Strong Sorption of Native PAHs to Pyrogenic and Unburned Carbonaceous Geosorbents in Sediments

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It has recently been shown that the presence of carbonaceous geosorbents (CG, including black carbon (BC), unburned coal, and kerogen) can cause strong sorption of polycyclic aromatic hydrocarbons (PAHs) in sediments. We studied sorption of native PAHs in four Norwegian harbor sediments of which high fractions (21−56%) of the total organic carbon (TOC) consisted of CG carbon (CGC), as shown by organic petrography. PAH sorption coefficients were 1−2 orders of magnitude above predictions based on amorphous organic carbon partitioning alone. In recent studies, such strong sorption was attributed solely to BC sorption under the implicit assumption that sorption is linear for coal and kerogen. The most important result of the present study is that total sorption is better explained by considering all three nonlinearly sorbing CGC materials than by only considering BC. In addition, it was evaluated whether activated carbon (AC) amendments could be effective in reducing the freely dissolved pore-water concentrations (C_W) and thus the environmental risks of the PAHs in such strongly sorbing sediments. The results indicated that an addition of 2 weight % AC reduced the C_W by factors of 21−153 for the four sediments (average values for all PAHs). It was shown that phenanthrene sorption to AC was, on average, reduced by a factor of 6 in sediment−AC mixtures compared to pure AC.

Introduction

Some years ago it was shown that sorption of hydrophobic organic chemicals (HOCs) to sediments and soils could be strong and nonlinear, and could be described by "dual-mode" sorption (*1, 2*). According to the dual-mode sorption paradigm, the organic matter (OM) of sediments and soils consists of two domains: (i) soft, amorphous materials (e.g., *1−3*), showing linear and noncompetitive *ab*sorption and (ii) hard, condensed, and aromatic materials that show nonlinear, extensive, and competitive *ad*sorption (e.g., *1, 2*). One "school" of sorption scientists interprets the latter adsorption domain as consisting of carbonaceous geosorbents (CG), such as unburned coal particles (here defined as lignite, bitumi-

nous coal, and anthracite, but not peat) (e.g., *3−8*), kerogen (e.g., *1, 8*), as well as soot and charcoal (the residuals of incomplete combustion, commonly termed "black carbon" or BC) (e.g., *3, 5, 6−15*). The terms amorphous organic carbon (AOC) and carbonaceous geosorbent carbon (CGC) refer to the carbon-normalized amounts of these two classes of organic carbon (OC).

Several authors have shown that the inclusion of a BC sorption term in the overall sorption equation significantly improves the description of total sorption (*4, 5, 10, 11, 13, 14*). Mostly, only the BC part of the CGC has been included in such descriptions, where BC was quantified by chemo-thermal oxidation at 375 °C (*10, 11, 13, 14*), or as the inertinite content obtained by organic petrography (*5*). In one instance, the total CG has been assessed by considering "opaque" particles (*4*) as identified by organic petrography.

In the present study, we evaluate sorption behavior of native PAHs in four Norwegian harbor sediments with high CG levels. We interpret the sorption results both in terms of a BC-inclusive and a CGC-inclusive sorption model. The most important aim of the study is to compare evaluations of native PAH sorption, that includes either all three types of CGC (coal, BC, and kerogen), or only BC, attributing all strong and nonlinear sorption to this moiety, such as in refs *10−14*.

Recent research has shown that sediment risk assessment can be improved by basing it on freely dissolved porewater concentrations rather than on total sediment contents (e.g., *8, 16, 17*). As a consequence, engineering approaches to reduce in situ freely dissolved concentrations should lead to a reduced risk of contaminated sediments. Luthy and co-workers were the first to explore the amendment of activated carbon (AC) to HOC-polluted sediments (*17−20*). Their results were encouraging: for PAHs and PCBs it was shown that amendment of a contaminated harbor sediment with 3.4 wt % of AC led to reductions of about 1 order of magnitude in aqueous concentrations, uptake by semipermeable membrane devices, fluxes to overlying water (*17*), and bioaccumulation by polychaetes, amphipods (*18*), and clams (*19*).

The presence of many natural and anthropogenic compounds in the sediment probably leads to a reduction of AC sorption strength (*21, 22*). The most important innovation of the present study compared to those in refs *17−20* is that the sorption behavior of pure AC is compared to that of AC mixed with sediment to understand the sediment−AC interaction processes. Other novel aspects include (i) the extent of equilibrium in the sediment−AC−water system, (ii) the viability of the AC amendment approach to sediments of which sorption is already strong due to the presence of CG, and (iii) the use of a state-of-the-art passive sampler method to quantify freely dissolved concentrations (in ref *17*, a flocculation method was employed, where fractions of natural dissolved organic matter (DOM) may not have been removed, resulting in an overestimation of the freely dissolved concentration (Ten Hulscher, unpublished results)).

The above considerations were addressed as follows: (i) sorption was quantified for both pure AC and for AC mixed in sediment mixtures, (ii) the extent of equilibration is tested by a time series as well as by incubations at elevated temperature, (iii) the effectiveness of AC is tested for sediments showing strong intrinsic sorption, and (iv) polyoxymethylene solid-phase extraction (POM−SPE (*15*)) is used to quantify freely dissolved concentrations.

Materials and Methods

Sediments. Samples were from four Norwegian harbors with variable degrees of native PAH pollution (Table 1): Oslo (OS),

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TABLE 1. Characteristics of the Four Sediments Used in This Study

	latitude	longitude	TOC[a] %	TON[a] %	BC[a] %	BC:TOC[a] %	<2 μm[a] %	>63 μm[a] %	total-PAH[b] mg/kg dw[c]
OS	59° 54′ 21″ N	10° 45′ 01″ E	4.2	0.26	0.25	6.1	19	8	31.1 ± 1.5
BG	60° 23′ 26″ N	05° 18′ 15″ E	7.4	0.27	0.90	12.1	9	48	161 ± 31
TR	69° 39′ 03″ N	18° 15′ 42″ E	1.7	0.13	0.12	6.7	10	62	8.9 ± 1.1
DR	59° 53′ 53″ N	10° 14′ 32″ E	2.0	0.08	0.09	4.3	5	69	2.1 ± 0.6

Petrographic Analyses (all in volume-% of TOC[h])						
	inertinites	coal OC[e]	unburned coal	carbonized coal	total carbonized OC[f]	total CGC[g]
OS[d]	6.3	44.9	27.9	17.0	23.0	50.9
BG[d]	4.2	51.6	20.8	30.8	35.0	55.8
TR[d]	3.6	24.3	11.8	12.5	15.1	27.9
DR	2.2	19.0	5.6	13.4	16.1	20.7

The complete petrographic data and PAH quantifications are in the Supporting Information (Tables SI-1 and SI-2, respectively). [a] From Oen et al. (23). [b] Sum of PHE, ANT, FLU, PYR, BAA, CHR, BBF, BKF, BEP, BAP, PER, IND, and BGP (measured in the present study). [c] dw, dry weight. [d] Partly published in Oen et al. (26). [e] Unburned coal carbon + carbonized coal carbon. [f] Carbonized coal carbon + inertinites − funginites. [g] Total carbonized OC + unburned coal carbon. [h] Calculated on the basis of 90 wt % C for inertinites, 70 wt % C for unburned coal, 80 wt % C for carbonized coal.

Bergen (BG), Tromsø (TR), and Drammen (DR). Sediment sampling locations and characteristics (Table 1) have been described in detail in Oen et al. (23).

Organic Petrography. Micropetrographic (maceral) analysis provides insight into the origin, morphology, and maturity of organic particles. Procedures were exactly the same as in ref 24. Briefly, the light (organic-rich) fraction was separated off by density separation (1.814 g/cm³) followed by ultrasonication, centrifugation, careful washing, and drying. The organic-rich fraction was embedded with epoxy resin, ground, polished, and examined under oil immersion. As many as 500 macerals were identified and counted. The recognizable macerals were grouped according to the classification of the International Committee for Coal and Organic Petrology (25). An intrinsic problem of these analyses is that no standard errors in the contents of the various macerals can be reported.

In this case, special attention was given to distinguish between modern OM and coal-derived OM.

The term modern organic matter refers to the recently accumulated organic debris, which originates mostly from plants but also from algae material. Depending on the environment of deposition, the modern organic matter reveals variable degrees of humification as well as of oxidation (inertinites). It can be postulated that the modern OM identified under the microscope is either unaltered (fresh tissues) or partially humified and displays coalification features (maturation) features similar to the peat stage. On the contrary, coal-derived OM includes the residues of incomplete combustion of coals (e.g., chars) termed as carbonized coal and "unburned" coal particles. The term coal refers to the organic matter (originating from terrestrial plants) that underwent advanced coalification processes (stages of lignite to anthracite), which, additionally, is probably material that shows strong and nonlinear sorption. Therefore, the coal part of CGC is here referring to lignite, coal, and anthracite, but not to fresh tissues, peat, and charcoal (inertinites of modern OM).

However, in this study the total carbonized OM also includes naturally carbonized modern OM, quantified as the inertinites of the modern OM without the funginite. Thus, the total CGC content is calculated as the sum of carbonized coal carbon + unburned coal carbon + inertinite carbon − funginite carbon (Table 1), normalized to carbon content. Because kerogen is part of the huminites/vitrinites of the unburned coal, it is included in the CGC, under the category "unburned coal".

In the derivation of CGC contents from organic−petrographic data, the assumption is made that all CGC materials have the same density. This is reasonable, as the average densities of huminites/vitrinites are 1.35 g/cm³, inertinites 1.5 g/cm³, and liptinites 1.2 g/cm³ (25). This implies that the error from this assumption is a maximum of 20−25%. To normalize the maceral wt % to C values, we used different C contents for the different groups (i.e., 90 wt % C for inertinites, 70 wt % C for unburned coal, and 80 wt % C for carbonized coal). The error resulting from the use of average C contents for the different groups is probably on the order of 10%. Thus, together these two factors will yield an uncertainty of <0.15 log-unit in the reported CGC sorption coefficients.

Sorption Studies: Method Evaluation. All sorption studies were carried out in triplicate, in 50 mL all glass flasks, in the presence of 100 mg NaN_3 (biocide) and NaCl (1.5 g, i.e., 3%, providing a constant ionic strength comparable to the in situ conditions at the sampling sites), using the POM−SPE method (15) with slight modifications (12). One can deduce freely dissolved aqueous concentrations (C_W) from the sorbate contents in POM with concentration-independent POM−water distribution ratios (K_{POM}).

In the present study, K_{POM} was measured without sediment to evaluate the POM−water distribution coefficients in a saline system. PAH stock solution (individual PAH concentrations of 50−200 ng/L) and POM (25 mg) were shaken end-over-end (6 rpm; 22 ± 1 °C; 78 d). After equilibration, the POM-strips were treated exactly as described in ref 12, i.e., extracted by horizontal shaking (180 rpm; 22 ± 1 °C; 48 h) with hexane in the presence of an internal standard (40 ng d_{10}−PHE). The aqueous phase was extracted with 10 mL hexane.

Sediment Sorption Experiments: K_{TOC}. POM (100−500 mg), wet sediment (2−5 g), and distilled water (50 mL) were shaken end-over-end as decribed above (78 d). No PAHs were spiked as we studied native compounds. After equilibration, the POM strips were extracted as described above. The native PAHs were extracted from the sediment phases ($n = 12$) by hexane (40 mL)−acetone (10 mL) reflux (6 h) as described in ref 12 (internal standard 400 ng d_{10}−PHE).

Sorption to Pure Activated Carbon (AC). Pilot experiments showed that the currently used AC (Sigma-Aldrich "untreated powder, 100−400 mesh", i.e., 37−149 μm) would sink in water at 22 °C within 10 min. In contrast to refs 17−19, where the AC was boiled in water prior to use we, therefore, added dry AC to our experimental systems, as boiling the AC is probably cumbersome and cost-prohibitive for field applications.

We measured a sorption isotherm for d_{10}−PHE on AC over a >10³ concentration interval. Aqueous d_{10}−PHE stock solution [(0.1−50 mL), POM (100 mg), AC (1−2 mg), distilled

water (0−50 mL)] was shaken as described above (78 d). After equilibration, the POM strips were inspected under a microscope and found to be smooth, clean, and white, similar to previous observations on POM−AC systems (6). Subsequently, they were extracted as described above (internal standard $^{13}C_2$−PHE). The AC + water phases ($n = 9$) were extracted by hexane−acetone reflux (6 h) as described above (internal standard $^{13}C_2$−PHE).

Equilibration Time of Sediment-AC Mixtures. Equilibration times were evaluated as follows: (i) OS samples with 2 wt % AC were equilibrated for 31, 48, 63, and 78 d, and (ii) OS, BG, TR, and DR samples with 2% AC were equilibrated for 31 d at 60 ± 1 °C followed by 47 d at 22 ± 1 °C. At 60 °C, slow desorption is 40−100 times faster than at 20 °C (27). Therefore, the process of redistribution of PAHs over sediment and AC, which consists of desorption from sediment followed by adsorption to the AC, will probably be accelerated significantly by the elevated temperature; with the help of activation enthalpies of slow desorption and the Arrhenius equation as in (27), one month of equilibration at 60 °C can be estimated to mimic 3−10 years of equilibration at 20 °C. Thus, incubations at 60 °C can yield insight in the long-term equilibration of AC−sediment systems.

POM (100−500 mg), wet sediment (2−5 g), distilled water (50 mL), and AC (2.0 ± 0.1 wt %) were shaken as described above. After equilibration, the POM strips were extracted as described above. Mass balances were checked for the 60 °C incubations ($n = 12$) by extracting the sediment/AC/water phases with hexane−acetone reflux as described above.

Effect of AC on Porewater Concentrations. The effect of 2.0 ± 0.1 wt % AC on freely dissolved porewater concentrations was measured for all four sediments. In addition, the effect of AC dosage was tested by amending the OS sediment with 0.20 ± 0.01%, 0.50 ± 0.02%, 2.0 ± 0.1%, and 4.0 ± 0.1% of AC. This experiment was designed in exactly the same manner as the equilibration time experiment described immediately above, with the only exception that the sediment/AC phase was not extracted.

PAH Quantification. After extraction, the hexane phases were cleaned up by shaking overnight with activated Cu, passage through a silica column, and drying with Na_2SO_4. Quantification was done on a GC−MS (Fisons FI MD 800 in electron impact mode). Mass balances for the PAHs were 80−120%. We chose to report sorption coefficients for a saline system and not correct the sorption coefficients for the "salt effect" caused by the NaCl concentration.

Results and Discussion

Throughout this section, the results for four representative PAHs will be presented (PHE, PYR, BAP, and BGP). Numerical results for all measured PAHs are in the Supporting Information.

Organic Petrography. Significant CGC contents (21−56% of TOC) were found in all four sediments (Table 1). A plot of the total carbonized OC (Table 1) identified by petrography vs the BC:TOC fractions derived from chemo−thermal oxidation at 375 °C (CTO−375) showed that these parameters were significantly related for the four currently studied sediments plus two previously studied ones (12, 28) (Figure 1; $p = 0.004$; $r^2 = 0.90$). However, the CTO−375 method yielded values for BC:TOC that were a factor 2.5 ± 0.4 lower. The reasons for this is, probably, that the less condensed part of BC, especially char, could be oxidized at 375 °C (e.g., refs 6, 29). Moreover, the partially carbonized particles (identified petrographically) could contain less C than the chars, thus affecting the correlation with the BC. In conclusion, for the quantification of BC, advantages of CTO−375 over organic petrography are that the method is fast and simple, multiple analyses can be performed, and small sub-μm sized particles are not missed. Disadvantages include
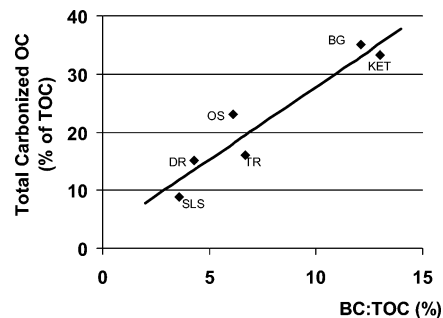
FIGURE 1. Petrography-derived content of carbonized coal carbon (as a fraction of TOC) vs BC:TOC ratio obtained by chemothermal oxidation at 375 °C (BC:TOC data from ref 23). Line derived by linear regression. Results for two other sediments from Sweden (Slussen, SLS) and The Netherlands (Ketelmeer, KET) are included as well; for these sediments, petrography data were reported in ref 28 and BC:TOC ratios in ref 12.

that losses at the less condensed end of the BC spectrum occur with CTO−375 and that unburned coal is not analyzed.

POM−Water Distribution Ratios. K_{POM} values were slightly lower than the ones previously reported (15) (Table 2). An explanation could lie in the POM cleaning procedure; we use a nonsurfactant detergent (12), in contrast to the organic solvents used in ref 15.

TOC−Water and BC−Water Distribution Ratios. K_{TOC} was 1−2 orders of magnitude higher than the values obtained through a widely used linear free energy relationship (31) (Table 2).

This is in accordance with earlier studies on freely dissolved concentrations in contaminated harbor sediments (10, 11, 13, 15). It is probably the CGC (BC, coal, kerogen) that caused this strong sorption (8, 10, 11, 13, 15).

First, we calculated how it would work out for the currently used sediments if K_{TOC} was reinterpreted with a BC-inclusive Freundlich sorption model, analogous to the modeling in refs 10, 13, 14.

$$C_S = f_{AOC}K_{AOC}C_W + f_{BC}K_{F,BC}C_W^{n_{F,BC}} \qquad (1)$$

where C_S is the concentration in the sediment (μg/kg dw), f_{AOC} and f_{BC} are the sediment mass fractions of AOC and BC, respectively, K_{AOC} is the AOC−water distribution coefficient (L/kg), C_W is the freely dissolved aqueous concentration (μg/L), $K_{F,BC}$ is the Freundlich BC−water distribution ratio ((μg/kg_{BC})/(μg/L)^n), and $n_{F,BC}$ is the Freundlich exponent of BC sorption.

Note that in this model, coal and kerogen are included in the linearly absorbing AOC, and all nonlinear sorption is attributed to BC. In the next section, we will describe sorption in terms of a CGC-inclusive model, where coal and kerogen are included in the CGC instead of in the AOC. Often a range of $n_{F,BC}$ values has been tested in previous BC-inclusive sorption data modeling (0.4−1.0, refs 13, 14). However, a recent elaborate literature study (8) showed that the median $n_{F,BC}$ of 21 measurements was 0.61 for PHE (interquartile range (IQR), 0.58−0.64). Therefore, we used this value for the calculation of $K_{F,BC}$ from our sorption data (Table 2), under the assumption that $n_{F,BC}$ is similar for various PAHs in the same BC. To test the validity of this assumption, we did a sensitivity analysis and calculated $K_{F,BC}$ with $n_{F,BC}$ values of 0.5 and 0.8 as well. It turned out that the value of $K_{F,BC}$ at 1 ng/L varied maximally 0.2 log unit between $n_{F,BC}$ of 0.5 and 0.8.

The inferred values of $K_{F,BC}$ were rather high compared to previous literature values (Table 2) and even compared to literature values for BC isolates and pure soot (Table 2), especially when realizing that $K_{F,BC}$ of "environmental" BC

TABLE 2. PAH Sorption Data for POM, TOC, BC and CGC

		PHE	PYR	BAP	BGP
$\log K_{AOC}$ (L/kg)[a]		4.2	4.7	5.7	6.1
$\log K_{POM}$ (L/kg)		3.37 ± 0.09	3.59 ± 0.02	4.46 ± 0.08	4.74 ± 0.05
literature $\log K_{POM}$ (L/kg)[b]		3.29 ± 0.07	3.76 ± 0.05	4.99 ± 0.12	4.90 ± 0.14
$\log K_{TOC}$ (L/kg)	OS	6.19 ± 0.09	6.24 ± 0.09	7.45 ± 0.10	8.06 ± 0.05
	BG	5.79 ± 0.17	6.09 ± 0.14	7.47 ± 0.04	8.06 ± 0.14
	TR	6.13 ± 0.12	6.28 ± 0.16	6.78 ± 0.01	7.67 ± 0.01
	DR	5.97 ± 0.05	5.89 ± 0.12	7.28 ± 0.12	7.6 ± 0.3
	KET (lit.)[b]	5.70 ± 0.04	6.05 ± 0.01	7.96 ± 0.03	7.84 ± 0.02
	BH (lit.)[c]	5.4 ± 0.1	5.8 ± 0.2	7.0 ± 0.2	
	NYH (lit.)[c]	5.1 ± 0.1	6.0 ± 0.1	$\leq 7.5 \pm 0.1$	
$\log K_{F,BC}$ $(\mu g/kg_{BC})/(\mu g/L)^n$	OS	6.78 ± 0.13	7.00 ± 0.13	7.86 ± 0.14	8.16 ± 0.09
	BG	6.3 ± 0.3	6.7 ± 0.3	7.8 ± 0.2	7.9 ± 0.3
	TR	6.8 ± 0.2	6.9 ± 0.3	7.08 ± 0.13	7.66 ± 0.13
	DR	6.44 ± 0.07	6.75 ± 0.14	7.48 ± 0.14	7.6 ± 0.3
	BH (lit.)[c,d]	6.1 ± 0.2	6.4 ± 0.3	7.1 ± 0.3	
	NYH (lit.)[c,d]	5.6 ± 0.3	6.4 ± 0.2	$\leq 7.4 \pm 0.2$	
	BC isolate (lit.)	5.62 ± 0.04[e]	6.25 ± 0.14[f]		
	pure soot (lit.)[g]	5.68	6.55		
	pure BC (lit.)[h]	5.9			
$\log K_{F,CGC}$[i] $(\mu g/kg_{CGC})/(\mu g/L)^n$	OS	5.9	6.1	7.1	7.3
	BG	5.8	6.3	7.1	7.3
	TR	6.3	6.4	6.5	7.2
	DR	5.8	6.1	6.9	7.0
	pure CG (lit.)[j]	6.0			

Log K_{POM}, log K_{TOC}, and log $K_{F,CG}$ of the other PAHs are in the Supporting Information (Tables SI-3, SI-4, and SI-5, respectively). [a] AOC, amorphous organic carbon. Values derived from a linear free energy relationship especially derived for PAHs: log K_{TOC} = 0.98 log K_{OW} − 0.32 (31), with log K_{OW} from ref 32. [b] From ref 15. [c] From ref 13. [d] Calculated on the basis of $n_{F,BC}$ = 0.7. [e] From ref 12. [f] From ref 14. [g] From ref 11. [h] Median of 38 literature values, from ref 8. [i] No standard deviations calculated because of a lack of standard deviations in CGC contents (Table 1). [j] Median of 72 literature values, from ref 8.

(i.e., BC as it is present in sediments) has been reported to be up to a factor of 10 *lower* than $K_{F,BC}$ of pure soots and BC isolates (8, 9, 12) due to competition for BC sorption sites by native PAHs and biomolecules. Therefore, the $K_{F,BC}$ values in Table 2 are probably overestimations. We propose that the reason for this overestimation is that not only BC, but also other CGC (unburned coal and kerogen) exhibited strong PAH sorption (3–8). Therefore, the K_{TOC} was reinterpreted by considering the *total* CGC content instead of only BC.

CGC-Inclusive Sorption. Inclusion of CGC in the total sorption equation was thus described by a CGC-inclusive Freundlich equation (8)

$$C_S = f_{AOC}K_{AOC}C_W + \sum_{CGC} f_{CGC}K_{F,CGC}C_W^{n_{F,CGC}} \quad (2)$$

where f_{CGC} denotes the fractions of the various CGC moieties (BC, coal, and kerogen), $K_{F,CGC}$ are the CGC Freundlich sorption coefficients $[(\mu g/kg_X)/(\mu g/L)^{n_{F,CGC}}]$, and $n_{F,CGC}$ are the Freundlich nonlinearity coefficients of sorption to CGC. This way, coal and kerogen are included in the nonlinear adsorption part of the equation, as opposed to eq 1.

As a measure of f_{CGC}, we used the petrography-derived fractions of total coal (unburned + carbonized) plus naturally carbonized modern OM (Table 1). On the basis of an extensive data set (n = 45), it has recently been shown that $n_{F,CGC}$ is not significantly different for PHE in BC, coal, and kerogen (8), the median value being 0.64. Therefore, we used this value in the calculation of $K_{F,CGC}$, again assuming that $n_{F,CGC}$ is similar for various PAHs in the same CGC. To test the validity of this approximation, we did a sensitivity analysis of $K_{F,CGC}$ and calculated this parameter with $n_{F,CGC}$ values of 0.5 and 0.8. It turned out that $K_{F,CGC}$ at 1 ng/L varied maximally 0.2 log unit between $n_{F,CGC}$ of 0.5 and 0.8, respectively.

The $K_{F,CGC}$ values for PHE in the currently studied sediments were on the order of or just below $K_{F,CGC}$ for pure and isolated CGC materials (the median log $K_{F,CGC}$ value of

72 literature values was 6.0 (IQR 5.6−6.4), Table 2 and ref 8). Because, the sorption to environmental CGC is probably attenuated by competition effects as well, this seemed reasonable. We, therefore, conclude that not only the BC but probably also the other CGC materials should be considered for the correct interpretation of sorption in sediments where several types of CGC are present.

The above approach is related to the approaches of Karapanagioti and co-workers who used the content of opaque (i.e., nontransparent) particles (4) or inertinites (5) as a measure for the content of strongly adsorbing material. However, in our present study, the sediments were enriched in coal-derived OM (Table 1) and, therefore, we chose to use the total coal-derived OM to derive our $K_{F,CGC}$ instead of only the oxidized (inertinite) and carbonized fraction.

With the help of eq 2, it could be calculated that 91−99% of the total PAHs was sorbed to CGC, with only a minor fraction in the non-carbonaceous AOC. This is in accordance with earlier observations that carbonaceous materials can completely dominate PAH sorption (8, 13, 14, 24).

AC Sorption Isotherm. The sorption isotherm of PHE in pure AC was fitted with a Polanyi−Dubinin−Manes (PDM) model (Figure 2)

$$C_{AC} = V_0\rho_0 \exp\left[\frac{-RT\ln\dfrac{C_W}{S}}{E}\right]^b \quad (3)$$

where C_{AC} is concentration in the AC (g kg^{-1} dw), V_0 is AC pore volume (cm^3 kg^{-1}), ρ_0 is PHE density (1.02 g cm^{-3}), R is the gas constant (Jmol^{-1}K^{-1}), T is the temperature (K), S is the maximum solubility (mg L^{-1}), E is the free energy of adsorption (J mol^{-1}), and b is a dimensionless fitting exponent set to 2 (3). V_0 and E were fitted to the experimental C_{AC} data by minimizing the sum of the squared residuals. The PDM model proved to fit the data well (r^2 = 0.995), with V_0 of 46.2 cm^3 kg^{-1} and E = 16.4 kJ mol^{-1}. The value of E was close to
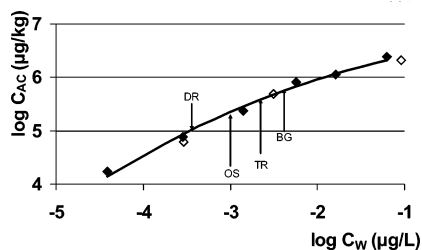
FIGURE 2. Sorption isotherm of PHE on pure AC. Plotted is the log of the concentration in the AC, log C_{AC} vs log C_W. Solid line obtained by fitting to the PDM model (eq 3). Closed symbols: equilibration at 22 °C for 78 d; open symbols: equilibration at 60 °C (31 d) followed by 20 °C (47 d). The arrows indicate the freely dissolved PHE concentrations in the sediments with 2% AC.
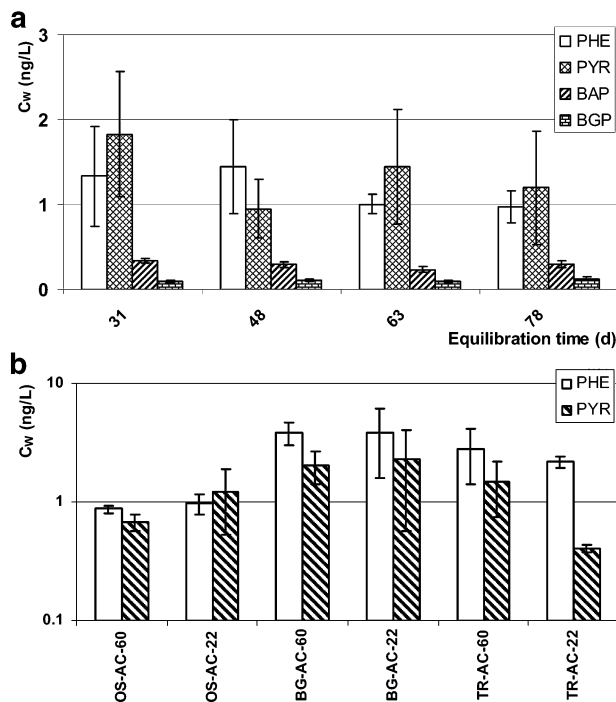

FIGURE 3. Part a: Freely dissolved porewater concentrations (C_W) in OS sediment amended with 2% AC after four equilibration times. Part b: Freely dissolved porewater concentrations (C_W) in OS, BG, and TR sediments amended with 2% AC after equilibration at 60 °C followed by 22 °C and after equilibration at 22 °C only.

the value obtained in ref *3* for PHE sorbed to AC (12.4 kJ mol^{-1}), whereas the value of V_0 was lower than the 415 cm^3 kg^{-1} observed in that study. The equilibration at 60 °C for 31 d followed by 47 d at 22 °C did not result in significantly different sorption to the AC (t-test on regression parameters, 95%; Figure 2).

Addition of AC: Equilibration Time and Temperature. It appeared that C_W did not significantly vary between 31, 48, 63, and 78 d for any of the selected PAHs in OS sediment (t-test, 95%; Figure 3a). In addition, the equilibrations at 60 °C (30 d) followed by 22 °C (47 d) did not result in a lower C_W (Figure 3b). For all analyzed individual PAHs in OS, BG, and TR sediments, C_W was significantly higher after 60 °C equilibration than after 22 °C equilibration for 4 PAH/ sediment combinations, significantly lower for 4 combinations, whereas there was no significant difference for 22 out of 30 comparisons (t-test, 95%). This confirms that equilibrium probably existed in the systems incubated at only 22 °C: although desorption from the sediment and thus sediment−AC redistribution was probably much faster at 60 °C than at 22 °C, this did not result in significantly lower C_W.
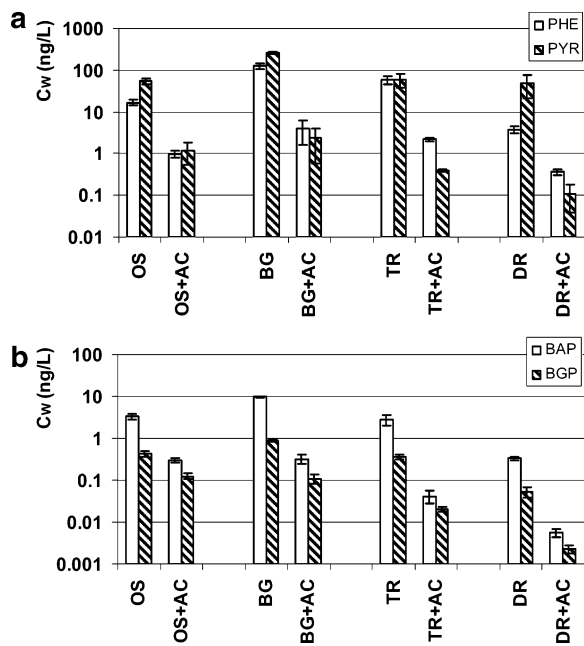
FIGURE 4. Part a: Effect on C_W of 2% AC in OS, BG, TR, and DR sediments for PHE and PYR. Numerical values for C_W of all measured PAHs with and without AC amendments are in the Supporting Information (Table SI-6). Part b: Same as part a, for BAP and BGP.
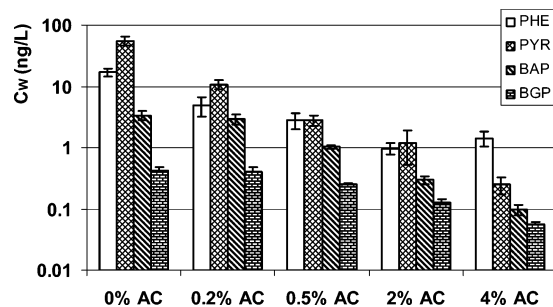
FIGURE 5. Effect on C_W of four dosages of AC in OS sediment. Numerical values for C_W of all measured PAHs with and without AC amendments are in the Supporting Information (Table SI-6).

Effect of AC Amendment. The amendment of AC was effective in reducing freely dissolved aqueous concentrations C_W (Figure 4); an addition of 2% AC reduced the C_W by factors of 21, 47, 73, and 153 for OS, BG, TR, and DR sediment, respectively (average values for all PAHs). This effect was larger than the effect observed by Zimmerman (*17*), who reported a 6-fold reduction of PAH C_W upon the amendment of 3.4% AC. This discrepancy might be explained by (i) variations in sediment and AC characteristics, and (ii) the different method employed in ref *17* to quantify C_W (flocculation vs the currently used POM−SPE).

Note that the strongest effect of AC addition was observed for DR sediment (Figure 4 and Table SI-6) with the lowest fractions of BC and CGC, as well as the lowest PAH contents (Table 1). Due to the nonlinearity of the AC sorption isotherm, lower PAH concentrations will probably result in stronger sorption to AC.

Effect of AC Dosage (Only OS Sediment). Even the lower dosages led to significant reductions in C_W: the reductions averaged over all measured PAHs amounted to factors of 2.5 (0.2% AC), 9 (0.5% AC), 21 (2% AC), and 56 (4% AC). There appeared to be a strong relation ($p = 0.01$, $r^2 = 0.97$) between dosage and the relative reduction in C_W, for this particular sediment−AC combination:

$$\text{reduction factor} = (1350 \pm 160)f_{AC} - (0.5 \pm 3.5) \quad (5)$$

where f_{AC} is the mass fraction of AC amended to OS sediment. This shows that the amounts of AC amended to sediments could probably be adjusted to meet the relevant water quality criteria.

Attenuation of AC Sorption in Sediment−AC Systems. It was anticipated that sorption to AC mixed into sediment is less strong than sorption to pure AC, because of sorptive attenuation by native natural and anthropogenic compounds present in the sediment (e.g., biomolecules and PAHs), which is analogous to sorptive attenuation of BC (9, 12) and coal (9) as well as fouling of AC filters by organic molecules (21, 22).

To this end, we compared actually measured C_W values for sediment−AC mixtures to "expected" values calculated on the basis of additive sorption to pure AC and to the sediment (i.e., AOC and CGC). Therefore eq 2 was extended with a PDM-based AC term (eq 3).

$$C_S = f_{AOC}K_{AOC}C_W + f_{CGC}K_{F,CGC}C_W^{n_{f,CGC}} + f_{AC}V_0\rho_0 \exp\left[\frac{-RT\ln\frac{C_W}{S}}{E}\right]^b \quad (6)$$

The "expected" values of C_W were found by varying C_W in this equation until the measured total sediment contents (C_S) were found. This calculation was done for PHE since the pure AC sorption isotherm was measured for this compound. For the various dosages of AC in OS sediment, it was found that the actually observed values of $C_{W,PHE}$ were 2−20 times higher than the values expected on the basis of pure AC sorption. For BG, TR, and DR sediments, the observed C_W values were 2, 13, and 53 times higher than expected, respectively. On a median basis, AC sorption was attenuated by a factor of 6 by the presence of sediment ($n = 7$; IQR 3−16). It is concluded that there is indeed some degree of site blockage and/or competition on the AC due to the presence of native biomolecules, and that the sorption to AC in sediment−AC mixtures is not as strong as sorption to pure AC.

Implications. The next step that should be taken is to test the viability of the AC amendment approach in the field. Considerations include (i) how to mix the AC into sediment without spreading the contamination to less polluted adjacent sites (33), and (ii) the influence of the AC on the nutritional value of the sediments to organisms at the bottom of the food chain (33). In addition, it needs to be checked whether AC will serve as a source or a sink of heavy metals, and whether it will not remove essential trace metals from the benthic ecosystem.

In the present study it appeared that amendments on the order of 0.5−1% already give reductions of porewater concentrations of over 1 order of magnitude, probably enough to meet environmental objectives in most cases. In a rough first approximation, it can be assumed that, in many cases without net sediment erosion, AC amendment into the uppermost bioturbated layer (10 cm) could suffice. Assuming 50% sediment dry weight and a sediment density of 2 g/cm^3, the amount of AC needed would then be 0.5−1 kg/m^2, yielding a material cost of only a few US$ per m^2 of treated sediment surface.

Acknowledgments

Supporting Information Available

Detailed organic petrographic data and numerical data for all PAHs. This material is available free of charge via the Internet at http://pubs.acs.org.

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