Concentrations and Biomagnification of Cyclodiene Pesticides including Chlordane Compounds, Dieldrin and Mirex in a Pelagic Food Web in the northern part of the Baltic Sea.

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INTRODUCTION

Chlordane and dieldrin are among the most common and important environmental contaminants. Both chlordane and dieldrin have been used for many different reasons both for residental and agricultural applications[1,2]. Mirex has been used for control of pests e.g. ants, although more widely used as a flame retardant and additive agent in plastics[3]. The usage of chlordane, dieldrin and mirex is phased out or strongly restricted in many countries e.g. Europe, USA and Japan but their use is continuing and even increasing in developing countries in tropical regions[4]. We are not aware of applications of either chlordane[5] nor mirex in the northern European countries, and there is very limited knowledge of concentrations and the fate of chlordane, dieldrin and mirex compounds in the Baltic Sea marine ecosystem.

The Baltic Sea has special physical features e.g. shallow, low salinity, slow water exchange and is a vulnerable ecosystem very poor in species abundance. Zooplankton, mysis (*Mysis sp.*) and herring (*Clupea harengus*) are important components of the pelagic marine food web in the Baltic Sea. The diet of mysis is dominated by zooplankton and mysis is an important food item for herring.

Biomagnification is defined as the increase of a compounds concentration with each trophic level in a food web[6]. A biomagnification factor (BMF), measured as the ratio between predator and prey on lipid weight basis, larger than 1 indicate that the compound biomagnifies. In the case metabolism is higher than the biomagnification potential for a compound the BMF can be lower than 1.

Chlordane components (CHLs) including heptachlor, U81, U82, U83, MC4, *trans*-chlordane, MC5, *cis*-chlordane, MC7, MC6, *trans*-nonachlor and *cis*-nonachlor, and their metabolites *cis*-heptachlorepoxide and oxychlordane and photoconversion products such as photoheptachlor and photo-*cis*-chlordanes, as well as dieldrin and mirex were quantified and the BMF determined in the pelagic food web consisting of zooplankton, mysis and herring at two locations in the northern part of the Baltic Sea.

MATERIALS and METHOD

Samples of zooplankton, mysis and herring were collected at two pelagic stations in the autumn of 1991, one in the Bothnian Bay (F9) and one in the Bothnian Sea (SR5) (Figure 1). The geographical coordinates of the sampling sites are given in detail elsewhere[7].

Zooplankton and mysis were pooled samples of organisms of mixed sizes. The herring were pooled samples with three fishe species in each. In order to limit biological variations all fishes were of similar sizes and weights.

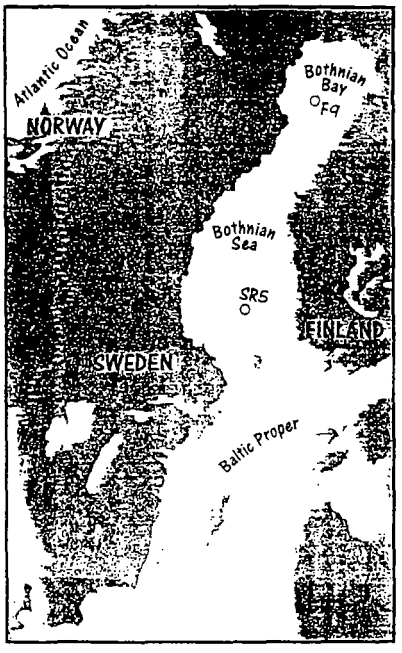

Figure 1. Sampling locations in the Baltic Sea.

The sample enrichment process was a multi-residue method aimed to target a multitude of organochlorines and polyaromatic hydrocarbons[8,9]. Briefly, the samples were homogenised and soxhlet extracted (Dean-Stark) with toluene (24h) and a mixture of hexane and acetone (59/41, 24h). Before extraction an internal standard mixture containing ^{13}C-labelled lindane, *p,p'*-DDT, dieldrin, PCB#80 and#153 were added to the samples. Bulk lipid removal was effected by means of a polyethylene film dialysis method[10,11]. This dialysis fraction was split into two parts, of which 10% was used for analysis of organochlorine pesticides (included those discussed herein) and (Cl_3-Cl_{10}) PCBs. The 90% fraction was analysed for mono- and non-*ortho* PCBs, PCDD/Fs and PCNs. The 10% fraction was further enriched on a Florisil column[12]. Finally, analysis and detection was accomplished using high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS). The MS instrument, a Fisons MD 800 coupled to a Fisons GC 8000 (DB-5 column, 60x0.32 i.d.) was used in electron impact (EI) mode with selected ion recording (SIR).

MC4, MC5, MC6, MC7, and U81, U82 and U83 are abbreviations of CHLs compounds identified by Miyazaki *et al.*[13] and Dearth & Hites[14], respectively. All compounds except the chlordane U and MC abbreviations and photoconversion products were identified and quantified against authenticated standards. The U and MC compounds were identified in a technical chlordane mixture and/or to the scientific literature[1,15,16], and quantified against native related compounds in the autenticated standard. The chlordane photoconversion products were tentatively identified according to Buser *et al.*[17].

RESULTS and DISCUSSION

CHLs and dieldrin were detected in all three specimen at both stations, but mirex was found only in trace levels in the herring samples. Concentration mean values (ng/g lipid) of CHLs, dieldrin and mirex as well as detection limit for mirex in zooplankton and mysis, are presented in Table 1. The analytical repeatability expressed by standard deviations of analysed compounds for the replicates was generally acceptable, 30% or better on lipid weight basis.

Table 1. Concentration (ng/g lipid) of cyclodiene pesticides including chlordanes (CHLs), dieldrin and mirex in zooplankton, mysis and herring at two stations in the northern Baltic Sea.

Specimen	Zooplankto	Mysis	Herring	Zooplankton	Mysis	Herring
Station	F9	F9	F9	SR5	SR5	SR5
	(n=4)	(n=2)	(n=3)	(n=4)	(n=3)	(n=4)
CHLs	3.8	44	73	6.2	28	154
Dieldrin	15	38	36	21	33	121
Mirex	ND (<0.25)	ND (<0.15)	0.48	ND (<0.20)	ND (<0.25)	1.4
Lipid weight (g)	0.65	4.6	2.3	0.42	1.0	1.3
% Lipid phase (%)	3.5	9.5	6.6	2.7	13.1	4.0

n-number of samples, ND-not detected

Among the CHLs, *cis*-chlordane and *trans*-nonachlor were found in the highest concentration in most of the analysed samples. All CHLs studied were found in herring except that of U81 and heptachlor. Heptachlor is however seldom found in the environment or in organisms since it is metabolised or converted to *cis*-heptachlorepoxide or photoheptachlor[17]. The two studied photo-*cis*-chlordanes were found among the CHLs components as relatively abundant peaks in both mysis and herring. Photoheptachlor however was only found in trace levels in herring samples and the concentrations were approximated to about 0.5-1.2 ng/g lipids.

Figure 2 display the BMF for CHLs, dieldrin and mirex in the Baltic pelagic food web including zooplankton/mysis/herring for the two locations, respectively. BMF values should however be regarded more as indicators than exact values. For mirex (bars denoted with *), the detection limit values were used for zooplankton and mysis when the BMF value were calculated to herring, respectively. The "true" BMF value for mirex should therefore be equal to or even higher than the bars are showing.

According to Figure 2 the three pesticides seem to biomagnify (BMF>1) in the food web, except for dieldrin from mysis to herring in F9, where the concentrations were similar in both predator and prey. CHLs seem to biomagnify to a larger extent than dieldrin, and mirex similar or larger than dieldrin. Interestingly, dieldrin has higher concentration than CHLs in zooplankton although in herring it is the contrary.

Various CHLs components can have markedly different accumulation behaviour and various organisms can differ in possibilities to metabolise parent chlordanes. For example, mysis contains less of octa chlorinated CHLs compared to herring, which indicates a higher BMF of those compounds compared to nona chlorinated CHLs. Both of the photo-*cis*-chlordanes had approximately similar BMF as their parent compound, *cis*-chlordane. Surprisingly, when the ratio of the parent compounds (sum of *trans*- and *cis*- chlordane and nonachlor) to the metabolites

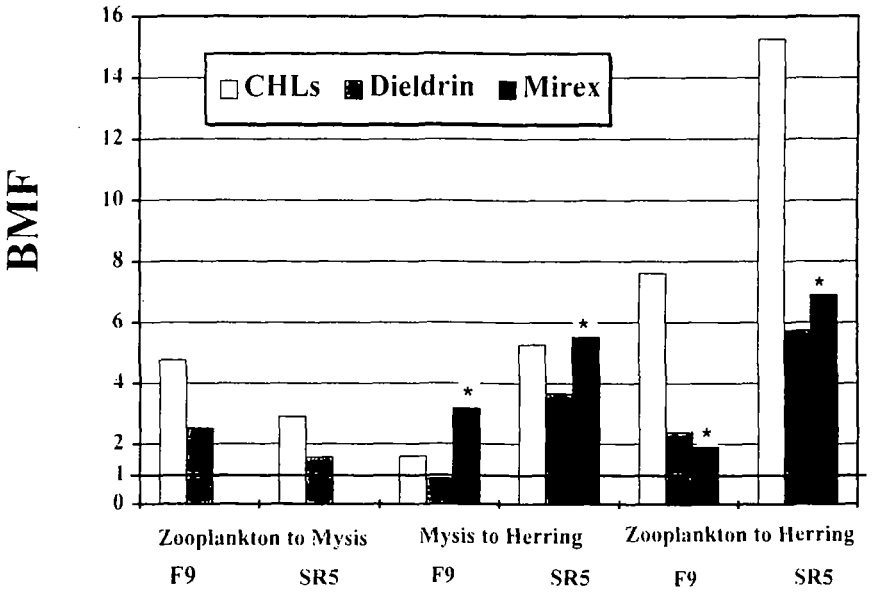

Figure 2. Biomagnification factors (BMF) for chlordane (CHLs), dieldrin and mirex in the Baltic pelagic food web zooplankton/mysis/herring for two locations (F9 and SR5) in the Baltic Sea. Bars denoted with * are calculated to not detected values for zooplankton and mysis, respectively. A BMF>1 indicates biomagnification.

(heptachlorepoxide and oxychlordane) where compared for mysis and herring, mysis seemed to have a factor of 3-4 higher metabolism than herring.

Finally, biomagnification differences between the two studied stations were noted. For all three studied pesticides the herring in the southernmost station (SR5) displayed approximately 2-4 times higher biomagnification than the herring from station F9.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support of the Kempe Foundation, the Swedish Forest Industries, the Finnish National Board of Water and the Environment, the Swedish Environmental Protection Agency, the Boliden Mineral AB and the Center for Environmental Research in Umeå, Sweden, and technical assistance from Per Jonsson and Olle Sandström.

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