Lipid-Filled Semipermeable Membrane Devices and Mussels as Samplers of Organochlorine Compounds in Lake Water

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Abstract
Semipermeable membrane sampling devices (SPMDs) and caged lake mussels (Anodonta piscinalis) were simultaneously deployed at four lake watercourse sites in Central Finland four weeks in August 1992. This study was part of the regular annual monitoring of the organochlorine compounds (OCC) in pulp-mill recipient watercourses of Finland with bivalves. Chlorohydrocarbons (CHCs), chlorophenol compounds (PCPs), chloroanisoles (PCAs) and chloroveratroles (PCVs) were analyzed from lipid extract of mussels and from the synthetic triolein lipid of the SPMDs. Hexane-diethyl ether (9:1, v/v) dialysis using polyethylene membrane was applied in clean up of the SPMD lipids and, for comparison, to six sets of the mussel fat. Dialysis recovered CHCs but not PCPs from the mussel fat. CHCs, PCPs, PCAs and PCVs were all recovered in dialysis of the SPMD lipid. Handling of SPMDs in the transport and deployment operations caused significant OCC contamination for the blank SPMDs. Similar trends were revealed in the OCC profiles for mussels and SPMDs. An exception was the lack of PCPs appearing in SPMDs that did appear in mussels and in a complementary manner the appearance of the PCAs and PCVs in SPMDs.

Key words: Biomonitoring; organochlorine compounds (OCC); chlorohydrocarbons (CHCs); chlorophenol compounds (PCPs); chloroanisoles (PCAs); chloroveratroles (PCVs); semipermeable membrane sampling devices (SPMDs); mussels, lipid extract; SPMDs, synthetic triolein lipid

1 Introduction
Caged lake mussels (Anodonta piscinalis) have been successful for monitoring purposes in concentrating organochlorine compounds (OCCs) from lakes and waterways in Finland [1, 2]. Previous concerted deployments of mussels and hexane-filled, hydrophilic dialysis membranes designed by SÖDERGREN [3, 4] showed little accumulation of DDE and PCBs [5]. Another type of semipermeable membrane device (SPMD), thin walled polyethylene layfat tubes filled with synthetic (triolein) lipid, developed by HUCKINS et al. [6], has been shown to be successful in accumulating traces of lipophilic organochlorine pesticides, PCBs, PCDDs and PCDFs in simultaneous deployment with clams [7]. This paper presents results of the deployment of triolein-filled polyethylene layfat SPMDs in concert with the regular mussel incubation monitoring of OCCs in a pulp mill recipient watercourse in Central Finland.

2 Materials and Methods
The sampling locations (MAT, KUU, TOR and KAR) are shown in Fig. 1. Fifteen mussels were incubated four weeks at each station in August 1992 using procedures in pretreatment, incubation, transportation, storage and analyses as described previously [2, 8, 9]. At the end of the exposure mussels from all sites were divided into three separate samples, each with five individuals. At stations KUU and KAR, additional fifteen mussels were incubated for comparative analyses by dialysis as three sets of five individuals, respectively.

The SPMDs were 229 cm long, 5 cm wide, 0.05 mm thick polyethylene layfat tubings filled with 5 mL of triolein. They were prepared for deployment in Santa Cruz, CA following the procedure described by PREST et al. [7]. The SPMDs were transported in closed glass containers to the deployment site. At the beginning of each exposure period, each SPMD was suspended inside a polyethylene basket. At each site, four baskets were incubated for four weeks together with mussels.

For a deployment method blank, one SPMD (OS-AKV) was kept four weeks inside an incubation basket in a laboratory aquarium of the Water and Environment District of Central Finland. Two SPMDs (OS-KUU and OS-TOR) were transported with the other SPMDs in their glass container to the incubation site but left in the container after removing the test SPMDs. The blanks were intentionally exposed with the incubated SPMDs; i.e. the transport container was opened while SPMDs were placed in the incubation basket. At TOR there was a heavy rain during employment while at KUU there was no rain during the operation. Then the containers were closed and the blank SPMDs were transported...
back to the laboratory and kept there frozen in glass containers during the incubation period. After the fourweek exposure period the mussels and SPMDs were brought to the laboratory in glass containers and kept frozen until analysis. Two containers (labelled 1 and 2) each containing two SPMDs were brought from each of the four stations.

SPMD membranes in the containers were allowed to thaw to room temperature and then inspected on aluminium foil for possible leaks. Most of the superficial biofouling was removed by drawing the membrane through the fingers of polyethylene gloved hands. One end of the membrane was cut open and the triolein inside was collected by three 40 mL rinses of hexane. The hexane rinses from each set of the four SPMDs deployed at a location were composited to be treated as a single sample. The hexane rinses of the three blank SPMDs were treated as separate samples. The solutions were concentrated by rotary evaporation and transferred into 100 mL measuring bottles. A 5 mL aliquot from these was evaporated under dry nitrogen and the residue weighed to give lipid present in each composite or blank sample.

The remaining 95 mL hexane-lipid solutions were evaporated to small volumes of mostly lipid and an internal standard, 2,4,6-tribromophenol, was added. Each lipid sample was transferred with small volumes of hexane into both ends of a hexane-washed polyethylene (PE) membrane (86 cm long, 5 cm wide, 0.05 mm wall layfat tube) using a long pipette. Similarly, lipid extracts from mussel composites of five individual bivalves were also transferred to polyethylene dialysis membranes; three replicates from station KUU and three from station KAR.

PE membranes containing combined extracts from deployed SPMDs were dialyzed in 2 L glass cylinders, the blank SPMD samples and lipid extracts from mussels in 1 L cylinders, with hexane: diethyl ether (9:1 v/v). The volumetric ratio of dialytic solvent to extract exceeded 50/1 in all cases. The dialysis was done with magnetic stirring for 24 hours. Then the solvent was replaced with another lot and the dialysis repeated for 24 hours and dialyzed as described above. The combined dialysate solutions from SPMDs and from the mussel composites were evaporated to 100 mL in rotary evaporation and then analyzed. Analysis of OCCs in dialysates were done using the same methods as in OCC determinations from mussel lipid extracts [2,8,9]. The compounds studied and their limits of determination (LDs) are listed in Table 1.