

PAHS AND DIOXINS IN SEDIMENT: IMPROVED RISK ASSESSMENT THROUGH FREE CONCENTRATIONS AND IN SITU REMEDIATION BY ACTIVE CARBON AMENDMENT

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Introduction

Strong sorption to carbonaceous geosorbents

It has recently been shown that the presence of carbonaceous geosorbents (CG, including black carbon (BC; soot and charcoal), unburned coal and kerogen) can cause strong sorption of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and dioxins in sediments¹. 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 carbonaceous materials, as shown by organic petrography. PAH sorption coefficients were 1-2 orders of magnitude above predictions based on amorphous organic carbon (AOC) partitioning alone⁵. Thus, strong sorption to carbonaceous geosorbents causes PAHs to be sorbed much more strongly to sediment than expected on the basis of K_{OC} -values, and than assumed in current risk assessment that is based on these K_{OC} values.

Improved risk assessment

In many countries, namely, human and ecotoxicological risk assessment of organic contaminants is based on quality criteria developed for the total contaminant content¹⁻⁴. However, freely dissolved contaminant concentrations in soils and sediments are found to be much better measures of human and ecotoxicological risks¹⁻⁴, because these take into account the abovementioned strong sorption. Such freely dissolved concentrations can therefore be directly compared to toxicity-based water quality criteria to improve the assessment of actual risks.

Activated carbon amendment

Luthy and coworkers were the first to recognize that the strong sorption to carbonaceous materials could be used in an engineering perspective⁸⁻¹¹: by the in situ addition of the carbonaceous material activated carbon (AC), one should be able to increase the sediment's sorption and therefore reduce the actual risk of present PAHs and other organic contaminants.

Methods

Passive samplers for Norwegian harbour sediments and dioxin-contaminated sites in Sweden

We used the passive sampler Polyoxymethylene (POM) to measure freely dissolved PAH concentrations for three priority Norwegian harbour locations^{5,6} (characteristics in Table 1).

At the moment we employ several types of passive samplers to monitor freely dissolved aqueous concentrations in the field. In addition, their applicability is tested for dioxins in Swedish dioxin-contaminated pentachlorophenol wood-doping sites.

Activated carbon amendment

In addition, we tested the addition of active carbon (AC) as an in-situ remediation method for PAH contamination in sediments⁵⁻¹¹. We studied this technique for three Norwegian harbor sediments, by measuring freely dissolved concentrations and bioaccumulation in two organisms in the presence and absence of AC.

TABLE 1: Sediment characteristics of Oslo (OS), Bergen (BG) and Tromsø (TR) sediments, partly from ref. 7.

	OS	BG	TR
Latitude	59° 54' 21" N	60° 23' 26" N	69° 39' 03" N
Longitude	10° 45' 01" E	05° 18' 15" E	18° 15' 42" E
Total Organic Carbon (TOC;%)	4.2	7.4	1.7
Total Organic Nitrogen (%)	0.26	0.27	0.13
Black Carbon (BC;%)^a	0.25	0.90	0.12
BC:TOC	6.1	12.1	6.7
CGC:TOC^b	50.9	55.8	27.9
Total-PAH (mg/kg dw^c)	31.1 ± 1.5	161 ± 31	9.0 ± 1.1

^a BC, Black Carbon, soot and charcoal that show strong sorption of PAHs, PCBs and dioxins.

^b CGC, Carbonaceous Geosorbent Carbon, i.e., the total carbonized organic matter + the unburned coal carbon, derived from organic micropetrography⁵.

^c dw, dry weight

Results and discussion

Freely dissolved concentrations and risk assessment

It appeared that the sediment-water distribution ratios for all PAHs were around 100 times higher than the values used to derive sediment quality criteria in risk assessment (Table 2). These high values could be explained on the basis of high soot and coal contents in the sediments⁵. Thus, risks were approximately as much as a factor of 100 lower than predicted on the basis of total sediment contents. As a consequence, current risk assessment practice would grossly overestimate PAH risk of these sediments. Bioaccumulation tests with two organisms confirmed these findings: uptake by these organisms was very limited, with biota to sediment accumulation factors (BSAFs) as low as around 0.01. On the basis of total bioavailability, the theoretical BSAF is around 1. Therefore uptake was also a factor of 100 lower than expected based on total PAH contents and total availability⁶ (Table 3). The reason is strong sorption to carbonaceous materials^{1,5,6,7}.

Thus, freely dissolved concentrations explained the organisms' contents well⁶. Therefore novel passive sampler methods will lead to a reduction of the uncertainty in risk assessments, a better prioritization of limited remediation resources, and improvements of the optimal design for monitoring.

TABLE 2: PAH distribution coefficients for four representative native PAHs in four Norwegian Harbour sediments. The K_{OC} used in current risk assessment is almost two orders of magnitude lower than the K_{OC} measured in all four field-contaminated harbour sediments. The reason is strong sorption to carbonaceous materials.

	Phenanthrene	Pyrene	Benzo[a]pyrene	Benzo[ghi]perylene
log K_{OC} risk assessment (L/kg)	4.2	4.7	5.7	6.1
log K_{TOC} field (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

Active Carbon addition to reduce bioavailability and actual risk

It was shown that AC amendments of 2 wt-% reduced freely dissolved concentrations by a factor of 10-50 (Figures 1,2). This implies that actual risks of PAHs in the three sediments were reduced by that factor. Reductions of uptake in organisms were around a factor of five⁶ (Table 4). Thus, actual risks are reduced by AC amendment^{5,6}. This technique has been shown to be effective for PCBs as well⁸⁻¹¹. It will be tested for dioxins in soil and sediment, as dioxins are strongly sorbed by AC.

TABLE 3: Biota sediment accumulation factors (BSAF) of original Oslo (OS), Bergen (BG) and Tromsø (TR) sediments ($\text{kg}_{\text{OC}}/\text{kg}_{\text{lipid}}$), as well as ratios between theoretical and empiric BSAFs ($\text{BSAF}_{\text{theory}} / \text{BSAF}_{\text{measured}}$) and between BSAFs calculated on the basis of freely dissolved concentrations and empiric ones ($\text{BSAF}_{\text{free}} / \text{BSAF}_{\text{measured}}$). It is observed that the freely dissolved concentrations much better predict the low BSAFs (within a factor of 2-6) than theoretical BSAFs based on total sediment contents (factor of 10-200 off).

		<i>Nereis diversicolor</i> (Polychaeta)			<i>Hinia reticulata</i> (Gastropoda)		
			Ratio	Ratio		Ratio	Ratio
		$\text{BSAF}_{\text{measured}}$	$\text{BSAF}_{\text{theory}} / \text{BSAF}_{\text{measured}}$	$\text{BSAF}_{\text{free}} / \text{BSAF}_{\text{measured}}$	$\text{BSAF}_{\text{measured}}$	$\text{BSAF}_{\text{theory}} / \text{BSAF}_{\text{measured}}$	$\text{BSAF}_{\text{free}} / \text{BSAF}_{\text{measured}}$
OS	PYR	0.095 ± 0.010^c	10.5 ± 1.1	0.30 ± 0.02	0.077 ± 0.009	13 ± 2	0.40 ± 0.02
	BAP	0.0042 ± 0.0015	240 ± 86	3.4 ± 1.0	0.0064 ± 0.0037	156 ± 89	2.2 ± 1.1
	BGP	0.0036 ± 0.0014	274 ± 105	6 ± 2	0.012 ± 0.009	81 ± 59	1.8 ± 1.3
BG	PYR	0.11 ± 0.04	9 ± 4	0.36 ± 0.05	0.032 ± 0.012	31 ± 11	1.3 ± 0.1
	BAP	0.006 ± 0.003	167 ± 72	2.2 ± 0.7	0.006 ± 0.002	156 ± 46	2.1 ± 0.4
	BGP	0.009 ± 0.006	114 ± 72	2.5 ± 0.9	0.018 ± 0.007	56 ± 22	1.2 ± 0.2
TR	PYR	0.058 ± 0.013	17 ± 6	0.45 ± 0.03	0.015 ± 0.004	69 ± 21	1.8 ± 0.3
	BAP	0.011 ± 0.007	86 ± 50	6 ± 2	0.008 ± 0.007	120 ± 96	8 ± 5
	BGP	0.007 ± 0.004	146 ± 86	8 ± 4	0.010 ± 0.006	96 ± 56	5 ± 2

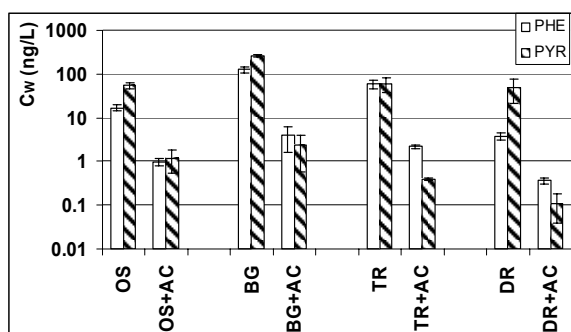


FIGURE 1: Effect on C_w of 2% AC in OS, BG, TR and DR sediments, for four PAHs.

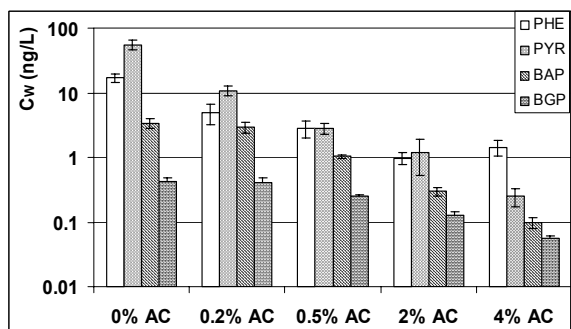


FIGURE 2: Effect on C_w of four dosages of AC in OS sediment.

Implications: AC as an in situ remediation technology

The advantages of the new environmental technology of AC amendment over many other remediation methods include i) it can be used as an in situ risk reduction method, ii) the price is low, and iii) it overcomes significant controversies associated with disposal of dredged materials. Also, unlike dredging, AC amendment of sediment need only treat the upper sediment layer comprising the biologically active zone. Much money can be saved if the cost of cleaning up contaminated soils and sediments is reduced by a cost-effective, innovative technique such as AC amendment⁵⁻¹¹.

TABLE 4: Biota sediment accumulation values (BSAF; kg OC/kg lipid) after activated carbon (AC) addition (2%), and reduction factors of lipid-normalized organism contents ($C_{\text{biota, lipid}}$) due to 2% AC amendment, for Oslo (OS), Bergen (BG) and Tromsø (TR) sediments. For example, $C_{\text{biota, lipid}}$ of pyrene (PYR) in OS sediment was reduced 29-fold by the addition of 2% AC⁶.

		<i>N. diversicolor</i>		<i>H. reticulata</i>	
		Reduction factor		Reduction factor	
		BSAF _{AC} ^a	$C_{\text{biota, lipid}}$ ^b	BSAF _{AC}	$C_{\text{biota, lipid}}$
OS	PYR	0.0048 ± 0.0033 ^f	29 ± 20	0.010 ± 0.002	11 ± 2
	BAP	0.0023 ± 0.0016	2.5 ± 2	0.007 ± 0.002	1.3 ± 0.8
	BGP	0.0006 ± 0.0002	9 ± 6	0.014 ± 0.003	1.3 ± 1.1
BG	PYR	0.008 ± 0.006	19 ± 14	0.009 ± 0.008	4 ± 3
	BAP	0.007 ± 0.006	1.1 ± 1.2	0.007 ± 0.005	1.1 ± 0.8
	BGP	0.014 ± 0.012	0.8 ± 0.7	0.018 ± 0.014	1.2 ± 0.7
TR	PYR	0.003 ± 0.002	43 ± 33	0.02 ± 0.03	2 ± 2
	BAP	0.010 ± 0.004	2.0 ± 1.2	0.05 ± 0.06	0.4 ± 0.6
	BGP	0.009 ± 0.001	1.5 ± 0.7	0.04 ± 0.04	0.6 ± 0.8

^a BSAF in the presence of 2% AC.

^b Reduction factor in concentrations in biota on a lipid basis.

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