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ACCUMULATION AND DISTRIBUTION OF PAH AND PCB IN DIFFERENT PARTICLE SIZE FRACTIONS OF CONTAMINATED MARINE SEDIMENTS

Akkumulering og fordeling av PAH og PCB i ulike partikkelstørrelsesfraksjoner av forurensede marine sedimenter

by LARS J. HEM[1], EILEN A. VIK[1], HANS-JACOB SVENSEN[2], and TORE LUNDH[3]*
1 Aquateam AS, P.O Box 6875 Rodeløkka, N-0504 Oslo, Norway
2 Alfa Laval AS, P.O Box 96, N-1300 Sandvika, Norway
3 NETT, P.O Box 1512, N- 3206 Sandefjord, Norway
** Corresponding author (lars.hem@aquateam.no)*

Abstract

The accumulation and distribution of PAH and PCB in different size fractions of contaminated sediments from The Norwegian Fjord Sandefjord and the bioaccumulation of these contaminants in sediment reworkers have been studied using dredged sediments.

The sediment reworker *Corophium volutator* (a sediment reworker included in OSPAR's toxicity test battery for chemicals used and discharged offshore in the North Sea) was used in the bioaccumulation study. Centrifugation was used for fractionating the sediment into suitable fractions prior to exposing the sediment reworkers in laboratory tests. The distribution of PAH and PCB in sediments and organisms was monitored.

The results showed that centrifugation was a suitable technology for separation of the relatively fine sediment, which is typical for Norwegian Fjords, into different sizes fractions where the majority of the PAH could be recovered from the dry solids from the centrifuge while the PCB still was equally distributed in the different size fractions of the dry solids and the water fraction from the centrifuge. The measured bioaccumulation concentration of PAH and PCB in *Corophium volutator* feeding on the dry solid from the centrifuge was almost twice the concentration found in the water phase from the centrifuge.

The results confirm that a proper prestudy is necessary to determine the effect of a physical pretreatment. The results also show that the effect on the bioavailability may differ from the effect on the contaminant concentration. Therefore, determination of the bioavailability of contaminants in sediments may add valuable information to physical and chemical analysis. The results did not give reason to conclude that neither the concentrate nor the centrate could be regarded as considerably less contaminated than the original sediment.

Key words – PAH, PCB, bioavailability, bioaccumulation, *Corophium volutator*, fractioning, distribution, contaminated sediments, particle size.

Sammendrag

Det er gjennomført studier av akkumulering og fordeling av PAH og PCB i ulike partikkelstørrelsesfraksjoner av forurensede marine sedimenter fra Sandefjorden i Norge, og bioakkumuleringen av disse forurensningene i sedimentlevende organismer.

Corophium volutator, en sedimentbearbeidende amfipode som inngår i OSPARs batteri av toksisitetstester for kjemikalier som brukes og slippes ut fra offshore installasjoner i Nordsjøen, ble benyttet i testene. Sentrifugering ble brukt for å fraksjonere sedimentene i forkant av disse testene. Fordelingen av PAH og PCB i fraksjonene av sedimentene og i organismene ble så målt.

Resultatene viste at sentrifugering var en egnet metodikk for å separere de relativt finkornige sedimentene, som er typiske for norske fjorder, i ulike fraksjoner ut fra partikkelstørrelse. Mesteparten av PAH fulgte fraksjonen med de største partiklene (konsentrat), mens PCB var jevnere fordelt på de ulike fraksjonene. Konsentrasjonene av PAH og PCB i *Corophium volutator* var omtrent dobbelt så stor i organismene som levde i konsentratet som i organismene som levde i rejektet (vannfasen).

Resultatene bekreftet at grundig forstudie er nødvendig for å bestemme effekten av en fysisk separasjon/forbehandling av sedimentene. Resultatene viste også at effekten på bioakkumulering av slik separasjon kan være forskjellig fra effekten på forurensningskonsentrasjonen. Måling av bioakkumulering av forurensningene i sedimentene kan være et verdifullt supplement til fysiske og kjemiske analyser. Resultatene ga ikke grunn til å konkludere med at verken konsentratet eller vannfasen var vesentlig mindre forurenset enn det ubehandlede sedimentet.

1 Introduction

The costs associated with remediation of contaminated sediments is highly dependent on the amount of sediments needed to be remediated and the technology required for the purpose. Any action which can reduce the amount of sediments needing remediation has therefore a potential for being economically beneficial. Such actions includes investigations which can identify less contaminated parts of the sediments as well as technology (physical, chemical or biological) suitable for fractionating the sediments into a contaminated and a noncontaminated fraction. This requires, however, thorough knowledge and understanding of acceptable levels of contamination at the site, the distribution of the contaminants in different size fractions as well as of technological possibilities for separating the sediments into relevant size fractions and treating the water without increasing spreading the contaminants during operation.

Adsorption and desorption mechanisms play an important role in transport and availability of the contaminants in soils and sediments (Schlebaum et al. 1999). It has further been documented that the availability mainly depend on the desorption process (Alexander 1995). In general, desorption of a pollutant is more difficult than adsorption. Some degree of reversibility has been reported (DiToro and Horzempa 1982, Fall et al. 2000). The greater the amount of organic content in soil and greater hydrophobicity (higher n-octanol/water partition coefficient, P_{ow} or K_{ow} of the contaminant), the greater retention in the soil matrix whereas desorption can be negligible. The irreversibility can also be increased by ageing phenomena (Alexander 1995). It is expected that the same processes occur in the sediment matrix as in the soil. Poggi-Varaldo et al (2002) documented a good correlation between the hysteresis coefficient and organic carbon, as well as with ageing time for phenanthrene and pentachlorophenol. The hysteresis coefficient was defined as the ratio between the derivatives of the adsorption and desorption coefficient. Concentration levels of micro pollutants in surface sediments are known mainly to be controlled by distance from pollutant source (present and past) and by sediment grain size. It is well known that the preferential association of most micro pollutants is with fine materials due to the larger surface area. Similar general information is available for the bioaccumulation

An example of physical treatment of contaminants is separation of coarser particles from smaller ones. The efficacy is, however, on fractioning of the contaminants. Sand can be removed by wet sieving, while other separation technologies like settling or sand cyclones can be used for separation of clay from silt (Francingues 2000). This has been used in Hamburg, where sand cyclones were used to separate less contaminated sand from more contaminated silt (Detzner 1995).

Norwegian sediments are typically contaminated by heavy metals, PAH and/or PCB. The sediments are typically mixtures of clay, silt and sand, with variable content of organic carbon. Relevant separation technologies are sedimentation, centrifugation or sand cyclones.

In a previously study the suitability of using a centrifuge for separating highly contaminated sediments from the harbour of Sandefjord from less contaminated sediments was studied (Hem et al. 2002). The study showed that PAH and PCB were mainly associated with larger particles, and by varying the operational parameters for the centrifuge it was possible to separate fine sediments into different particle size fractions.

The bioavailability of particle-bound contaminants may also depend upon the particle size, i.e. particles that may be utilised directly by the sediment reworker *Corophium volutator* have typically a diameter of 4–63 µm (Nijkamp 1992). Particle size fractioning of the contaminated sediments may then not only divide the sediments into more and less contaminated fractions, but also have an effect by reducing the bioavailability and the potential for bioaccumulation.

2 Objectives

The scope of the work presented in this paper was to study the distribution of PAH, PCB and the bioaccumulation potential of these contaminants in the concentrate (treated sediment) and centrate (water phase) from centrifugation of dredged sediments from the Sandefjord harbour. This work was done partly to understand if the particle size of the contaminated sediments influence the bioaccumulation potential, and partly to understand if the physical shear forces involved in the separation step may change the bioaccumulation potential for the whole sediment.

3 Materials and Methods

3.1 Sediments tested

The sediments chosen for the laboratory tests and for the pilot study was from Kilen in the Sandefjord harbour. In this harbour area there are restrictions on intake of seafood due to PCB content in the livers of the fish. The urban development of the harbour area implies considerable dredging. Possible restrictions on the disposal of the sediments will affect the development costs.

3.2 Particle size fractioning

The particle size fractioning was performed using a pilot scale centrifuge from Alfa Laval with a load of 600 l sediments/h. The G value of the centrifuge was 1900, and the differential speed was 18 rpm. One part of dredged

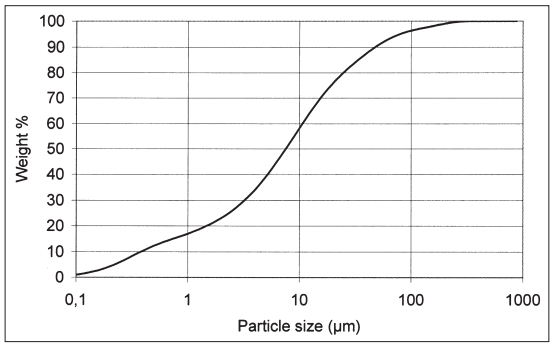

Figure 1. *Particle size distribution in dredged sediment.*

sediments from the harbour (dry solids (DS) content of approximately 35 %) were diluted with two parts unpolluted seawater prior to the test to achieve optimal conditions for the operation of the centrifuge. No chemical additives were used.

3.3 Physical and chemical analysis

The particle size distribution was measured with a Malvern Mastersizer particle counter.

The various fractions of the sediments were categorized for its size distribution, dry solids (DS), volatile dry solids (VDS), total organic carbon (TOC), polycyclic aromatic hydrocarbons (PAH_{16}) and polychlorinated biphenyls (PCB_7). DS and VDS was analysed according to NS (Norwegian Standard) 4764. TOC was analysed according to NS 1484. PAH_{16} was extracted with cyclohexane and ethyl acetate (1:1) for 2 hours in shaker followed by 5 min in ultrasonic bath. The organic phase was analysed on GC-MS with El-ionisation. PAH_{16} includes the 16 USEPA PAHs. PCB_7 was extracted with acetone followed by extraction with hexane. The organic phase was washed with distilled water, concentrated with rotavapor, cleaned for sulphur with tetra-butyl-ammonium hydrogen sulphate and for hydrocarbons with sulphuric acid. The organic phase was analysed on GC-µECD.

3.4 Bioaccumulation

The amphipod specie *Corophium volutator* was chosen for the bioaccumulation study. The bioaccumulation procedure was according to AnalyCen Ecotox (2001), which is based on PARCOM (1994). A 2 cm sediment layer was added to 1-litre glass beakers. Fresh seawater and 20 species of *Corophium volutator* were added to the beakers. The test duration was 15 days, with continuous aeration, and with control of temperature, salinity, oxygen and pH after 0, 6, 9 and 15 days. The length of the exposure was based on Krauss et al. (2000).

Pre-treatment of *Corophium volutator* prior to PAH and PCB analysis was performed according to NS (Norwegian Standard) 9812. Because of the limited amount of samples the pre-treatment of biota prior to PAH and PCB analysis was performed by mixing all the 20 species of *Corophium volutator*. 3 mL of the biota was frozen, grinded, hydrolysed in 5 mL 2 M KOH in methanol-water (1:1), extracted for two hours in a shaker followed by 5 min in an ultrasonic bath. 2 mL distilled water was added, and the sample was shaken. Undissolved material and water was removed in the centrifuge, and the sample was divided in two fractions for the analyses of PAH and PCB.

A blank control sample of *Corophium volutator* was also analysed for PAH and PCB. Bioaccumulated PAH and PCB was defined as the content in the sample subtracted the content in the control.

4 Results and Discussion

4.1 Sediment characteristics

The dry solids content of the sediment was 11.3 %, and the organic content of the sediment was 92 g VDS/kg DS. The organic carbon content was 37 % of VDS (3,4 % of DS). The measured contents of PAH and PCB are summarised in Tables 1 and 2 and compared with reported literature data for bioaccumulation. The amount of the more volatile PAHs was in general low.

4.2 Characteristics of fractioned sediments

53 % of the particulate DS was recovered in the concentrate. All particles larger than 60 µm and 30–70 % of the particles in the smaller particle size fractions were recovered in the concentrate (Figure 2).

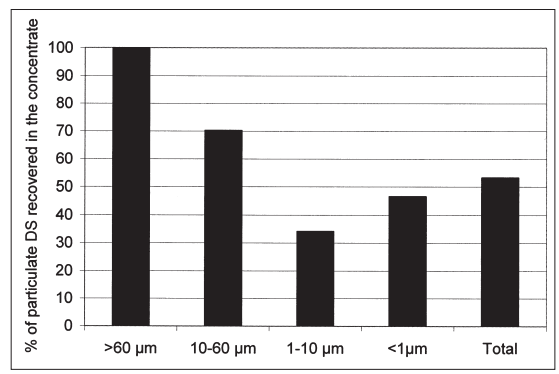

Figure 2. *Distribution of particulate matter between the concentrate (sediment fraction) and the centrate (water fraction); particulate matter recovered in the concentrate.*

Table 1. *PAH in dredged sediment.*

	Measured conc. (mg/kgDS)	Log P_{ow}	Calculated bioaccumulation factor (BAF)[3] (kg DS (sediment)/kg ww (biota))	Measured biota-sediment accumulation factor (BSAF)[4] (kg TOC/kg lipid)	
				[5]	[6]
Naphtalene	0.05	3.32[1]	1.0		
Acenaphtylen	0.20				
Acenaphtene	0.08	3.92[2]	1.0		
Fluoren	0.15	4.38[2]	1.5		
Phenantrene	0.60			0.6–1.2	1.0
Anthracene	0.30	4.49[1]		1.6	1.0
Fluoranthene	1.50	4.95[1]	2.0		1.4
Pyrene	2.13	4.88[2]	1.9	0.4–1.0	1.7
Benzo(a)anthracene	0.75	5.61[2]	2.7		0.3
Crysene	0.75				
Benzo(b)fluorantene	1.40				0.5
Benzo(k)fluoranthene	0.98				0.6
Benzo(a)pyrene	1.10	6.12[1]	3.7		0.5
Indeno(1,2,3,c,d)pyrene	1.45				
Dibenzo(a,h)anthracene	0.40				
Benzo(g,h,i)perylene	0.95				
PAH_{16}	12.8				

[1] Müller and Klein, 1992
[2] Mackay, 1982
[3] Calculated from log P_{ow} as described by Jager and Hamers (1997) for earthworms, assuming an organic content of 40 g TOC/kg DS.
[4] BSAF= $(Q_{biota}/l_{biota})/(Q_{sediment}/f_{oc})$, where Q_{biota} is contaminant uptake rate in biota given per ww, $Q_{sediment}$ is contaminant elimination rate in sediment given per DS, l_{biota} is lipid content in biota given as g/g ww, f_{oc} is organic content in sediment given as g TOC/g DS.
[5] Reible et al. (2002). Bentic worms.
[6] Kraaij et al. (2001). *Corophium volutator.*

75 % of the PAH_{16} and 48 % of PCB_7 in the sediment treated with a centrifuge was recovered in the concentrate. The recovery of the more chlorinated PCB congeners in the concentrate was higher than of the less chlorinated congeners (Figure 4), while the variation of the recovery of various PAHs did not seem to follow any particular pattern (Figure 3).

4.3 Bioaccumulation of PAH and PCB

The DS content in the dredged sediment going into the centrifuge was 13 % on average. The DS content was 50 % in the concentrate (treated sediment) and 8 % in the centrate (water phase). VDS was 11±1 % of the DS. TOC was 3.9±0.3 % of DS. The DS content in *Corophium volutator* was 17.8±0.3 %.

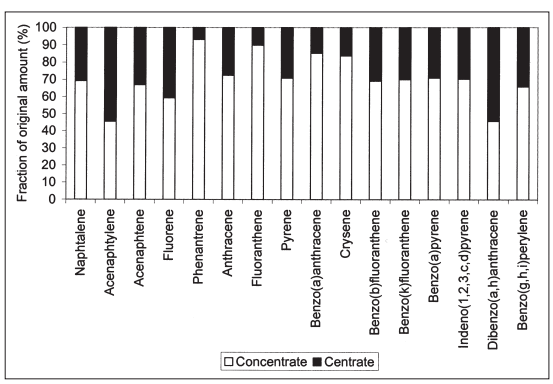

Figure 3. *Distribution of PAHs between the concentrate (treated sediment) and the centrate (water phase) after centrifugation.*

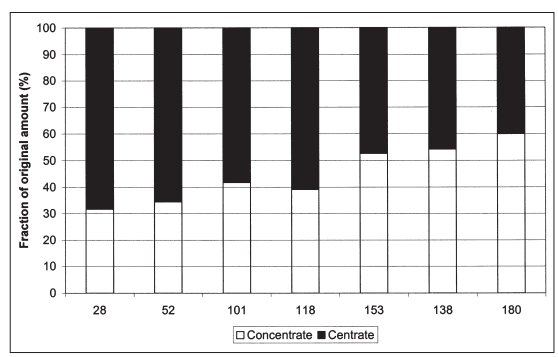

Figure 4. *Distribution of PCBs between the concentrate (treated sediment) and the centrate (water phase) after centrifugation.*

Table 2. *PCB in dredged sediment.*

PCB congener	Measured concentration (mg/kg DS)	Log P_{ow}	Calculated bioaccumulation factor[2] (kg DS (sediment)/ kg ww (biota))
28	0.01	5.71[1]	2.9
52	0.03	5.79[1]	3.0
101	0.05	6.40[1]	4.2
118	0.03	6.74[1]	4.9
138	0.05	6.73[1]	4.9
153	0.05	6.80[1]	5.1
180	0.03	7.21[1]	5.6
PCB_7	0.25		

[1] Mackay et al. 1992

[2] Calculated from log P_{ow} as described by Jager and Hamers (1997) for earthworms, assuming an organic content of 40 g TOC/kg DS.

The concentrations of PAH and PCB in the dredged sediment and in concentrate (treated sediment) and centrate (water phase) from centrifugation are shown in Figures 5 and 6. For the most volatile PAHs and least chlorinated PCBs the concentrations in biota were not significantly different from the values measured in the control, and therefore the accumulation of these compounds appears as zero. The bioaccumulation concentration was considerable in untreated and treated sediments as well as in the water phase, with no major reduction in neither of the fractions from centrifugation compared to the bioaccumulation in the dredged sediment, even though the bioaccumulation of PCB in the centrate was lower than in the dredged sediment and the concentrate. The results did not give reason to conclude that neither of the fractions from centrifugation was harmless and could be discharged to the recipient.

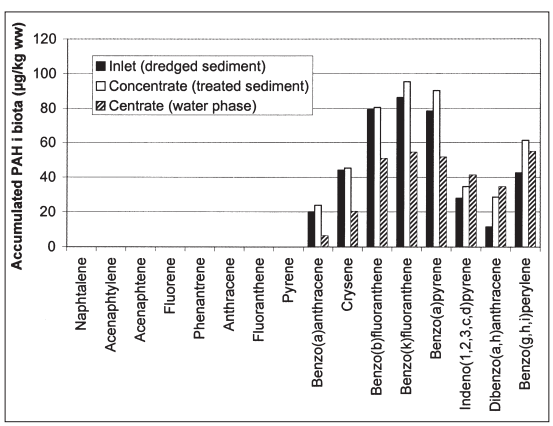

Figure 5. Bioaccumulation of PAH in *Corophium volutator* in inlet (dredged sediment), concentrate (treated sediment) and centrate (water phase) after centrifugation.

5 Conclusions

The results from this study confirm that a proper prestudy is necessary to determine the effect of a physical pretreatment. The results also show that the effect on the bioavailability may differ from the effect on the contaminant concentration. Therefore, determination of the bioavailability of contaminants in sediments may add valuable information to physical and chemical analysis.

When the bioavailability of PAH and PCB in a fine-grained sediment from a Norwegian harbour was measured before and after physical separation with a centrifuge, the results did not give reason to conclude that neither the concentrate nor the centrate could be regarded as considerably less contaminated than the original sediment. This means that for this specific sediment, a physical separation carried out to divide the sediment based on particle size would not give any major benefit since all of the fractions could be defined as being potential harmful to the environment.

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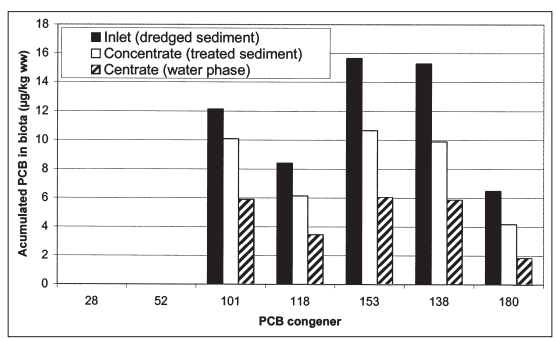

Figure 6. Bioaccumulation of PCB in *Corophium volutator* in inlet (dredged sediment), concentrate (treated sediment) and centrate (water phase) after centrifugation.

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