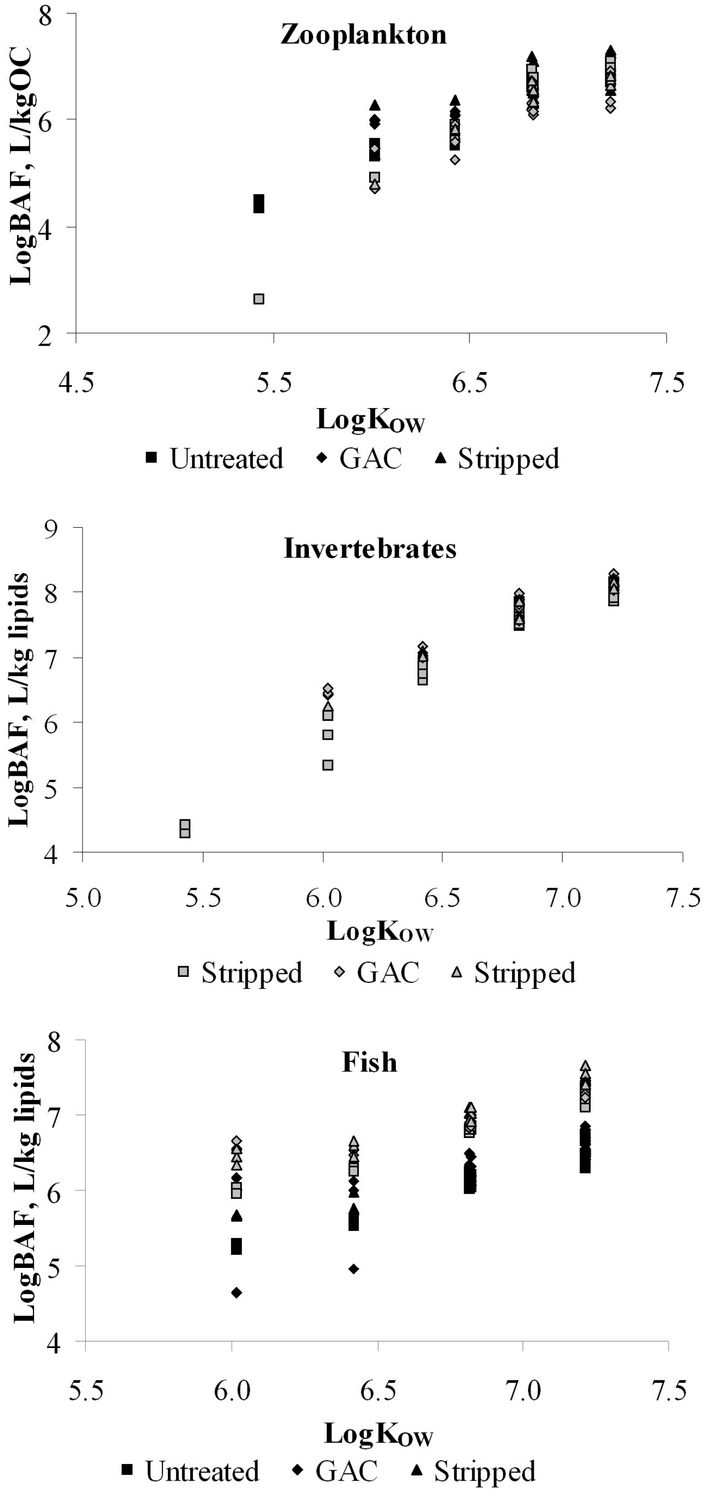

Figure 3. PCB LogBAF for fish based on pore water concentrations determined with the POM-SPE method. The black symbols and grey symbols relate to the measurements done after 1 and 3 months of exposure (i.e. 4 and 6 post-treatment), respectively.

These differences, however, were not statically significant (1 month: one-way ANOVA, F (3, 8) = 3.830, p = 0.057; 3 months: one-way ANOVA, F (3, 8) = 3.214, p = 0.083).

Analysis of lipid content revealed a decrease in lipids in time due to growth (Figure S9). The observed variability is attributed to natural variability among fish individuals. No treatment effects on lipids content were identified after 1 and 3 months of exposure (one-way ANOVA, F (3, 8) = 0.930, p = 0.470 and F (3, 8) = 2.893, p = 0.102, 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 water (presence of lower chlorinated congeners, e.g. 49 and 52) and that of sediment (higher chlorinated congeners, e.g. 149 and 153) (Figure S10). 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 LogK_{OW} PCB congeners, whereas uptake from food dominates in adult fish and higher LogK_{OW} PCBs *(21, 38, 39)*. 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.

The concentration of ∑PCBs in fish after 1 month ranged from 0.23 (PAC) to 2.19 (GAC) µg/g lipids with levels in the PAC treatment being statistically lower than those in the other treatments (one-way ANOVA, F (3, 8) = 5.746, p =0.021) (Figure 2). After 3 months, ∑PCBs concentrations in all treatments had increased by a factor of 4 to 5, except for the PAC treatment where ∑PCBs concentrations increased only a factor of 2. Bioaccumulation in the PAC treatment was significantly lower than in untreated, GAC treated and stripped sediment (one-way ANOVA, F (3, 8) = 126.8, p = $4.4 \cdot 10^{-7}$). These concentrations can be compared to lethal body burden (LBB) *(40)* concentrations in order to evaluate the effects of the treatments on the reduction of risk for these 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 lethal levels, also because ∑PCB in fish underestimates total HOC exposure, because PAH exposure was not accounted for. ∑PCB body burdens in the systems with GAC stripped sediment were lower than the LBB, but not significantly given the error in ∑PCB. In the PAC treatments however, ∑PCBs molar concentrations were reduced substantially by a factor of 16 (factor reduction range 3 - 89, for individual congeners), compared to lethal body burdens 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 and reduces originally lethal exposure levels, to levels much lower than lethal concentrations that would occur under field conditions. The data also show that 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 four variables correlate significantly with PCB concentrations in fish (p = 0.031, 0.005, 0.016, and 0.001, respectively), indicating the importance of these routes of exposure to PCB bioaccumulation in fish. Probably, these significance levels also reflect the relative importance of the exposure pathways, invertebrates being more important than aqueous exposure and finally zooplankton.

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 2, varied between 5.3 and 7.5 (Figure 3) and again increased linearly with LogK_{OW}: LogBAF = (0.95 ± 0.12)LogK_{OW} + (0.05 ± 0.80) (R^2=0.431, $p = 4.9 \cdot 10^{-12}$). This trend was observed for all treatments at both time points. No treatment effect on LogBAF was observed. This implies that the differences in PCB bioaccumulation were determined only by the differences in PCB concentration in water, invertebrates and in 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.

The treatment effects on 3 month bioaccumulation in golden orfe can quantitatively be explained as follows. GAC treatment and GAC stripping did not affect PCB concentrations in invertebrates, caused a factor 2 to 3 decrease in zooplankton PCB concentrations and a decrease in pore water PCB concentrations by only a factor of 4. Because of these limited effects, exposure through water and feeding was not significantly affected overall. In contrast, PAC treatment caused a factor of 4 decrease in invertebrate PCB concentrations, a factor of 10 lower zooplankton PCB concentrations and an almost 100% reduction in sediment pore water concentration. Given that orfe is a pelagic fish and feeds mainly on zooplankton, the factor 16 reduction in PCB accumulation may have been driven by the same factor reduction of PCB concentrations in zooplankton.

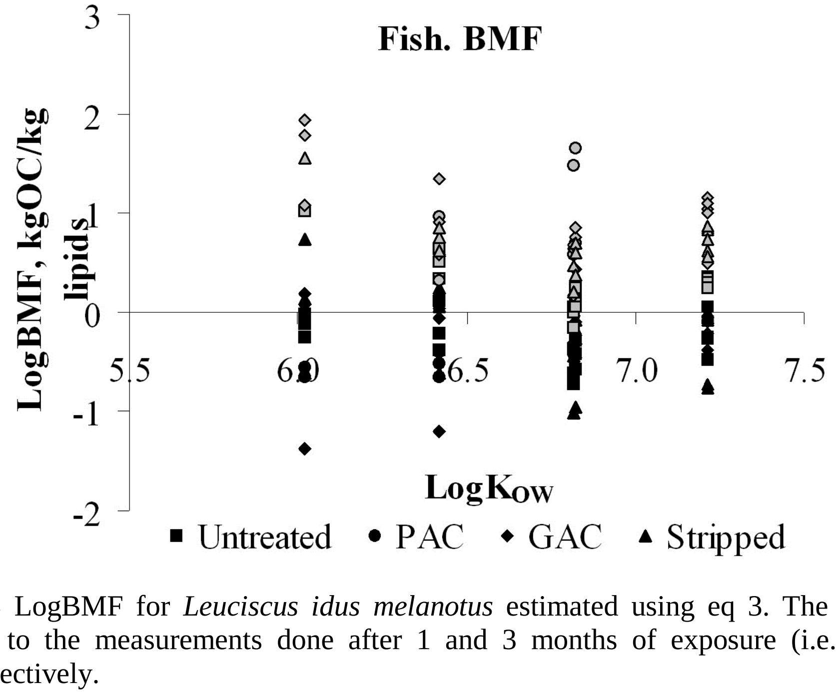

Figure 4. PCB LogBMF for *Leuciscus idus melanotus* estimated using eq 3. The black and grey symbols relate to the measurements done after 1 and 3 months of exposure (i.e. 4 and 6 post-treatment), respectively.

After 1 month of exposure the LogBMFs ranged from -2 to 0, being lower than values predicted with equilibrium partitioning theory. After 3 months the LogBMF values were approaching 1, thus indicating biomagnifiation, whereas LogBMF for some congeners with low LogK_{OW} already reached values up to 1.76 (Figure 4). There are several explanations for the increase in apparent BAF and BMF values. First, PCB uptake is known to be slow, leading to higher levels over time, especially for the more hydrophobic congeners. Equilibration of PCBs may take weeks to months dependent on LogK_{OW} *(38, 41)*. Furthermore, growth dilution may result in lower then equilibrium steady state concentrations, especially for PCBs with higher LogK_{OW} *(38, 42)*.

Conclusions

Sediment treatment with AC resulted in a significant decrease of HOC pore water concentrations, with PAC being the most efficient, followed by sediment stripping and GAC. In the short term, the effectiveness of the treatments decreased with increasing LogK_{OW} of the compounds. POM-SPE passive sampling showed better results in predicting exposure concentration than polyacrylate SPME fibers that did not reach equilibrium within 30 days. Sediment treatment with PAC effectively reduced PCB bioaccumulation in zooplankton, invertebrates and fish. PCB concentrations in fish were reduced to concentrations far below thresholds for baseline toxicity, which proves the capacity of PAC treatment to eliminate HOC associated risks for fish. Presence of PAC in the ecosystems caused lower lipid contents in invertebrates but did not negatively affect the condition and growth of the fish. Sediment stripping as well as sediment treatment with GAC turned out to be not efficient in reducing PCB bioaccumulation in biota but was not harmful to any of the biota either.

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Supporting Information

Table S1. Concentration 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[*a*]anthracene	1.2	0.07	CB-31	43 (1.2)	
Chrysene	1.4	0.11	CB-44	14 (0.7)	
Benzo[*k*]fluoranthene	1.0	0.06	CB-52	82 (1.2)	
Benzo[*a*]pyrene	1.1	0.09	CB-101	75 (4.1)	
Benzo[*ghi*]perylene	0.78		CB-105	17 (0.8)	
Indeno[1,2,3-*cd*]pyrene	0.64		CB-118	29 (0.7)	
∑PAHs	**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	**∑PCBs**	**700 (28)**	**22**
Mineral oil	**700**		**TOC, %**	**5.86 (0.51)**	**-**
∑DDT/DDE/DDD	**0.22**	**0.0045**	**BC, %**	**1.15 (0.19)**	**-**

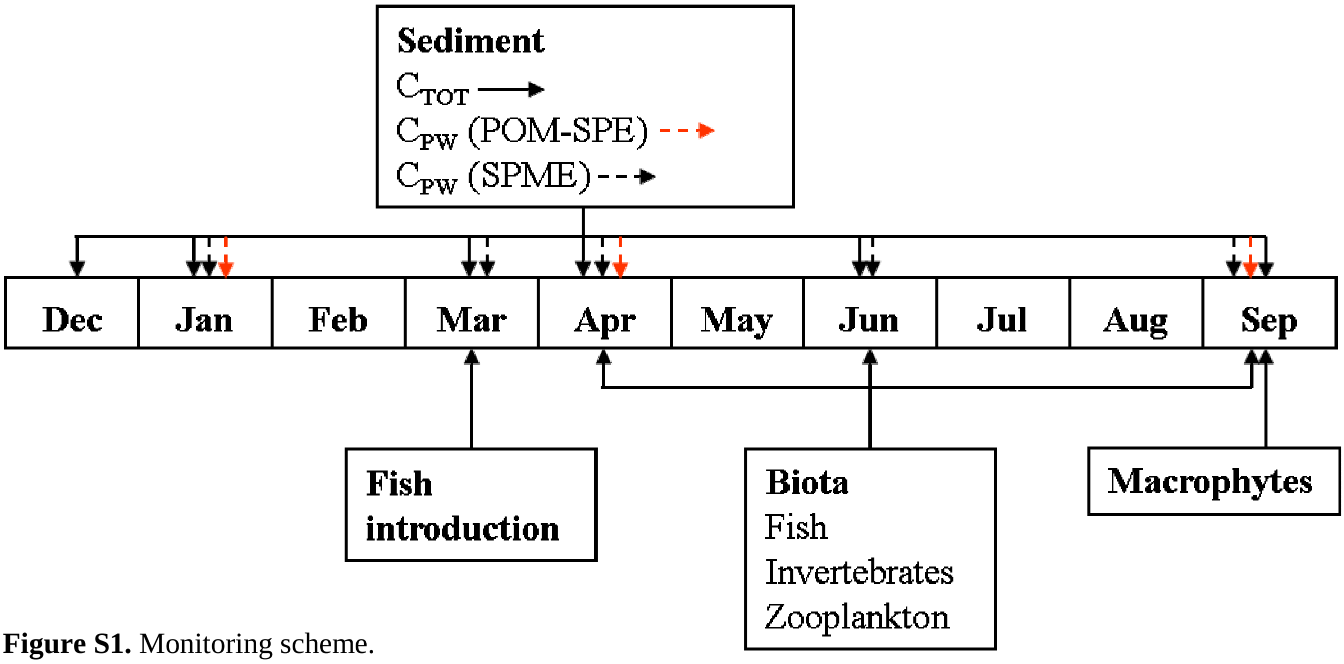


Figure S1. Monitoring scheme.

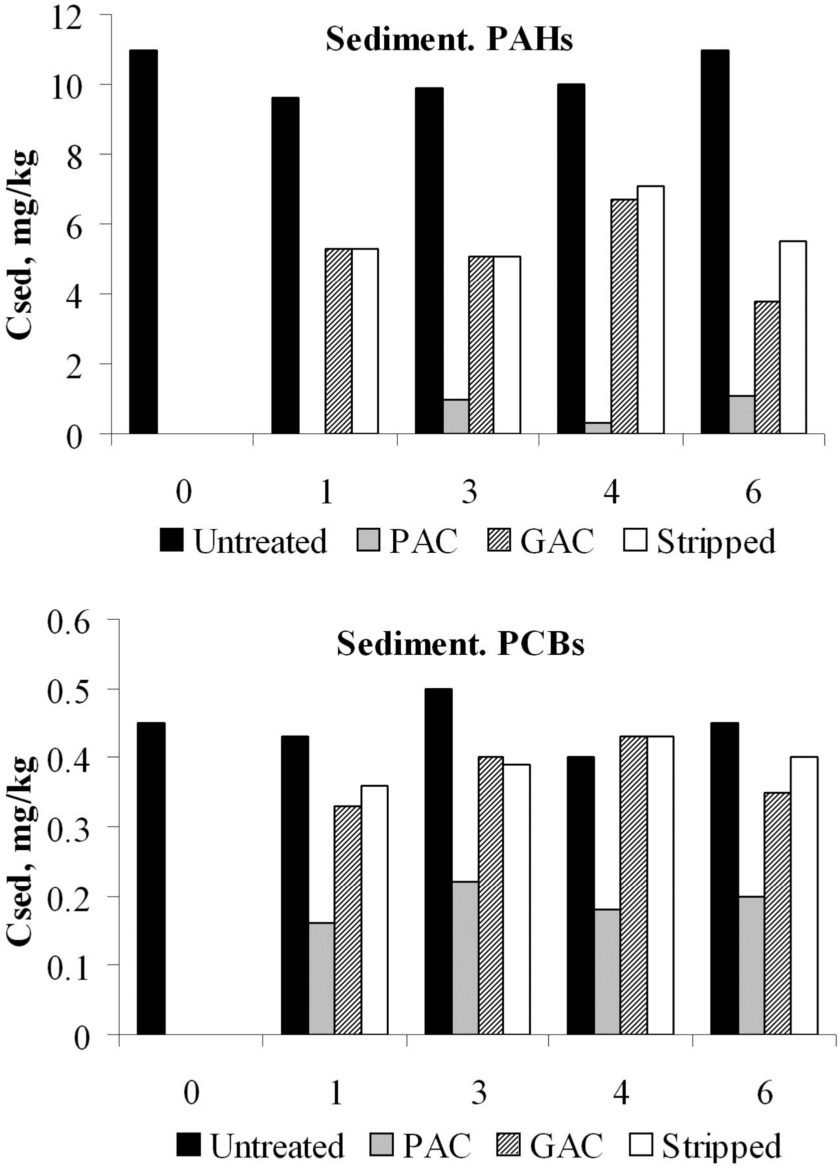


Figure S2. $\sum_{13}$PAH and $\sum_{7}$PCB concentration in untreated, PAC, GAC, and stripped sediment.

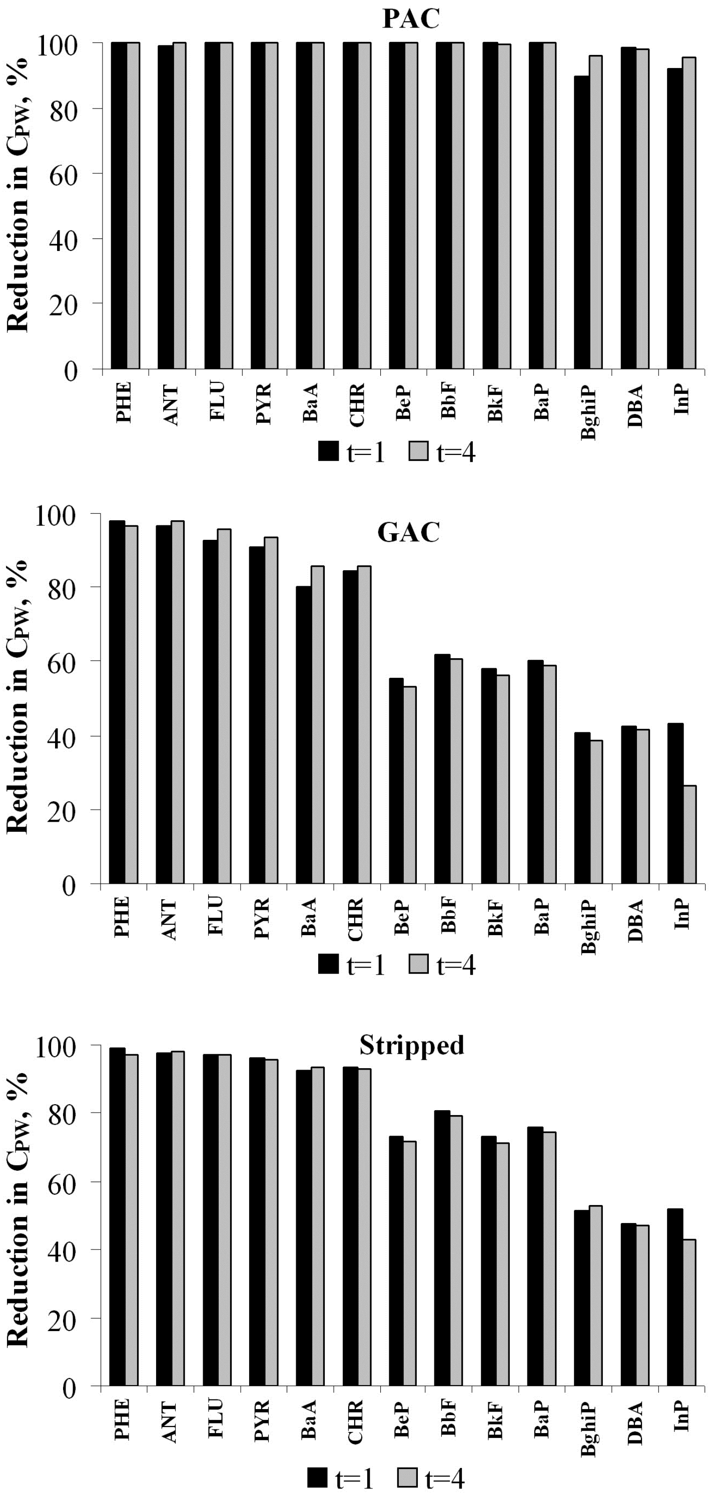


Figure S3. Reduction in PAH pore water concentrations as measured with POM-SPE passive samplers.

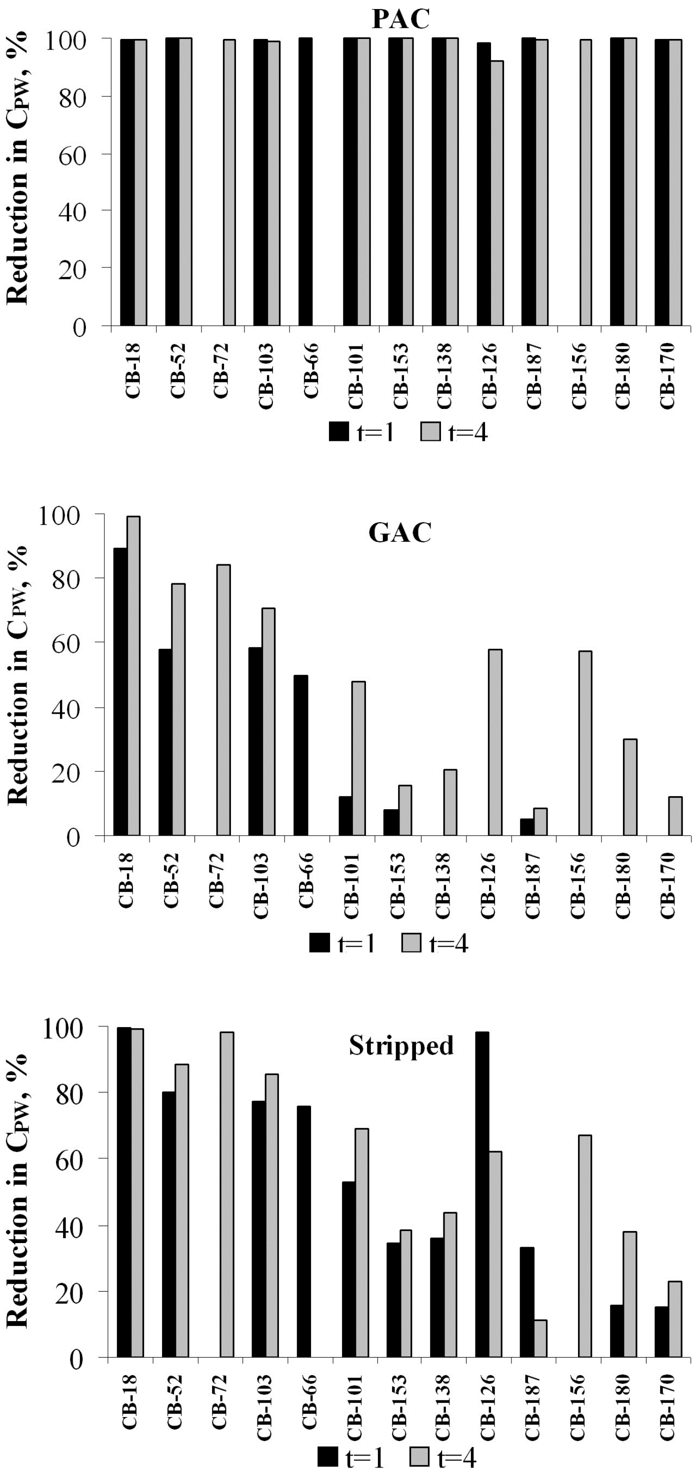


Figure S4. Reduction in PCB pore water concentrations as measured with POM-SPE passive samplers.

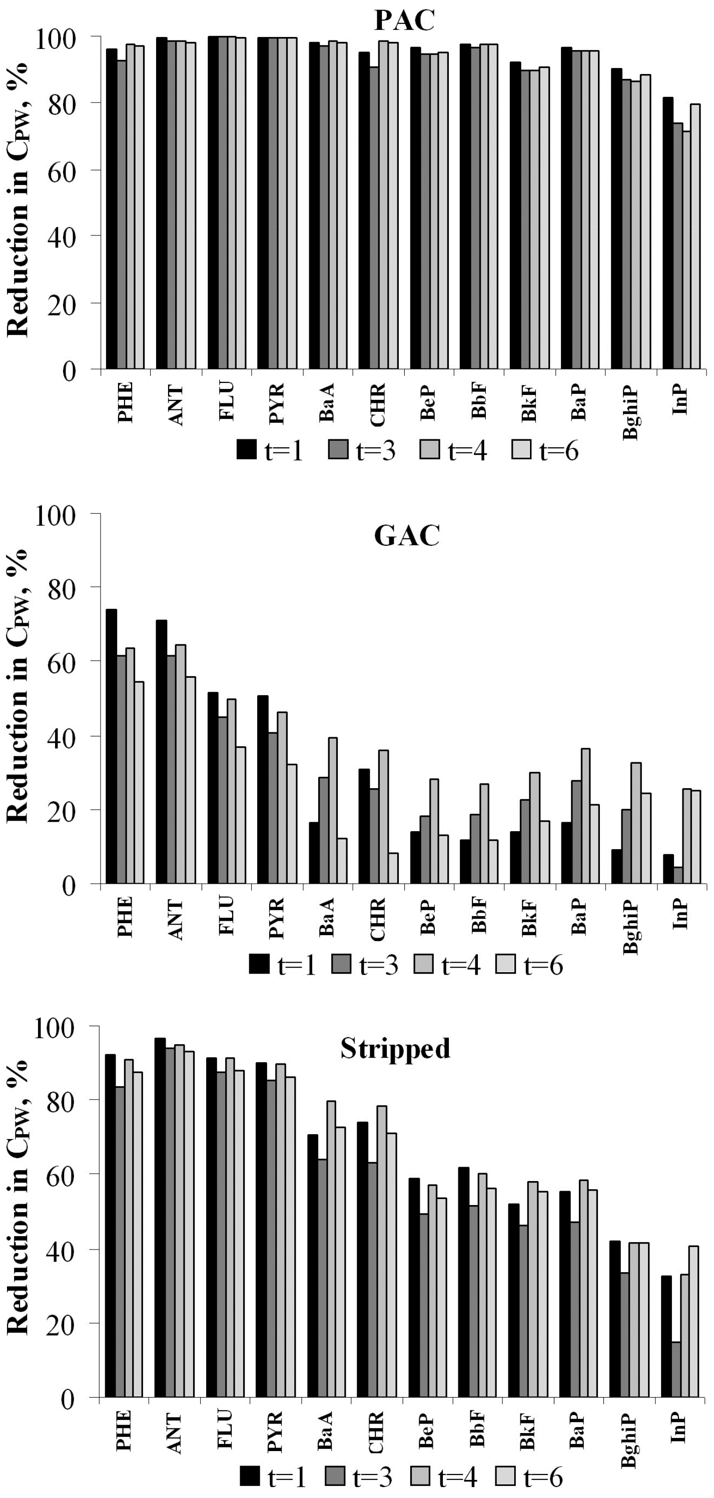


Figure S5. Reduction in PAH pore water concentrations as measured with SPME passive samplers.

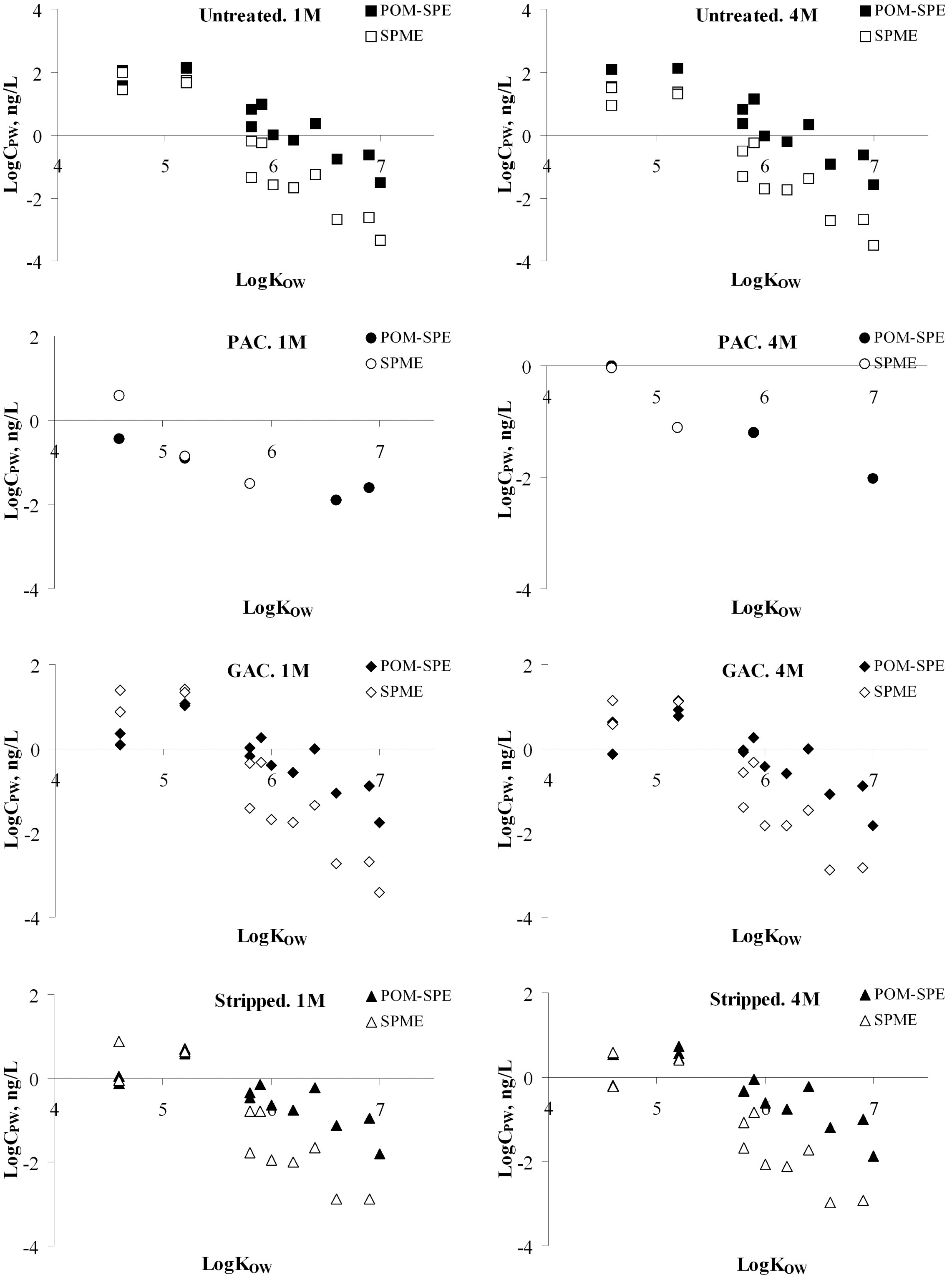
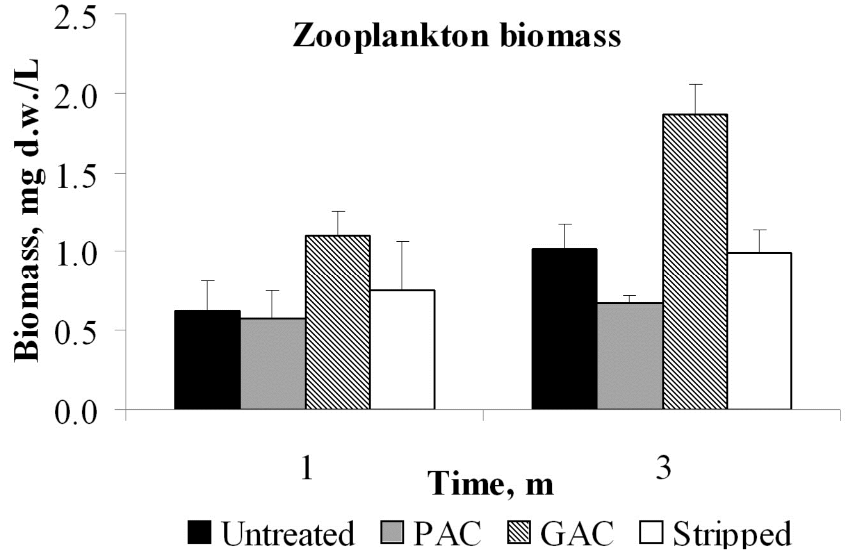


Figure S6. PAH LogC_{PW} measured *ex situ* with POM-SPE and *in situ* with SPME passive samplers in untreated, PAC, GAC, and stripped sediment at 1 and 4 months post-treatment.



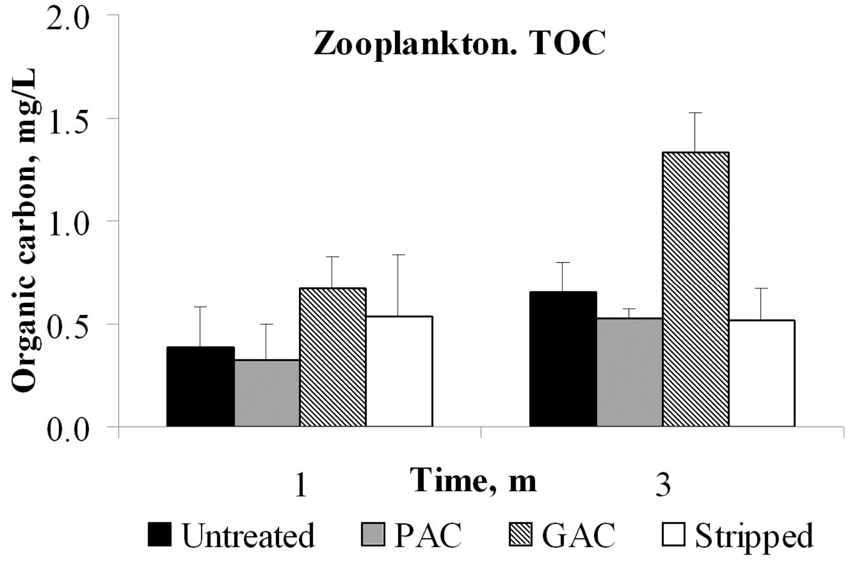


Figure S7. Biomass and total organic carbon in zooplankton from the ditches with untreated, PAC, GAC, and stripped sediment after 1 and 3 months of exposure (i.e. 4 and 6 months post-treatment).

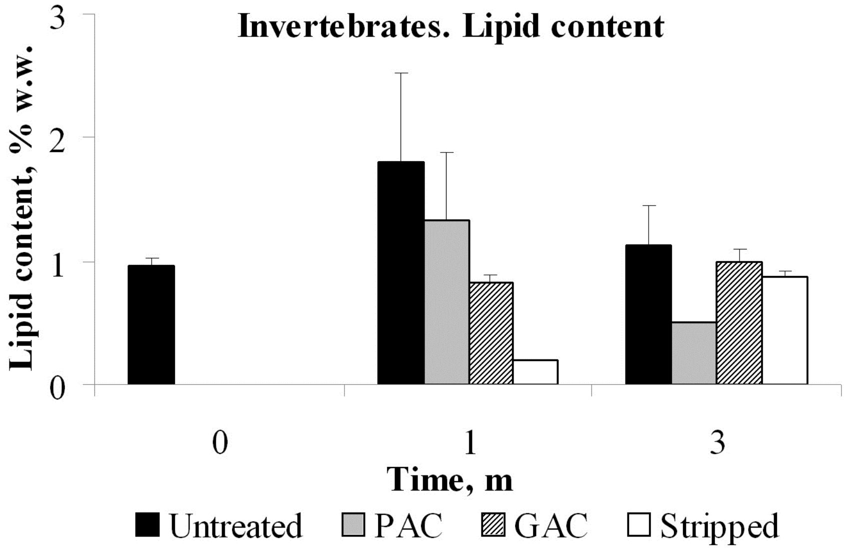


Figure S8. Lipids content of benthic invertebrates from the ditches with untreated, PAC, GAC, and stripped sediment before and after 1 and 3 months of exposure (i.e. 4 and 6 months post-treatment).

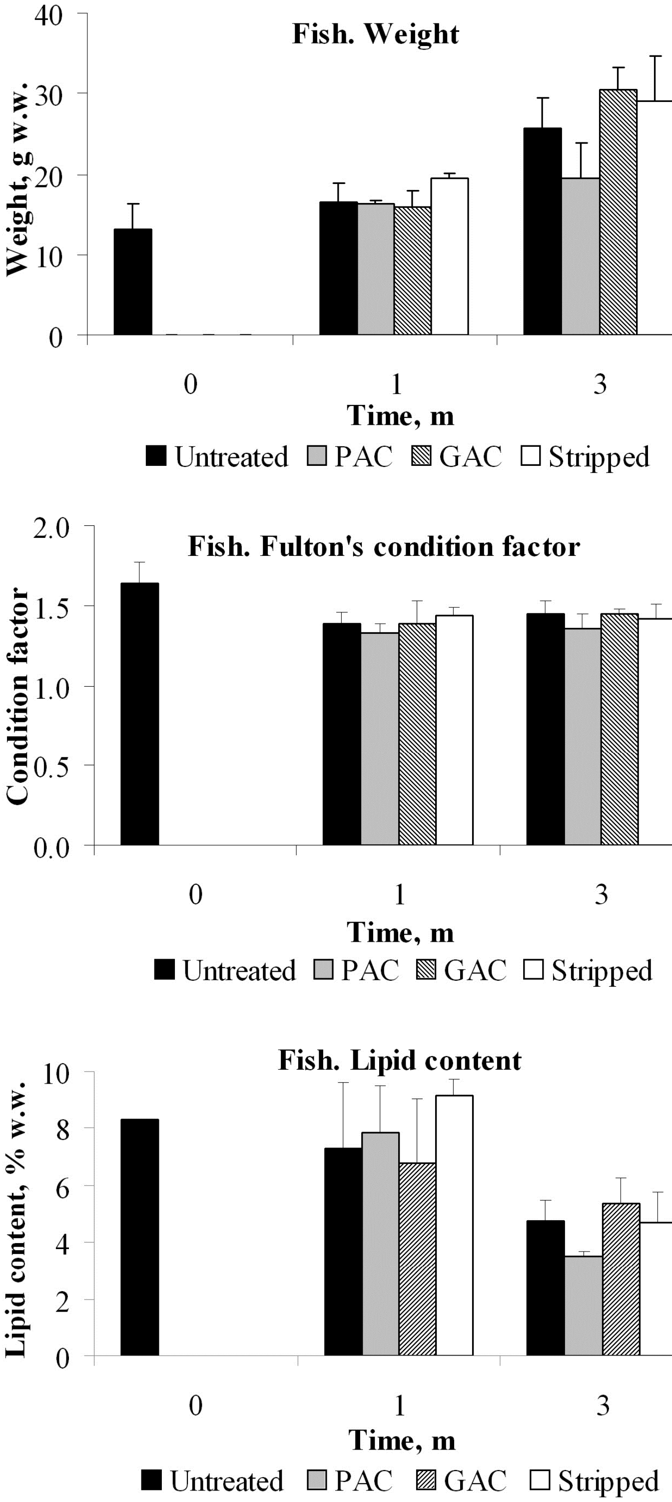


Figure S9. Fulton’s condition factor, weight and lipids content of fish from the ditches with untreated, PAC, GAC, and stripped sediment before after 1 and 3 months of exposure (i.e. 4 and 6 months post-treatment).

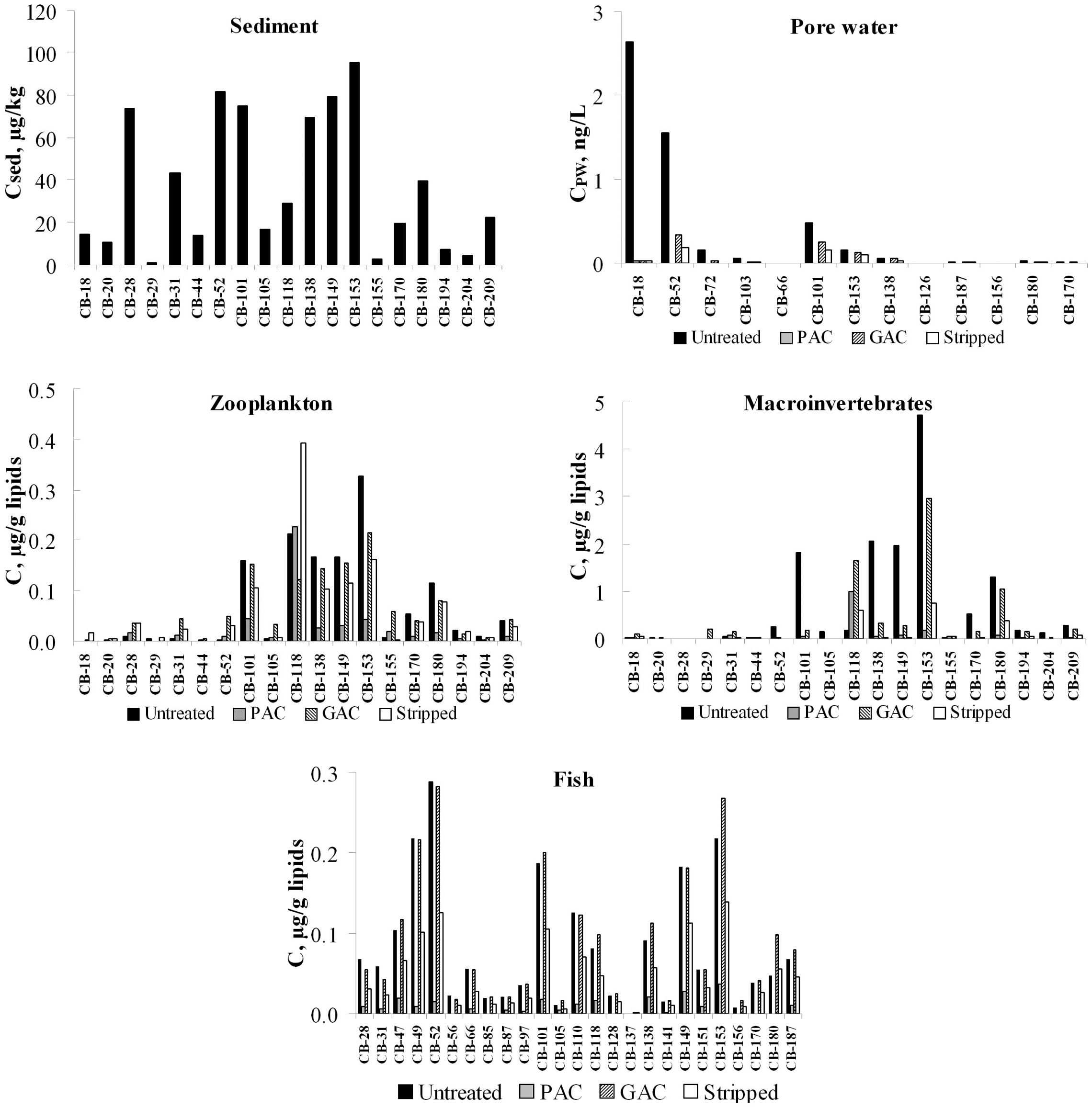


Figure S10. PCB profile in sediment, pore water, zooplankton, invertebrates, and fish.

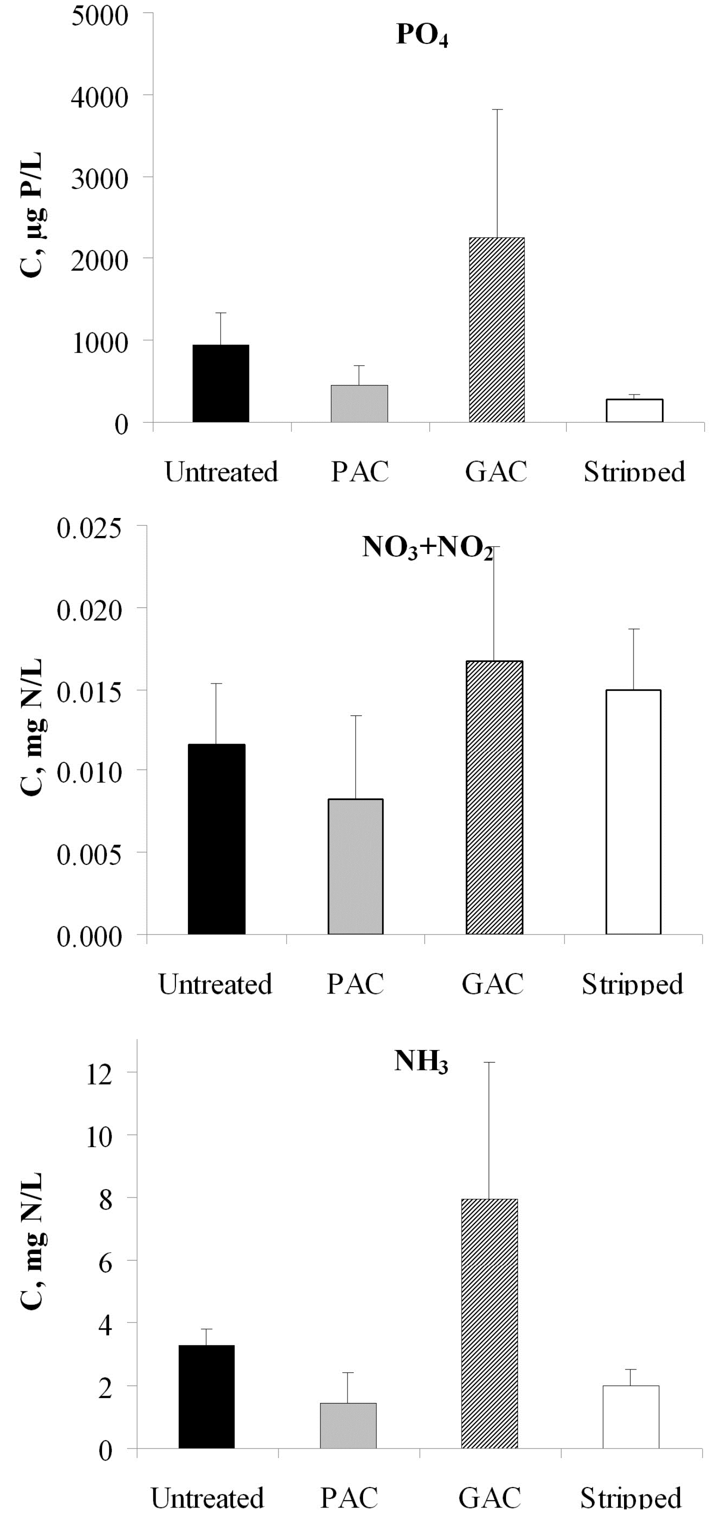


Figure S11. Concentration of nutrients in the ditches with untreated, PAC, GAC, and stripped sediment.

CHAPTER 9

SUMMARIZING DISCUSSION

Summary

Sediments contaminated with hydrophobic organic contaminants (HOCs) may pose health risks to aquatic organisms and humans. The routes of exposure include uptake from sediment pore and overlying water, direct contact with contaminated sediment as well as consumption of organisms that have accumulated contaminants from the sediments. The potential adverse effects of HOCs are the main reasons to reduce exposure and thus risks associated with these contaminants. Selection and implementation of a remediation strategy (and combinations thereof) mainly depend on site conditions *(1)*. Contaminated sediments can occur in small, localized areas like streams, rivers, and small lakes and ponds or in vast areas like wetlands, harbours, lakes and ocean basins. In some cases, contamination is relatively local but in other cases contamination may extend throughout a watershed and may have several more diffuse sources, e.g. industrial discharges, agricultural runoff, and atmospheric deposition. The thickness of the contaminated sediment layer as well as the degree of contamination are highly variable *(2)*. Furthermore, the nature of the sediments may vary widely and depends on geological, hydrological characteristics of the site, as well as human activities in the area. In summary, the nature of sediments, the environments in which they occur, and the type and degree of contamination are highly variable. Taking into account this variability, remediation methods that are flexible and widely applicable in contaminated sediment management are urgently needed. While traditional methods have and will continue to prove useful and be used, they have limitations. A physical limitation is that they are not feasible or appropriate in hard-to-reach environments or in ecologically sensitive sites. An ecological limitation is that they are highly disruptive and very often do not reduce the risks associated with HOCs. An economical limitation is that they are very expensive and energy-intensive. Societal limitations relate to public fear for leaching from depots or risks to ecosystems. These limitations make all parties involved in the process of sediment remediation, e.g. policy makers, engineers, sediment managers, and scientists, to look for new alternatives to existing remediation approaches that would be more efficient, less disruptive, and less expensive than traditional methods.

The primary aim of this thesis was to increase understanding of the effects of alternative methods of AC deployment and application on HOC exposure and risks reduction for benthic species and communities. The results of this research may help to improve risk assessment of contaminated sediments, to reduce risks caused by polluted sediment sites, to get regulatory acceptance of this emerging remediation technique, and finally take away public resistance against contaminated sediments and sediment remediation.

Amendment of contaminated sediments with *in situ* sorbents is a developing management strategy for addressing ecological and human health risks posed by HOCs in sediments. The current state of the art in AC sorbent amendment technology as a method for sediment remediation was reviewed in **Chapter 2**. This review is based on literature and datasets from laboratory as well as field studies with AC application. The review provided a discussion of how factors such as AC type, particle size and dosage, sediment characteristics, and adsorbates (i.e. HOC) properties affect the efficiency of AC amendments in reducing sediment pore water HOC concentrations. Furthermore, the effectiveness of AC in reducing HOC bioaccumulation and toxicity to benthic species was reviewed. Finally negative ecological side effects of AC application like mortality or growth inhibition on benthic species and communities were addressed. The literature suggests that the effectiveness of AC decreases in the presence of other carbonaceous materials like BC, OM, and oil. Important factors increasing the efficiency of AC remediation are sufficient mixing, small AC particle size, and optimal dose. Literature data suggest that a dose of 4% AC is sufficient to reduce aqueous concentration of HOCs, as well as HOC bioaccumulation and toxicity to benthic species. Available reports show that the addition of 4% AC to sediments has only mild direct effects on benthic organisms. 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 the benthic species and communities, especially in highly contaminated areas where the beneficial toxicity reduction outweighs any negative ecological side effects.

The effectiveness of AC may be less if BC is already present in the sediment. Therefore, published datasets from AC amendment trials were analysed to identify variation in the effectiveness of AC for different BC concentrations (**Chapter 3**). A conceptual model framework was provided to assess *in situ* affinity constants for HOC sorption to BC and AC. It was demonstrated that HOC sorption to AC is stronger than to BC for PCBs and PAHs with LogK_{OW} below 6.3 and 6.6. This can be advantageous from a risk reduction perspective because less hydrophobic HOCs are more soluble and thus more bioavailable compared to more hydrophobic HOCs, and will be sequestered faster by AC. The developed model and optimized *in situ* K_{BC} and K_{AC} can be used to design AC dosages given native OM and BC contents of aquatic sediments. It appeared that 1% of AC is sufficient to reduce pore water concentration by 99%.

The effectiveness of remediation with AC may be different for different types of AC treatment. In **Chapter 4**, effects of three different sediment treatments with AC, viz. powdered AC (PAC) addition, granular AC (GAC) addition and addition and subsequent removal of granular AC (sediment stripping), on PCB pore water concentrations, sediment-to-water fluxes and mass transfer coefficients were assessed. It appeared that all these sediment treatments with AC decrease pore water concentrations of PCBs. The efficiency of the AC treatments decreased in the order PAC > sediment stripping > GAC. AC addition was shown to decrease mass fluxes but to increase apparent mass transfer coefficients due to dissolved organic carbon (DOC) facilitated transport across the benthic boundary layer (BBL) at the sediment-water interface. The presence of bioturbators tolerant to AC addition (e.g. *A. aquaticus*) may also stimulate DOC facilitated transport of HOC, increase fluxes and thus decrease the efficiency of sediment treatment with AC. If bioturbators are sensitive to AC (e.g. *L. variegatus* in PAC sediment), AC might cause a decrease in biological activity, which would have no effect on sediment-to-water fluxes of HOCs. A dual BBL resistance model combining AC effects on PCB concentration gradients, DOC facilitated transport and biodiffusion was evaluated against the experimental data. The analysis of the results illustrated the variation in resistance among treatments and PCB congeners with different hydrophobicity. The results of laboratory experiments and simulations showed the complex interplay between AC and contaminant toxicity to benthic species, and showed how differences in species sensitivity can affect mass fluxes from sediment to the water column. This should be taken into account, (a) when evaluating the effectiveness of AC treatment or, (b) in the risk assessment of contaminated sediments, since traditional pore water concentration alone may underestimate HOC bioavailability and risk reduction.

If ecological side-effects of AC treatment exist, they may be visible through monitoring of sublethal behavioural endpoints, which can be considered to be more sensitive than traditional endpoints such as growth inhibition or mortality. In **Chapter 5**, we provide data on effects of AC addition on locomotion and ventilation, sediment avoidance, mortality and growth of two benthic species, *Gammarus pulex* and *Asellus aquaticus*, in clean versus polycyclic aromatic hydrocarbon (PAH) contaminated sediment. The series of whole-sediment behavioural toxicity tests with clean sediment demonstrated the absence of behavioural responses like locomotion, ventilation or avoidance. Our tests with *A. aquaticus* identified no negative effects for up to 28 d, whereas the application level of 2-4% would affect populations of *G. pulex* to a limited extent. It is not likely, however, that this would lead to extinction of this species. In contrast to the clean sediment, no survivors were detected in PAH contaminated sediment *without* AC. Addition of only 1% AC, however, already resulted in a substantial reduction of water exposure concentration and increased survival of *G. pulex* and *A. aquaticus*.

These series of laboratory single species bioassays showed that sediment treatment with AC reduces the risks associated with HOCs and substantially increases the habitat quality for benthic organisms (**Chapter 4** and **5**). At the same time it was shown that AC itself may have negative impacts on benthic organisms (**Chapter 4** and **5**). A key question is under what conditions the improvement of habitat quality due to HOC sequestration would compensate for the possible negative effects of AC. Therefore, in **Chapter 6**, a conceptual model to quantify the trade-off between the advantageous and the disadvantageous effects of AC on populations of two benthic species of different sensitivity was presented. The model describes population growth, incorporates concentration-effect relationships for PAHs in the pore water and for AC, and uses an equilibrium sorption model to estimate PAH pore water concentrations as a function of AC dosage. The model was calibrated using our bioassay data (**Chapter 5**) and evaluated by calculating isoclines of zero population growth for two species. The model framework was evaluated for a specific case, but may be used as a generic tool in risk assessment or as a tool in the design of sediment remediation. The framework is generally applicable to cases where sorbents are added to soils or sediments contaminated with HOCs.

AC effects observed in laboratory single species tests may be less severe in field settings, where recolonization occurs and where habitat quality may be maintained due to fresh input of nutrients and organic matter. Therefore, long term effects of AC application on benthic communities were investigated by evaluating the recolonization of AC treated sediment by benthic communities (**Chapter 7)**. Sediment from an unpolluted site was amended with increasing levels of AC, placed in trays and randomly embedded in the original site, which acted as a donor system for recolonization of benthic species. After 3 and 15 months, the trays were retrieved and benthic organisms identified. Using univariate and multivariate statistical analyses, a considerable recovery in terms of species diversity and abundance was observed already after 3 months, and full recovery of the community after 15 months. This was explained from migration of individuals from the donor system, followed by further migration and reproduction of the species in the next year. AC treatments explained 3% of the variance in the community data. Negative trends with AC were detected for Lumbriculidae and Pisidiidae which most probably relate to species-specific life-history traits. However, none of these species was extinct after 15 months post-treatment.

So far, the remediation effectiveness and ecological side effects have been studied for the benthic compartment only. It is not clear whether such effects can be observed on the level of an entire aquatic food chain (including fish), in real (i.e. not laboratory) aquatic ecosystems. In **Chapter 8**, the effects of three different AC treatments, viz. powdered AC addition, granular AC addition and addition and subsequent removal of granular AC (sediment stripping), on polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) concentrations in pore water, benthic invertebrates, zooplankton and fish (*Leuciscus idus melanotus*) were investigated. Sediment treatments with AC resulted in a significant decrease in freely dissolved PCB and PAH concentrations. The untreated sediment control showed concentrations in fish approaching lethal levels. Sediment treated with PAC, however, showed a reduction of accumulation of PCBs in fish by a factor of 16, which resulted in PCB levels below toxic thresholds. Furthermore, the treatments had no significant negative effect on fish condition. Bioaccumulation in fish was mainly explained by uptake from water and food (i.e. zooplankton) with fish-zooplankton LogBMFs being up to 1.76 after 3 months of exposure. Sediment amendment with GAC did not yield reductions in bioaccumulation in fish, due to limited reductions of bioaccumulation in zooplankton and invertebrates, whereas these components of the aquatic food web constituted the major uptake pathways for fish.

The effectiveness of AC application

The effectiveness of AC amendments mainly depends on desorption processes from the native sediment particles and subsequent sorption processes to AC. Thus, besides sediment geochemical characteristics, the efficiency of AC application depends on factors like particle size, AC concentration applied, AC pore structure and surface area.

The efficiency of AC application in sediment remediation can be evaluated by measuring the reduction in freely dissolved HOC concentrations in the overlying or pore water or by HOC analysis in target organisms like invertebrates, fish or plants.

In **Chapter 4**, **5**, and **8**, it has been shown that sediment treatment with 4% powdered AC results in almost complete, i.e. approaching 100%, removal of HOCs from the sediment pore water, closely followed by sediment stripping with granular AC and sediment treatment with 4% granular AC (reduction by 97 and 90%, respectively). Other studies applying up to

4% AC have shown significant reduction of aqueous concentrations of different classes of HOCs, i.e. PAH, PCB and DDT, by up to 99% *(3-10)*. However, in some cases AC application appeared to be not so efficient, which can be explained by a high contaminant to AC ratio resulting in saturation of the AC adsorption capacity, and as a result a lower affinity of HOCs for AC amendment *(10, 11)*.

As for reduction in bioaccumulation, the effects of different AC types, doses and particle sizes on bioaccumulation have been tested for a number of benthic invertebrates, zooplankton, and fish. The results showed that application of <4% of AC or similar carbonaceous materials lead to significant (i.e. up to 100%) decrease in bioaccumulation and in biota-to-sediment accumulation factors for invertebrates *(3, 9, 10, 12-26)*, (**Chapter 8**), and fish *(27)*, (**Chapter 8**). In this project, it is shown for the first time that AC treatment also reduces bioaccumulation in zooplankton and fish, using exposure for 3 months in outdoor model ecosystems (**Chapter 8**). These results compare to those from an early study *(27)*, which however was performed in the laboratory, only considered AC effects on bioconcentration by fish in the short term (5 days), and lacked the presence of natural prey species like zooplankton or invertebrate species.

In general, the effectiveness of AC to reduce bioaccumulation appeared to be species-specific, greatly depending on the physiology and behavior of the organisms, which drive factors such as ingestion rate, assimilation efficiency and elimination. Reduced bioaccumulation of HOCs agrees with reduced aqueous phase concentrations in response to AC additions up to 4-5% *(3, 13, 26)* but have been found to level off at AC dose >5% *(6)*. In long-term exposure experiments, reductions in HOC aqueous concentrations and bioaccumulation were observed in the first year *(3, 6)*. The non-significant improvement in bioaccumulation after one year might relate to the fact that HOCs with higher LogK_{OW} are subjected to slower mass transfer kinetics. AC particle size has been shown to have an effect on HOC bioaccumulation in the same way as on aqueous concentrations which was discussed in **Chapter 2** *(4, 26)*. In **Chapter 8**, it has been shown that at equal concentration, AC with a smaller particle and therefore higher surface area, facilitates HOC sequestration and results in lower bioaccumulation in aquatic organisms, which was also observed before *(18, 21)*. Granular activated carbon (GAC) will require months or even years to reach maximum treatment efficiencies (**Chapter 8**), *(28)*. To improve the short term effectiveness of GAC treatments, a higher GAC dose can be applied *(29, 30)*. A better efficiency of sediment treatment with AC can also be obtained by homogeneous distribution of AC particles in the sediment, which can be achieved by enhanced mixing or AC re-applications. Mixing may be insured as by mechanical mixing *(6, 12)*, natural processes, e.g. dispersion by water flow, wave pumping, or bioturbation. It has been shown that application of AC without mixing is nearly as effective as application with initial brief mixing *(31)*. In our field scale bioaccumulation experiments (**Chapter 8**) we also observed a high effectiveness of the PAC treatment after initial mixing only. We hypothesize that subsequent mixing by bioturbation *(32)*, turbulent dispersion due to wind induced pressure gradients *(33)* or direct wind-induced resuspension *(34)* ascertained sufficient mixing of AC.

There are several additional factors that may influence the effectivity of AC amendment like attenuation which can be a result of a competitive sorption or pore blocking by other dissolved compounds and particles, e.g., humic substances *(35)*. The degree of attenuation usually depends on AC characteristics like pore size distribution and the ability of target sorbates to compete with fouling substances, e.g. physical-chemical properties like molar volume and hydrophobicity, and the relative abundance of non-target species per available AC sorption site *(36)*. These processes can reduce the capacity of AC to sorb target compounds and/or slow down sorption kinetics *(7, 8, 17, 31, 35, 37)*.

Another important factor which potentially can affect AC efficiency under *in situ* conditions is bioturbation. In **Chapter 4**, it has been shown that the presence of bioturbators tolerant to AC addition, may on the one hand enhance mixing and facilitate HOC mass transport to AC particles, but on the other hand increase sediment-to-water fluxes of HOCs and thus reduce the effectiveness of AC in lowering overlying water concentrations. Consequently, this process should be taken into account when evaluating the effectiveness of AC treatment, since measuring pore water concentration alone may underestimate HOC mass fluxes and bioavailability.

It can be concluded that the maximum efficiency of 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 giving 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.

The ecological safety of AC application

In this work, the ecological effects of the presence of AC in sediments were tested for three benthic invertebrates, *Asellus aquaticus*, *Gammarus pulex*, and *Lumbriculus variegatus*, in three different sediments, one clean, one moderately polluted and one highly polluted, amended with two types of AC, powdered and granular, in AC concentrations up to 30% d.w., in 6 different experiments after 3 to 28 days of exposure (**Chapter 4** and **5**). In addition, effects of AC application on benthic communities were investigated by evaluating the recolonization of such communities (**Chapter 7**). Effects of AC on an aquatic food web were studied by evaluating invertebrate and zooplankton functional group abundances and lipid contents, and for fish, assessing effects on lipid content, length, weight and condition factors (**Chapter 8**). The series of sensitive whole-sediment behavioural toxicity tests with *clean* sediment demonstrated the absence of subtle behavioural responses like locomotion, ventilation or avoidance. Our tests with *Asellus aquaticus* identified no negative effects for up to 28 d, whereas the application level of 2-4% could affect populations of *Gammarus pulex* to some extent. It is not likely, however, that this would lead to extinction of this species. After all, mortality was not complete and in natural settings fresh inputs of organic matter and nutrients will dilute AC concentrations and improve the quality of the habitat for these species. Furthermore, AC will never be added to clean, unpolluted sediments. Addition of AC to *contaminated* sediment had a positive effect on the survival of benthic species. No negative effects of AC application of AC were identified on the community or ecosystem level.

In the literature, survival, growth, lipid content and behaviour are the main ecotoxicological endpoints used to test AC effects. These were mainly investigated for benthic species, mainly filter feeders, deposit and facultative deposit feeders and carnivores. Survival in sediments amended with AC in the range 0.7-30% was solely tested for benthic invertebrates. Most of the studies did not report any negative effect of AC amendment to *unpolluted* sediments on the survival of benthic species like the polychaete *Neanthes arenaceodentata*, the mussel *Mytilus eduli*, the clams *Macoma balthica* and *Macoma nasuta*, the amphipods *Leptocheirus plumulosus* and *Corophium volutator*, and the isopod *Asellus aquaticus (12, 19, 24, 38-42)*, (**Chapter 5**). A decreased survival was reported only for two species, viz. the clam *Macoma balthica* and the amphipid *Gammarus pulex (17, 41)*. However, in a series of experiments with *contaminated* sediment amended with AC, positive AC dose-response relationships, that is, an increased survival of tested species, e.g. the oligochaete *Lumbriculus variegatus*, the isopod *Asellus aquaticus*, the amphipods *Gammarus pulex* and *Ampelisca abdita*, the mysid shrimp *Americamysis bahia*, and the polychaete *Neanthes arenaceodentata*, with increasing AC dose was observed *(38, 39, 41, 43)*, (**Chapter 4** and **5**).

No or very mild effects on growth were observed for the clam *Macoma balthica*, the mussel *Mytilus edulis*, the amphipods *Leptocheirus plumulosus* and *Gammarus pulex*, the freshwater clam *Carbicula fluminea*, and the isopos *Asellus aquaticus* in sediment amended with <30% AC, and for the sea snail *Nassanus nitidus*, the clam *Abra nitida*, and the brittle star *Amphiura* spp. in sediment capped with AC *(17, 19, 24, 39, 41, 42, 44)*, (**Chapter 5**). The growth behavior of the polychaete *Neanthes arenaceodentata* showed a sediment-specific response to AC amendments *(19, 44)*. No negative effects on the growth or condition factor of *Leuciscus idus melanotus* (golden orfe) were reported in contaminated sediments amended with powdered and granular AC (**Chapter 8**).

Lumbriculus variegatus was shown to have a negative response to sediments treated with AC causing significant decrease in lipids content *(15, 40)*. For another worm, *Neanthes arenaceodentata*, inconsistent results were observed. That is, with the same sediment and AC type, tests showed absence of effects as well as significant effects of AC on lipids content which could not be explained by AC dose *(14, 39)*. Sediment amendment with <5% AC did not have an effect on lipid contents in a number of species: the clam *Macoma nasuta*, the amphipod *Leptocheirus plumulosus*, the snail *Hinia reticulate* and *Nassanus nitidus*, the worms *Nereis diversicolor*, *Lumbriculus variegatus*, and *Nereis* spp. *(8, 12, 18, 19, 42)*. In case growth, lipid and total biomass effects were observed, altered bioavailability of nutrients in sediment was suggested as a potential mechanism *(19, 44-46)*, (**Chapter 7**).

As for behavioral endpoints, preference/avoidance behavior was tested in two studies for three benthic invertebrate species, viz. the isopod *Asellus aquaticus* and the amphipods *Corophium volutator* and *Gammarus pulex*, using different sediments amended with up to 30% AC *(40, 41)*, (**Chapter 5**). The avoidance was either not observed *(41)*, (**Chapter 5**) or could not be proven from the data, because of inconsistent dose-response relationships *(40)*. No effects of AC on locomotion and ventilation were demonstrated for *Asellus aquaticus* and *Gammarus pulex* in whole-sediment behavioral toxicity tests *(41)*, (**Chapter 5**). A significant reduction in egestion rate was observed for the worm *Lumbriculus variegatus (40)*.

The influence of AC amendment on the diversity and abundance of macroinvertebrate communities has been assessed in four field pilot studies *(3, 46-48)*, (**Chapter 7**). Addition of 2-10% AC to the sediment did not show any effects on community abundance or diversity after up to 1.5 year of exposure *(3, 46)*, (**Chapter 7**), whereas the use of AC as a capping material showed a significant effect on diversity *(48)* as well as on diversity and abundance *(47)*. These effects of capping can partially be explained with seasonal variability or due to substantial exceeding of target AC dose during AC placement as a cap.

Only three studies investigated the impacts of AC amendments on bacterial communities. An AC amendment to uncontaminated and contaminated sediment with up to 20% AC had no effect on the bacterial community composition *(40, 49)*, whereas in another experiment some alteration of bacterial communities, i.e. an increase in bacterial production and respiration, was observed *(48)*. Notably, several studies showed the potential of AC to facilitate bacterial degradation of HOCs *(50, 51)*.

It can be concluded that, generally, AC amendments to contaminated sediment have a beneficial effect on the survival of aquatic organisms. Some reduction in survival was observed only for AC amendments to *uncontaminated* sediment for two species. The majority of tests with growth as an endpoint did not show any adverse effects of AC application. Studying AC effects on lipid contents revealed inconsistent results, i.e. negative effects were limited to two burrowing worm species out of the total 7 species tested. However, reduced growth and lipid content were the dominant secondary effects of AC amendments.

Evaluation of alternatives for the remediation of contaminated sediments

For contaminated sediments, the remediation process typically includes a site investigation, a comparison of remediation alternatives, and a selection and implementation of one remediation scenario *(52)*. An example of a qualitative comparative analysis of remediation alternatives is summarized in Table 1. Site characterisation was briefly discussed in the beginning of this chapter and usually covers the distribution, depth, types and concentrations of contaminants in sediments and contaminant concentrations in the aquatic biota. The comparison of remediation alternatives usually depends on several key factors, i.e. complexity and costs of remediation approaches, the benefits and associated risks that can arise during implementation and those that remain after remediation. The best option for a particular site will be the one that stays within the regulatory context and will help to achieve maximum efficiency with minimum adverse ecological effects, and investments of time and energy *(1)*.

Monitored natural recovery or ‘natural attenuation’ is the least difficult and least expensive *(1)*. It leaves contaminants in the aquatic environment but does not itself create new risks. However the process of natural recovery might take decades and the success of this remediation approach is difficult to predict. In addition, in aquatic systems with unfavourable hydrological conditions or physical disturbances causing resuspension and thus release of sediment-associated contaminants, natural recovery might be not the optimal remediation strategy.

In situ capping of contaminated sediment with clean silt or sand can be a good option in some areas. However, capping may not sufficiently reduce contaminant transport due to permeability or erosion of capping materials, for instance in areas with dynamic hydrological and topographical conditions *(46)*. The material costs of this approach can be high.

Dredging is the most complex, invasive and expensive *(46)*. Dredging may create extra exposure, for instance through the resuspension of buried contaminants. Dredging is a proven technology to remove contaminated sediments permanently from the aquatic environment, but shifts the problem to another place where further management is required. Dredging can be useful when applied to sediments liable to erosion and to variations in hydrologic conditions. However, dredging is very disruptive to the ecosystem. Inefficient removal of contaminated sediment during dredging may result in residual concentrations of contaminants in sediment and pore water still exceeding safe levels *(2)*.

AC amendment to contaminated sediments is a very efficient remediation technique that can be a successfully used for the sites with depositional and cohesive characteristics as well as in low energy environments, where the probability of sorbent translocation after incorporation into contaminated sediment is low *(11, 53, 54)*. 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, e.g. stabilization with additional layers of sand, gravel, or clay. Capping with such layers would decrease the risk of contaminated AC being dispersed within the aquatic environment. Moreover, AC can be applied when dredging is not feasible or appropriate as well as in ecologically sensitive sites such as wetlands *(53)*. Whenever ecological side-effects need to be considered, a prognostic conceptual framework is now available that may be further developed to a decision support tool capable of balancing the benefits against the ecological side effects of *in situ* AC treatments (**Chapter 6**). Another promising alternative to the *in situ* methods could be sediment stripping *(55)* that could be applied in combination with dredging as an alternative to bioremediation or physical separation cleaning techniques with subsequent reuse of the stripped material on land or as building materials. The material costs of sediment remediation with AC is one order of magnitude lower than that of dredging and disposal *(53)*, and even the cost for AC based remediation can be reduced by using alternative carbonaceous materials like biochar, coke breeze and fly ash, or AC produced from biomass waste products like pine chips or corn stalk *(10, 11, 19, 53, 56)*. A potential barrier for commercial use of AC based remediation technologies is the regulatory context. It is well known that addition of AC to sediments reduces bioavailable concentration of contaminants, but does not decrease their total concentrations in sediment. This implies that as long as permissions for sediment re-use or management are based on total concentrations, implementation of AC based technologies may be hampered *(57)*. Although regulatory institutions start considering bioavailability in risk assessment and management of contaminated sediment *(58, 59)*, there is still a bias against *in situ* methods.

In conclusion, AC based sediment remediation technologies offer great flexibility, i.e. can be used along or in combination with other approaches, *in situ* and *ex situ*, and can be applicable in a wide range of settings and sites with different characteristics, and would avoid some of the problems with traditional dredging and capping. Mild effects of AC itself, if any, will be overshadowed by the advantageous effects of AC to sequestrate HOC and reduce the risks associated with them.

Table 1. Comparison of remediation strategies.

Criteria	**MNA**	**Capping**	**Dredging**	**AC**		
				In situ		**Ex situ**
				PAC	**GAC**	**Stripping**
Complexity	-	++	+++	+	+	++
Costs	-	++	+++	+	+	+
Efficiency	---	+	+	+++	+	++
Risks	+	++	+++	+-	+	---
Applicability (type of sites)	sensitive, protected	stable, depositional	with dynamic hydrological conditions, liable to erosion	depositional, cohesive, low energy, sensitive, deeper waters*, sloping areas*, with low sediment stability*, and extreme erosion conditions*		n/a
Acceptance:						
(a) regulatory	+++	+++	+++	-	-	-
(b) public		+-	---	-	-	-

*****specific measures should be taken, e.g. stabilization with additional layers of sand, gravel, or clay
"+" refers to "high", "-" refers to "low".

Outlook and recommendations

The past years, considerable progress has been made in understanding benefits and risks associated with AC application in contaminated sediments. Overall, the mild negative effects of AC itself, if any, seem to be negligible compared to the ability of AC to sequestrate HOCs efficiently, to limit their mobility and therefore to reduce exposure of HOCs to aquatic organisms and indirectly - humans. The results from full scale AC application studies showed stability of AC in the environment and demonstrated its efficiency in binding contaminants in sediments several years after application *(3, 6, 12, 53)*. At the same time, AC did not show a significant impact on benthic communities based on taxa abundances and diversity *(3, 46)*, and on an aquatic ecosystem as a whole (**Chapter 8**). The recent ecological studies suggest that AC effects on the community and ecosystem level are absent or less severe compared to those observed in single species laboratory tests, known from earlier studies. Consequently, amendment of AC to contaminated sediment is considered as a serious and promising new remediation technique. However, since the main objective of any restoration process is to provide the utmost benefit with minimal risk, some additional remaining questions may be considered to further facilitate regulatory acceptance of this new remediation technique in full-scale applications.

Methods of AC delivery to the sediment remain to be a technological challenge. Ideally, AC delivery should be minimally invasive and avoid sediment resuspension and increase of pollutant mobilization in the aquatic environment. On the one hand, enhanced mixing will increase homogeneity of AC-sediment mixture and increase remediation efficiency. On the other hand, mixing can be considered to be disadvantageous from an ecological point of view since it may have a negative impact on benthic communities in the short term.

Another uncertainty relates to the long term stability of AC in aquatic sediments. Despite AC has been shown to be stable after 3 years *(3, 6, 53)*, stability of AC under unfavourable hydrological and geological conditions is still lacking.

So far, effects of AC application were mainly tested in laboratory bioassays with survival, growth, behavior and lipid content as ecotoxicological endpoints. To understand the mechanisms of AC effects on benthic organisms and to bridge the biological responses across different levels of biological organization, i.e. species, benthic communities and aquatic ecosystems, AC effects on reproduction of individuals as well as possible effects on following generations may be addressed in future studies.

Because the method of AC application in sediment remediation is still novel, more comprehensive studies including the community and ecosystem level like that in **Chapter 8** are required. Especially, long-term effects on community and food web structure and function need to be investigated after application of AC in real ecosystems. Consequently, full-scale AC application studies need to be carried out and monitored for a long period (e.g. for several years) to be able to give an answer to the abovementioned questions.

Further research may focus on developing modelling approaches for the purpose of understanding cause-effect mechanisms that underlie experimental data. Furthermore, system models may assist in predicting effects and benefits of a certain AC-based remediation strategy in the future. Such models should incorporate the fate of HOCs, the long-term performance of AC, and take into account the effects on benthic communities and aquatic food webs and their associated uncertainties *(60, 61)*. Models may better predict ecosystem recovery under various remediation scenarios and will help decision makers and sediment managers to select appropriate remediation approaches (e.g. AC addition, capping, stripping) at particular sites, define the extent of remediation, and make credible predictions of the chemical and biota impacts based on the best scientific information available *(62)*.

Comprehensive comparative analysis is needed to evaluate the benefits and risks of AC amendment with respect to other traditional remediation strategies, such as dredging and capping. Even though costs of AC applications appear to be lower than those of traditional methods, both pre-treatment and monitoring costs need to be considered. A framework for comparing decision criteria and the life cycle for different remediation strategies needs to be established in greater detail.

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SUMMARY

Aquatic sediments form an ultimate sink for legacy contaminants such as hydrophobic organic compounds (HOCs) and may become a source of secondary pollution, thus posing a risk to aquatic organisms and humans. Traditional remediation approaches of contaminated sediment, like dredging and *in situ* capping, are disruptive to benthic environments, not always efficient, and very expensive. Therefore, new developments in remediation approaches are needed that either supplement or provide less laborious, less expensive, and less disruptive alternatives to existing methods. Over the past years the potential of adding sorptive materials, like activated carbons (AC), to polluted sediment, as a means to reduce aqueous HOC concentrations, has been explored. The current research was meant to increase our understanding of the effects of AC application on HOC exposure and toxicity reduction for benthic species and communities, and to bridge the gap between laboratory and field settings for AC remediation.

In **Chapter 2**, we review the current state of the art for the use of AC as an extensive method for sediment remediation, covering both technical and ecological angles. In the review we discuss how factors such as AC type, particle size and dosage, sediment characteristics, properties of adsorbates, and presence of other carbonaceous materials like BC, OM, and oil affect the AC amendment efficiency to adsorb HOCs and to reduce HOC bioaccumulation in benthic macroinvertebrates. We also review to what extent AC may reduce toxicity of contaminants and whether it has negative effects on benthic species and communities. In the end we discuss if the effects of AC addition can be predicted using fate and transport models.

Since sediments and AC types differ in their characteristics, it is highly relevant to identify the affinity parameters for *in situ* sorption of HOCs to AC in order to be able to design and evaluate applications of AC in sediment remediation. A conceptual framework to assess affinity constants for HOC sorption to BC and AC is provided in **Chapter 3**. It appears that sorption to BC increases with LogK_{OW}, whereas sorption to AC shows a relatively narrow range of affinity properties with a median Freundlich Log$K_{F,AC}$ value of 7.2 for polychlorinated biphenyls (PCBs) and 8.6 for polycyclic aromatic hydrocarbons (PAHs). Sorption to AC is stronger than to BC for chemicals below LogK_{OW}=6.3–6.6. The developed model and optimized *in situ* K_{BC} and K_{AC} can be used, when designing an AC dosage, to predict the efficiency of AC amendments.

In **Chapter 4**, effects of three different sediment treatments with AC, viz. powdered AC addition, granular AC addition, and addition and subsequent removal of granular AC (sediment stripping), on PCB pore water concentrations, sediment-to-water fluxes, and mass transfer coefficients, are assessed. Sediment treatment with AC is shown to decrease pore water concentrations of PCBs. Moreover, the efficiency of the AC-treatments decrease in the order PAC > sediment stripping > GAC. AC addition is shown to decrease mass fluxes but increase apparent mass transfer coefficients due to dissolved organic carbon (DOC) facilitated transport across the benthic boundary layer (BBL). The presence of bioturbators may also stimulate DOC facilitated transport of HOC, increase fluxes and thus decrease efficiency of sediment treatment with AC. A dual BBL resistance model, combining AC effects on PCB concentration gradients, DOC facilitated transport and biodiffusion, is evaluated against the experimental data. The analysis of the results illustrates the variation in resistance between different treatments and PCB congeners with different hydrophobicity.

In **Chapter 5**, we provide data on effects of AC addition on locomotion and ventilation, sediment avoidance, mortality, and growth of two benthic species, *Gammarus pulex* and *Asellus aquaticus*, in clean versus polycyclic aromatic hydrocarbon (PAH) contaminated sediment. The series of whole-sediment behavioural toxicity tests with clean sediment demonstrates the absence of behavioural responses like locomotion, ventilation or avoidance. Our tests with *A. aquaticus* identify no negative effects for up to 28 d, whereas the application level of 2-4% AC would affect populations of *G. pulex* to some extent. It is not likely, however, that this would lead to extinction of this species.

Thus, a series of laboratory single species bioassays has shown that sediment treatment with AC reduces the risks associated with HOCs and increases the habitat quality for benthic organisms (**Chapter 4** and **5**). At the same time, it has been shown that AC itself may have negative impacts on benthic organisms (**Chapter 4** and **5**). A key question is under what conditions the improvement of habitat quality due to HOC sequestration would compensate for the possible negative effects of AC. In **Chapter 6**, a conceptual model to quantify the trade-off between the advantageous and the disadvantageous effects of AC on populations of two benthic species of different sensitivity has been presented. The model describes population growth, incorporates concentration-effect relationships for PAHs in the pore water and for AC, and uses an equilibrium sorption model to estimate PAH pore water concentrations as a function of AC dosage. The model is calibrated using bioassay data (**Chapter 5**) and evaluated by calculating isoclines of zero population growth for two species. The current framework is evaluated for a specific case, but may be used as a tool in risk assessment or when designing sediment remediation scenarios and can be generally applicable to cases where sorbents are added to soils or sediments contaminated with HOCs.

AC effects observed in laboratory single species tests may be less severe in field settings, where a better habitat quality may be maintained due to fresh input of nutrients and organic matter. Therefore, long term effects of AC application on benthic communities are investigated by evaluating the recolonization of benthic communities in **Chapter 7**. Sediment from an unpolluted site is amended with increasing levels of AC, placed in trays and randomly embedded in the original site, which acts as a donor system for recolonization of benthic species. After 3 and 15 months, the trays are retrieved and benthic organisms identified. From the univariate and multivariate statistical analyses, a considerable recovery in terms of species diversity and abundance is observed already after 3 months, and full recovery of the community after 15 months. This is explained by migration of individuals from the donor system, followed by further migration and reproduction of the species in the next year. AC treatments explain 3% of the variance in the community data. Negative trends with AC are detected for Lumbriculidae and Pisidiidae which most probably relate to species-specific life-history traits.

So far, the remediation effectiveness and ecological side effects have been studied for the benthic compartment only. It is not clear whether such effects can be observed on the level of an entire aquatic food chain (including fish), in full scale i.e. not laboratory aquatic ecosystems. In **Chapter 8**, the effects of three different AC treatments, viz. powdered AC addition, granular AC addition, and addition and subsequent removal of granular AC (sediment stripping), on polycyclic aromatic hydrocarbon (PAHs) and polychlorinated biphenyl (PCBs) concentrations in pore water, benthic invertebrates, zooplankton and fish (*Leuciscus idus melanotus*) are investigated. Sediment treatments with AC result in a significant decrease in freely dissolved PCB and PAH concentrations. Sediment treated with PAC shows a reduction of accumulation of PCBs in fish by a factor of 100, which results in PCB levels in fish below toxic thresholds and had no significant negative effects on fish condition. Bioaccumulation in fish is mainly explained by uptake from water and food (i.e. zooplankton) with fish-zooplankton LogBMFs being up to 1.76 after 3 months of exposure. Sediment amendment with GAC does not yield reductions in bioaccumulation in fish, due to limited reductions of bioaccumulation in zooplankton and invertebrates, whereas components of the aquatic food web are considered to be major uptake pathways for fish.

Finally, in **Chapter 9**, we summarize all benefits and risks associated with AC application, evaluate alternatives for the remediation of contaminated sediments, and give an outlook and recommendations for future studies.

SAMENVATTING

Klassieke verontreinigingen zoals hydrofobe organische verbindingen (HOCs) komen uiteindelijk vaak in waterbodems terecht. Deze waterbodems kunnen hierdoor zelf een bron van verontreiniging worden en zo een risico vormen voor aquatische organismen en voor de mens. Traditionele manieren om waterbodems te reinigen, zoals baggeren en *in situ* capping, zorgen voor een grote verstoring van het benthische milieu en zijn niet altijd effectief, terwijl zij wel hoge kosten met zich meebrengen. Daarom is het nodig om nieuwe methoden voor reiniging van waterbodems te ontwikkelen die makkelijker zijn, minder kosten en minder verstorend zijn dan de bestaande methoden. De afgelopen jaren is de mogelijkheid onderzocht om adsorberende materialen zoals actieve kool (AC) toe te voegen aan verontreinigde waterbodems om zo de HOC concentratie in het water te verminderen. Dit onderzoek heeft als doel om het effect van toevoegen van AC op HOC blootstelling en toxiciteitsafname voor bentische organismen en gemeenschappen beter te begrijpen, om zo het gat tussen laboratorium en veld te dichten.

In **Hoofdstuk 2** bespreken we de huidige stand van zaken voor wat betreft het gebruik van AC als een methode voor het saneren van waterbodems. Hier behandelen we hoe verschillende factoren de efficiëntie van AC om HOCs te binden veranderen en de HOC bioaccumulatie in benthische macroinvertebraten beïnvloeden. We bespreken factoren zoals AC type, deeltjesgrootte en -dosis, waterbodem karakteristieken, eigenschappen van HOCs en de aanwezigheid van andere vormen van koolstof zoals ‘black carbon’ (BC), organisch materiaal (OM) en olie. We bespreken ook in welke mate AC de toxiciteit van verontreinigingen vermindert, en of het negatieve effecten heeft op benthische soorten en gemeenschappen. Uiteindelijk bediscussiëren we de mogelijkheid om de effecten van het toevoegen van AC te voorspellen met modellen.

Door de verschillen in karakteristieken die waterbodems en AC hebben, is het hoogst relevant om de affiniteitsparameters te identificeren voor de *in situ* sorptie van HOCs aan AC. Hierdoor kan het mogelijk worden om toepassingen te ontwerpen en te evalueren voor sanering van waterbodems met AC. Een conceptueel raamwerk voor het schatten van affiniteitsconstanten voor HOC soprtie aan BC en AC wordt gegeven in **Hoofdstuk 3**. Het blijkt dat de sorptie aan BC toeneemt met LogK_{OW}. Terwijl de sorptie aan AC slechts een relatief nauw bereik van affiniteits eigenschappen laat zien met een mediane Freundlich Log$K_{F,AC}$ van 7.2 voor polychloorbifenylen (PCBs) en 8.6 voor polycyclische aromatische koolwaterstoffen (PAKs). Sorptie aan AC is sterker dan aan BC voor chemicaliën met een LogK_{OW} lager dan 6.3-6.6. Het ontwikkelde model en de geoptimaliseerde *in situ* K_{BC} en K_{AC} kunnen worden gebruikt voor het ontwerpen van een AC dosering en om de efficiëntie van de AC toevoeging te voorspellen.

In **Hoofdstuk 4** worden de effecten van drie verschillende waterbodembehandelingen met AC op PCB poriewaterconcentraties, sediment-water fluxen en massa-overdracht coëfficiënten getest. De drie behandelingen bestaan uit een toevoeging van AC poeder (PAC), een toevoeging van AC korrels (GAC) en de toevoeging en daaropvolgende verwijdering van AC korrels (sediment stripping). De waterbodembehandeling met AC blijkt de poriewater concentraties van PCBs te verlagen. Ook wordt de efficiency van de AC behandeling verlaagd in de volgorde PAC > sediment stripping > GAC. Toevoeging van AC verlaagt de massaflux, maar verhoogt de schijnbare massa-overdracht coëfficiënten als gevolg van transport door de benthische grenslaag (BBL) gefaciliteerd door het opgeloste organische koolstof (DOC). Ook de aanwezigheid van bioturbators kan het transport van HOC met behulp van DOC stimuleren, fluxen doen toenemen en daardoor de efficiency van de AC behandeling doen afnemen. Een dubbel BBL weerstandsmodel dat het effect van AC op PCB concentratiegradiënten combineert met DOC gefaciliteerd transport en biodifussie, wordt geëvalueerd met experimentele data. Uit analyse van de resultaten blijkt dat de transportweerstand verschilt voor verschillende behandelingen en PCB's met verschillende hydrophobiciteit.

In **Hoofdstuk 5** presenteren we gegevens over effecten van AC toevoeging op de beweging en ventilatie, het vermijden van de waterbodem, de mortaliteit en de groei van twee benthische soorten, *Gammarus pulex* en *Asellus aquaticus*, in schoon en met PAK vervuild sediment. De toxiciteitstesten met schoon sediment laten geen gedragsreactie, zoals motoriek, ventilatie of ontwijking. zien. Onze testen met *A. Aquaticus* laten geen negatieve effecten zien tot 28 dagen, maar de toevoeging van 2-4% AC heeft tot op zekere hoogte wel effect op de populatie van *G. Pulex*. Het is echter niet waarschijnlijk dat dit zou leiden tot uitsterven van deze soort.

Aldus heeft een serie van *single species* bioassays in het laboratorium laten zien dat waterbodembehandelingen met AC de risico's geassocieerd met HOCs verminderen en de kwaliteit van de leefomgeving van benthische organismen verbeteren (**Hoofdstuk 4** en **5**). Tegelijkertijd is aangetoond dat AC zelf negatieve effecten kan hebben op bentische organismen (**Hoofdstuk 4** en **5**). Een belangrijke vraag is onder welke omstandigheden de verbetering van de leefomgeving door de vastlegging van HOC de mogelijke negatieve effecten van AC zelf zal compenseren. In **Hoofdstuk 6** is een conceptueel model voor de kwantificering van de wisselwerking tussen de positieve en negatieve effecten van AC op de populatie van twee benthische organismen van verschillende gevoeligheid gepresenteerd. Het model beschrijft populatiegroei, dosis-effect relaties voor PAK's in het poriewater, en voor AC, en het maakt gebruik van een evenwichtssorptie model om de PAK concentratie in het poriewater als een functie van AC dosis te schatten. Het model is gekalibreerd met behulp van bioassay data (**Hoofdstuk 5**) en is geëvalueerd door middel van het berekenen van nullijnen voor populatiegroei van twee soorten. De huidige opzet is geëvalueerd voor een specifieke casus, maar zou ook gebruikt kunnen worden als een methode voor risicobeoordeling of voor het ontwerpen van sediment remediatie scenario's.

AC effecten die zijn aangetoond in *single species* laboratorium testen, zijn in het veld vermoedelijk minder groot, door de verse toevoer van nutriënten en organisch materiaal. De lange termijn effecten van AC toepassing op rekolonisatie van benthische gemeenschappen zijn bestudeerd in **Hoofdstuk 7**. Sediment van een verontreinigde locatie is behandeld met toenemende niveaus van AC, in bakken gedaan en willekeurig teruggeplaatst op de originele locatie, die nu als donor systeem dient voor de rekolonisatie van benthische soorten. Na 3 en 15 maanden zijn de bakken er uit gehaald en de benthische organismen zijn geïdentificeerd.

Via univariate en multivariate statistische analyses is al na 3 maanden een aanzienlijk herstel op basis van soortendiversiteit aangetoond en een volledig herstel van de gemeenschap na 15 maanden. Dit wordt verklaard door migratie van individuen vanuit het donor systeem, gevolgd door verder migratie en reproductie van soorten in het volgende jaar. AC behandeling verklaart 3% van de variatie in de benthische levensgemeenschap. Negatieve trends met AC zijn aangetroffen voor Lumbriculidae en Pisidiidae, hetgeen waarschijnlijk gerelateerd is aan specifieke eigenschappen van de levenscyclus van deze soorten.

Tot dusverre werden de effectiviteit van remediatie en de ecologische neven effecten van AC alleen bestudeerd voor het benthische compartiment. Het is niet duidelijk of AC effecten heeft op het niveau van een volledig aquatische voedselketen (inclusief vis). In **Hoofdstuk 8** zijn de effecten van drie verschillende AC behandelingen (toevoeging van AC in poedervorm (PAC) en korrelvorm (GAC), en toevoeging en opeenvolgend verwijdering van korrelvormig AC; sediment stripping) bestudeerd, op concentraties van polycyclische aromatische koolwaterstoffen (PAK's) en polychloorbifenylen (PCB's) in poriewater, benthische invertebraten, zoöplankton en vis (*Leuciscus idus melanotus*). Sediment behandelingen met AC resulteren in een sterke afname van vrij opgeloste PCB en PAK concentraties. Sedimentbehandeld met PAC vertoont een reductie in accumulatie van PCB's in vis met een factor 100, hetgeen resulteerde in PCB niveaus beneden de toxische grenzen en geen significante negatieve effecten had op de conditie van de vis. Bioaccumulatie in vis wordt hoofdzakelijk verklaard via opname vanuit water en voedsel (in dit geval zoöplankton) met vis-zoöplankton LogBMF's tot 1,76 na een blootstelling van 3 maanden. Sediment, bewerkt met GAC laat geen reductie van bioaccumulatie in vis zien, vanwege de beperkte afname van bioaccumulatie in zoöplankton en invertebraten. Deze componenten van de aquatische voedselketen worden gezien als de belangrijkste opnameroutes voor vis.

Tenslotte, vatten we in **Hoofdstuk 9** alle voordelen en risico's van sediment-behandeling met AC samen. Alternatieven voor remediatie van gecontamineerde waterbodems worden gegeven en een vooruitzicht en aanbevelingen voor toekomstige studies worden geïdentificeerd.

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ABOUT THE AUTHOR

Curriculum vitae

Darya Kupryianchyk was born in 1983 in Ivatsevichy, Belarus. She started studying Environmental Management at Belarusian National Technical University in 2001. Waste management, water purification and air cleaning systems were of particular interest to Darya. At her bachelor thesis, focusing on improving waste oil treatment methods, she worked at The Ball Bearing Factory, Minsk, and at The International Institute of Industrial Environmental Economics (IIIEE) at Lund University, Sweden. After obtaining her BSc in 2006 (*cum laude*), Darya was awarded a scholarship from The Swedish Institute and enrolled in Master's Program in Environmental Chemistry at Stockholm University, Sweden. During her studies she specialized in chemical processes in the environment and fate and effects of different contaminants on environmental and human health. In her thesis she investigated if indoor living and canned food increase exposure of pet cats to traditional and emerging organohalogen compounds. After graduation in 2008, Darya started her PhD research at the Aquatic Ecology and Water Quality Management Group of Wageningen University. It aimed at exploring potential of sorptive materials like activated carbon to reduce risks of sediment bound contaminants and to increase the quality of aquatic ecosystems.

List of publications

Kupryianchyk, D., Rakowska, M.I., Roessink, I., Grotenhuis, J.T.C., and Koelmans, A.A., 2012. In situ activated carbon amendment reduces bioaccumulation in aquatic food chains. Environmental Science and Technology, *in revision*.

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CERTIFICATE

The Netherlands Research School for the
Socio-Economic and Natural Sciences of the Environment
(SENSE), declares that

Darya Kupryianchyk

born on 13 November 1983 in Ivatsevichy, Belarus

has successfully fulfilled all requirements of the
Educational Programme of SENSE.

Wageningen, 1 February 2013

the Chairman of the SENSE board

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the SENSE Director of Education

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The SENSE Research School declares that **Ms. Darya Kupryianchyk** has successfully fulfilled all requirements of the Educational PhD Programme of SENSE with a work load of 45 ECTS, including the following activities:

SENSE PhD Courses

- Environmental Research in Context
- Research Context Activity: Co-organizing expert workshop "Innovations in sediment remediation technology", 17 October 2012, Wageningen
- Introduction to R for Statistical Analysis

Other PhD Courses

- PhD competence assessment
- Techniques for writing and presenting a scientific paper
- Teaching and supervision thesis students
- Career Assessment

Management and Didactic Skills Training

- Communication team Aquatic Ecology Department
- Co-organisation of Scientific Strategy Day; PhD Strategy Day;
- Supervising two MSc Thesis
- Assisting in the MSc courses *Practical aquatic ecology and water quality; Environmental quality and governance*; and *Chemical processes in soil-water-atmosphere*

Oral Presentations

- *Safe ranges of activated carbon application in sediment remediation.* SETAC Europe 20th Annual Meeting, 23-27 May 2010, Seville, Spain
- *Sediment remediation with activated carbon: Modeling the trade-off between PAH toxicity reduction and negative activated carbon effects on macroinvertebrate populations.* SETAC Europe 21st Annual Meeting , 15-19 May 2011, Milan , Italy
- *Sorbent amendments: Balancing benefits and limitations.* Workshop "Innovations in sediment remediation technology", 17 October 2012, Wageningen, The Netherlands

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