Bioavailability of polychlorinated diphenylethers (PCDEs) in contaminated sediments: Comparison of benthic organisms and semipermeable membrane devices (SPMDs)

Jussi V.K. Kukkonen*, Anna-Lea Rantalainen**, Pirjo Mikkelson**, Merja Lyytikäinen*, Heikki Hämäläinen* and Jaakko Paasivirta**

*University of Joensuu, Department of Biology, P.O.Box 111, FIN-80101 Joensuu, Finland
**University of Jyväskylä, Department of Chemistry, P.O.Box 35, FIN-40351 Jyväskylä, Finland

Introduction

It is well documented that sediments are a sink for hydrophobic halogenated organic pollutants discharged into the aquatic environment. Although mostly bound by sediment particles, these pollutants can be bioavailable to benthic organisms. Thus, sediment-associated contaminants can be toxic to benthic organisms or introduced in significant levels into the aquatic food chain. To monitor this potential accumulation, different approaches have been suggested.

Oligochaete worms, like *Lumbriculus variegatus*, meet most of the test criteria set for the organism used in the sediment toxicity and bioavailability tests [1]. They are also easy to culture and handle in laboratory conditions [2]. Oligochaetes have been employed both in field surveys as a bioindicator of pollution or trophic status [3] and in laboratory toxicity [4, 5] and bioaccumulation tests [6, 7]. Oligochaete species are also appropriate for measuring sublethal endpoints, such as growth and reproduction and behavioural responses such as sediment avoidance or feeding rate [8]. Among the bioassays proposed with *L. variegatus* is their use as a standard freshwater bioaccumulation organism [9].

Another approach for determining the bioavailable fraction of contaminants in the environment is to use different kind of passive samplers, which mimic organisms. Semipermeable membrane devices (SPMDs), developed by Huckins *et al.* [10], represent a further advancement of passive samplers such as Södergrens hexane-filled cellulose dialysis membranes, which have been shown to concentrate halogenated organic compounds [11]. SPDMs may have some advantages over living organisms: they do not metabolize and actively depurate accumulated compounds (although photooxidation may occur without precautions) and they are durable in severe environments. Disadvantages of SPMDs are that they do not actively move in sediment or soil and do not consume particles which may have a high load of hydrophobic pollutants sorbed. This may lead to underestimation of bioavailable fraction. SPMDs can be used in various compartments of ecosystem including water and sediment.

Some comparisons between organisms, mainly bivalves, and SPMDs have been performed in aquatic environments [12,13] but more is needed especially to establish the applicability of SPMDs in monitoring of bioavailable compounds in sediments. The objectives of this study were to compare the accumulation of sediment-associated polychlorinated diphenylethers into oligochaete worms, *L. variegatus*, and SPMDs at laboratory conditions and, further, relate the observed accumulation to the concentrations in benthic organisms collected from field at the same sites where sediment samples were collected.

Materials and Methods

River Kymijoki is heavily affected by pulp and paper as well as chemical industry. One of the pollution sources along the river is in Kuusankoski, the factory produced large amounts of a chlorophenol product called Ky-5 between 1940-1984. Ky-5 mainly consisted of penta-, tetra- and trichlorophenols [14] but it had PCDD/Fs as well as the other chlorinated compounds like polychlorinated diphenylethers as by-products and these compounds have also been leached into River Kymijoki [15]. The River Kymijoki was sampled at ten different stations. Sediment samples were obtained by Ekman type sampler and indigenous benthic organisms, midge (*Chironomus* spp.) larvae were collected by a pump sampler.

In the laboratory, sediment samples were sieved at 2 mm to remove animals and large debris and held at 4°C until use. This experiment was designed to evaluate the accumulation of chlorinated organic compounds in sediment into *L. variegatus* and SPMDs. The sediments were mixed for homogeneity, subsamples were taken for sediment characterization and chemical analyses, and 800 g of wet sediment was distributed to three 3-L exposure beakers per sampling station. Artificial freshwater (2 L) was then carefully added to each beaker with minimal sediment disturbance. On the following day, 80 test organisms were carefully added by pipetting to each beaker. These groups of *L. variegatus* were exposed at 21 ± 1 °C to sediment for 28 days [9]. The overlying water was continuously aerated. The SPMD exposure was done in duplicate in each sediment. One 21.5 cm long PE-tubing filled with 0.25 ml triolein was placed in 800 g wet sediment. The exposure time and conditions were the same as in worm exposure above.

Preparation of SPMDs and the first clean up after exposure to prepare the hexane dialysates have been described in detail by Rantalainen *et al.* [16]. Further analysis of dialysates, biota and sediment samples were the same as reported earlier for PCDEs [17]. PCDE standard used consisted of 32 congeners.

Results and Discussion

The sediment characteristics varied at different stations: dry weight %: 17% - 37%, organic carbon: 1.2% - 11.0%, percent of fine (< 63 µm) particles: 38.0% - 86.6%. Sums of the PCDE congeners above the limit of determination are collected in Table 1. Only these sum parameters (denoted as "PCDEs") are compared in the present report. The concentration of PCDEs in sediment was the highest at the stations closest to the old Ky-5 factory (site 2-4) and decreased downstream (Table 1). The PCDEs concentrations in the organisms and SPMDs had a similar trend (Table 1), but only the PCDEs concentrations in *L. variegatus* have a significant correlation ® = 0.73, P = 0.024) with sediment concentrations. This lack of correlation may indicate that there are other factors than the total concentration of compounds in sediment that affect bioavailability.

The PCDEs concentrations in the organisms and in SPMDs correlate with each others (Fig.1). The lipid normalized body residues in the indigenous midge larvae were very close to the concentrations measured in *L. variegatus* exposed to the sediments in the laboratory. The slightly lower concentrations in midge larvae can be explained by their different behaviour in the sediments compared to the oligochaete worms [18].

Table 1. Concentration of polychlorinated the sum of diphenylethers (PCDEs) in sediment (ng/g sed. dw), in indigenous midge larvae (*Chironomus* spp.; ng/g lipids), in oligochaete worms (*L. variegatus;* ng/g lipids) and in SPMDs (ng/g lipids) exposed in the laboratory to the sediments. The suspected source is between sites 1 and 2. Also, biota-sediment accumulation factors (BSAF; ng g^{-1} lipids / ng g^{-1} sediment organic carbon) are shown.

Site code	Sedim.	Midge	Worms	SPMDs	BSAF Midge	BSAF Worms	BSAF SPMDs
0	nd	nd	nd	1.0	nd	nd	nd
1	9	303	336	2.0	1.91	2.12	0.013
2	256	426	926	14.8	0.14	0.40	0.006
3	606	510	1325	9.0	0.09	0.23	0.002
5	328	248	493	6.1	0.06	0.11	0.001
7	183	589	913	5.4	0.40	0.62	0.004
9	29	nm	215	2.3	-	0.09	0.001
12	39	nm	882	5.2	-	0.27	0.002
14	14	348	568	4.8	0.64	1.04	0.009
15	24	223	260	3.8	0.54	0.63	0.009

nd = not detected, nm = not measured

The SPMDs accumulated much less PCDEs during the 28 days exposure period compared to oligochaetes (Table 1). The reasons for the low accumulation into the SPMDs can be that the diffusion is so slow that the equilibrium is not yet reached after 28 days exposure. Further, SPMDs uptake the compounds only from the pore water but organisms feed on the sediment

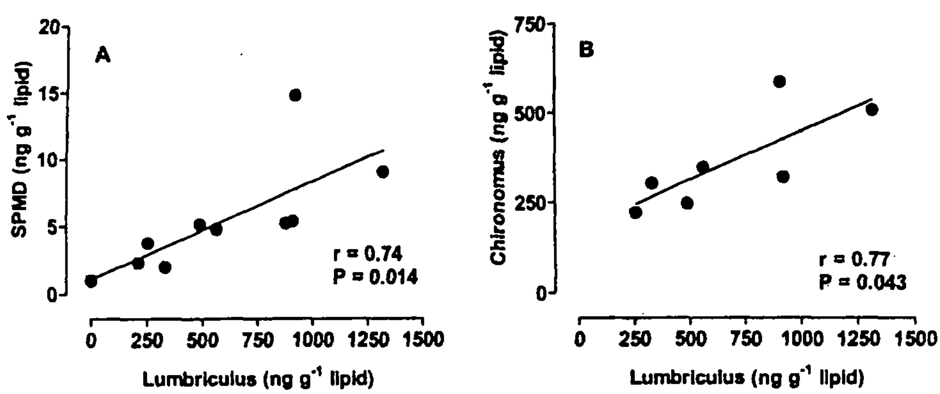

Figure 1. Relationship between PCDEs accumulated into SPMDs and *L. variegatus* exposed the same sediments in laboratory conditions (A) and relationship between lipid normalized PCDEs concentrations in laboratory exposed *L. variegatus* and in indigenous *Chironomus spp.* larvae collected from the same sites as the sediments (B).

particles and thus expose themselves to much larger pool of contaminants. However, the trend between body burden in *L. variegatus* and concentration in SPMDs was the same (Fig.1).

Acknowledgements

This research was supported by the Academy of Finland (project 38004) and UPM-Kymmene Co.

References

1. Burton G.A., Nelson M.K. and Ingersoll C.G. Chapter 10, p. 213-240, in *Sediment Toxicity Assessment*, Ed. G.A.Burton, Lewis Publishers, Ann Arbor, MI, **1992**; ISBN:0-87371-450-4
2. Phipps G.L., Ankley G.T. Benoit D.A. and Mattson V.R.; *Environ. Toxicol. Chem.* **1993**, 12, 269.
3. Lauritsen D.D., Mozley S.C. and White D.S.; *J. Great Lakes Res.* **1985**, 11, 67.
4. Wiederholm T., Wiederholm A.M. and Milbrink G.; *Water Air Soil Pollut.* **1987**, 36,131.
5. Wiederholm T. and Dave G.; Hydrobiologia **1989**, 176/177, 411
6. Kukkonen J. and Landrum P.F.; *Environ. Toxicol. Chem.* **1994**, 13, 1457.
7. Kukkonen J. and Landrum P.F.; *Environ. Toxicol. Chem.* **1995**, 14, 523.
8. White D.S. and Keilty T.J.; *Arch. Environ. Contam. Toxicol.* **1988**, 17, 673.
9. ASTM, Standard guide E1688-97a, p. 1072-1121, in *Annual Book of ASTM standards* vol 11.05, American Society for Testing and Materials, **1997**, ISBN: 0-8031-2448-1.
10. Huckins J.N., Tubergen M.W. and Manuweera G.K.; *Chemosphere* **1990**, 20, 533.
11. Södergren A.; *Environ. Sci. Technol.* **1987**, 21, 855.
12. Herve S., Prest H.F., Heinonen P., Hyötyläinen T., Koistinen J. and Paasivirta J.; *Environ. Sci. Pollut. Res.* **1995**, 2, 24.
13. Prest H.F., Jarman W.M., Burns S.A., Weismuller T., Martin M. and Huckins J.N.; *Chemosphere* **1992**, 25, 1811.
14. Vartiainen T., Lampi P., Tolonen K. and Tuomisto J.; *Chemosphere* **1995**, 30, 1429.
15. Verta M., Vartiainen T., Kiviranta H., Korhonen M., Kukkonen J.V.K., Hämäläinen H., Palm H. and Mikkelson P. 8th Annual Meeting of SETAC-Europe, Bordeaux, France, 14 - 18 April **1998.** Abstracts Book, p. 177, Abstract 3C/P008.
16. Rantalainen A.-L., Paasivirta J. and Herve S.; *Chemosphere* **1998**, 36, 1415.
17. Koistinen J., Paasivirta J., Suonperä M. and Hyvärinen H.; *Environ. Sci. Technol.* **1995**, 29, 2541.
18. Penttinen O.-P., Kukkonen J. and Pellinen J.; *Environ. Toxicol. Chem.* **1996**, 15, 160.