### BIOACCUMULATION OF CHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN SPIDER CRABS AND BLUE MUSSELS EXPOSED TO SEDIMENT POLLUTED BY PAPER PULP BLEACHING: PART I

Å. Granmo<sup>A</sup>, R. Ekelund<sup>A</sup>, M. Berggren<sup>A</sup>, K. Magnusson<sup>A</sup>, <u>C. de Wit<sup>B</sup></u>, C. Rappe<sup>C</sup>, S. Bergek<sup>C</sup> and M. Hjelt<sup>C</sup>

<sup>A</sup> Swedish Environmental Protection Agency, Kristineberg Marine Biological Station, S-450 34 Fiskebäckskil, Sweden

<sup>B</sup> Swedish Environmental Protection Agency, Special Analytical Laboratory, S-171 85 Solna, Sweden

<sup>C</sup> Institute of Environmental Chemistry, University of Umeå, S-901 87 Umeå, Sweden

#### ABSTRACT

To find out to what extent chlorinated dibenzo-p-dioxins and dibenzofurans occuring in a bleachery-contaminated sediment are bioavailable, spider crabs (*Hyas araneus*) and blue mussels (*Mytilus edulis*) were exposed to the suspended sediment. The crabs were exposed via both water and food. The food consisted of blue mussels that had been exposed in the same way. The results of the chemical analyses showed that the mussels and crabs exposed to the contaminated sediment contained elevated concentrations of PCDD and PCDF compared to the animals exposed to the control sediment. The PCDD/PCDF profiles were different in the animals than in the sediment and the most highly chlorinated congeners became less dominating in the animals, especially in the crabs.

#### INTRODUCTION

At present it is well-known that sediments formed in a receiving water for effluents from paper pulp mills using chlorine, contain high concentrations of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) (Jonsson et al., 1992) and of extractable organic chlorine (EOCl) (Håkansson et al., 1988). However, it is not well understood to what extent these sediment-stored compounds are bioavailable. To elucidate this, spider crabs (*Hyas araneus*) and blue mussels (*Mytilus edulis*) were exposed to a contaminated sediment and to a less contaminated control sediment and analyzed for PCDD and PCDF.

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### MATERIALS AND METHODS

Baltic Sea sediments collected four kilometers from the bleached pulp mill discharge (Iggesund) and from a control station 65 kilometers away were supplied suspended in running seawater to make them available to the filter-feeding mussels. The turbidity in the tanks (10 L) was  $12 \pm 2 \text{ mg/mL}$  and the water flow was 70 mL/min. The exposure lasted for 52 days at  $15 \pm 2^{\circ}$ C. The crabs were exposed via both water and food. The food consisted of blue mussels that had been exposed under the same conditions for 14 days. At the end of the exposure period, the hepatopancreas and ovaries of the crabs and whole soft tissues of the mussels were sampled and frozen at -20°C for analysis of PCDD and PCDF (Rappe et al., 1991). Sediment samples from both stations were also analyzed.

#### RESULTS

The results of the chemical analyses of PCDD and PCDF are shown in Table 1 and Fig. 1a and 1b. The mussels and crabs exposed to the contaminated sediment (Fig. 1b) contained elevated concentrations of PCDD and PCDF compared to the animals exposed to the control sediment (Fig 1a). A close examination of these figures reveals that the most toxic congeners such as 2,3,7,8-substituted tetra through hexa CDDs and CDFs dominate more in the biological samples than in the sediments. Additionally, the sediment sample collected in the vicinity of the pulp mill as well as the animals exposed to this sediment contained more 2,3,7,8- and 1,2,7,8-tetra CDF, a non-2,3,7,8-substituted congener (Table 1). Both of these congeners are well recognized indicators of effluents from bleaching operations at pulp mills (Jonsson et al., 1992; Swanson, 1988).

		Baltic				Iggesund			
	Sedi- ment	Muss- els	Crab hep.	Crab ov.	Sedi- ment	Muss- els	Crab hep.	Crab ov.	
IG or									
% lipid	7.4	0.9	14.7	4.5	14.4	1.0	14.3	4.8	
Congener									
2,3,7,8-TCDD	5.4	4.4	10	9.6	104	41	54	23	
2,3,7,8-TCDF	80	72	150	175	1500	470	550	330	
1,2,7,8-TCDF	41	28	27	44	760	200	120	120	

Table 1. Levels of bleached paper pulp-associated PCDD/PCDF in sediment (pg/g ignition loss, IG), blue mussels and crabs (pg/g lipid weight) exposed to a control (Baltic) and a paper mill-influenced (Iggesund) sediment.

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Fig. 1. PCDD and PCDF levels (lipid weight) in blue mussels, crab hepatopancreas (crab hep) and crab ovaries (crab ov) after exposure to a control sediment (a) and sediment (ignition loss) contaminated by a bleached pulp mill (b). TD=2378-TCDD, PD=12378-PeCDD, HxD4=123478-HxCDD, HxD6=123678-HxCDD, HxD9=123789-HxCDD, HpD=1234678-HpCDD, OD=OCDD, TF=2378-TCDF, 12TF=1278-TCDF, PF1=12378-PeCDF, PF4=23478-PeCDF, HxF4=123478-HxCDF, HxF6=123678-HxCDF, HxF9=123789-HxCDF, HxF2=234678-HxCDF, HpF6=1234678-HpCDF, HpF9=1234789-HpCDF, OF=OCDF.

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#### DISCUSSION

The sediment-associated PCDD and PCDF are markedly bioavailable with the exception of the most highly chlorinated congeners (hepta- and octachlorinated CDD and CDF), probably because their larger molecular size prevents free passage across the cell membranes. This implies that the most toxic congeners are the most bioavailable.

Knutzen and Oehme (1989) analyzed crabs and mussels from a fjord heavily polluted with primarily higher chlorinated PCDF, and from their results it is calculated that the ratio of TCDD-equivalents in crab hepatopancreas was 0.2 and in mussels 0.04 compared to the concentration in sediment (concentration fresh weight in tissue/concentration dry weight in sediment). The corresponding ratios from this experiment, 0.2 and 0.02 respectively, are comparable even if the sediment in the Knutzen and Oehme study probably did not function as a source to the same extent as in our laboratory investigation with suspended sediment.

Comparison of ovary and hepatopancreas tissue shows that the levels are a bit higher or the same in ovarian tissue in crabs exposed to the control sediment. Crabs exposed to the discharge sediment have higher levels in the hepatopancreas. In a previous study, mussels were exposed to the same sediments at a concentration of 70 mg/L for four weeks. No significant difference in the scope for growth index (Widdows, 1985) was detected between the two groups (Granmo et al., unpublished results).

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