TEMPORAL TRENDS OF A POLYBROMINATED DIPHENYL ETHER (PBDE), A METHOXYLATED PBDE, AND HEXABROMOCYCLO-DODECANE (HBCD) IN SWEDISH BIOTA

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Introduction

Previously reported time trend studies of tetra- and pentabrominated diphenyl ethers have shown both increasing and decreasing trends. Results from a sediment core from the Baltic Sea indicated increasing levels in the environment from the mid 1970s to 1989 (1). The levels in guillemot eggs, from the Baltic Sea, increased from the early 1970s to the late 1980s, but have decreased during the 1990s (2). Decreasing time trends of 2,2',4,4'-tetrabromodiphenyl ether (BDE47) were also reported in eel from River Rhine and River Meuze (1984-1993) and in cod liver from the North Sea (1983-1993) (3,4). PBDE numbering is in analogy to the system for PCB based on the substitution pattern (5). In eel from the River Roer however, increasing concentrations of BDE47 were found over the years 1983-1991 (3,4). In a temporal study of PBDE in Swedish human breast milk the concentrations increased exponentially from 1972 to 1997 (6).

Methoxylated PBDEs (MeO-PBDE) were first identified in fish and seal samples from the Baltic Sea (7,8). Possible origins of these may be anthropogenic sources, microbial methylation of hydroxylated PBDEs, or biogenic sources. For example, tetrabrominated MeO-BDEs have been identified in marine sponges from Indonesia and in green algae collected in Japan (9,10).

Hexabromocyclododecane is also used as a flame retardant. It has previously been reported in fish and sediment from Japan (11), and from a Swedish river where textile industries are located (12). HBCD was also detected in two high volume air samples collected in Sweden (13).

In this study the temporal variations of BDE47, 2-methoxy-2',4,4',6-tetrabromodiphenyl ether (MeO-BDE47) and HBCD in biota were investigated. The samples were part of the Swedish National Environmental Monitoring Program for contaminant analyses.

Material and Methods

Muscle tissue of pike *(Esox lucius)* from Lake Bolmen and roach *(Rutilus rutilus)* from Lake Krankesjön as well as homogenates of guillemot eggs *(Uria aalge*) from Stora Karlsö in the Baltic Proper, were analysed (Fig 1). Lake Bolmen is a mesotrophic lake situated in woodland with minor agricultural and industrial activities. Lake Krankesjön is eutrophied, located in an agricultural region. The pike and guillemot eggs have previously been analysed for PCB, DDT and PCDD/F within the Swedish environmental monitoring program (14,15). The guillemot eggs have also been analysed for PBDE (2). Pike extracts from 1974, 1981, 1987 and 1991-1997 were analysed
individually (9-11 ind./year). The other pike samples were pooled samples of 6-10 individuals. The analyses of guillemot eggs were performed on pooled samples (1969-1988, 1990, 1992) and

individually (1976, 1989, and 1992-1997, 10 ind./year). The roach samples were analysed individually (8 ind./year) from 1980, 1983, 1985, 1988, 1990, 1992, 1994 and 1996. The extraction and lipid determination of all samples was performed according to (16). The samples were analysed by GC/MS (ECNI) monitoring the bromide ions (12).

Results and Discussion

The concentrations of BDE47 in pike increase significantly from 1967 to the early 1980s (Fig. 2a). From 1984 to 1997, there are large variations in the mean concentrations between years as well as between individuals within each year and the trend is more or less stagnant. The three major congeners normally found in biota are BDE47, 99 and100.

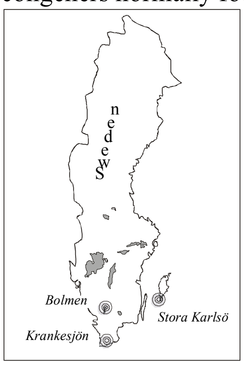

Figure 1. Location of sampling sites.

In pike, the mean concentration ratio of BDE47 to BDE99 was 1.8.

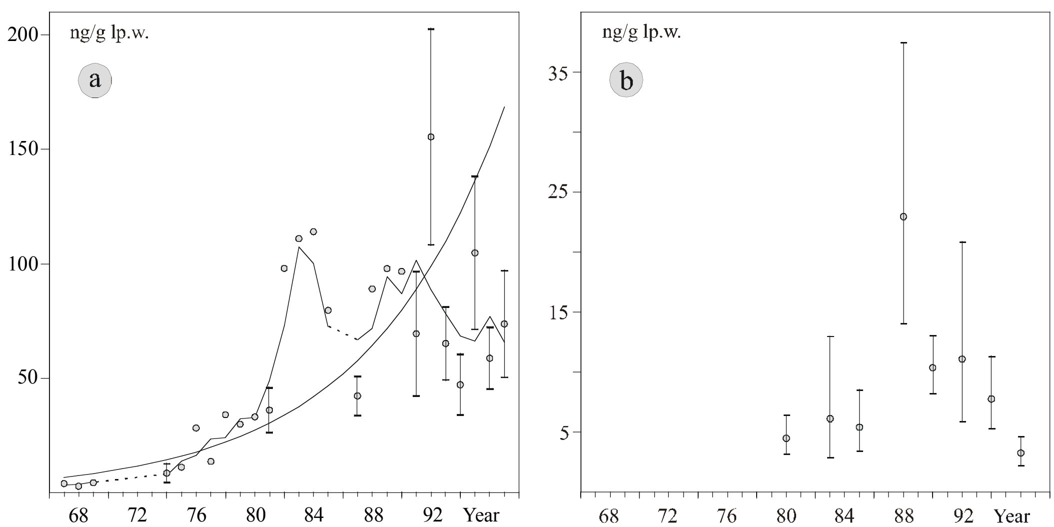

Figure 2. Temporal trends of BDE47 in a) pike from Lake Bolmen and b) roach from Lake Krankesjön. The line represents a three-point running mean smoother ($p<0.001$) and the dots the arithmetic means (pike) or the geometric means (roach) with 95 % confidence intervals indicated. The curve represents the log-linear regression line ($p<0.001$).

The concentrations of BDE47 in roach were generally lower than in pike (Fig. 2b). As in pike, the variation between years as well as within a given year is considerable (Fig. 2b). No significant trend was detected. The maximum concentrations appeared in 1988.
The congener profile in roach was somewhat different to that observed in pike. BDE47 dominated largely over BDE99, which was, with few exceptions, below the quantification limit. This congener profile is often observed in biological samples (2,3) except in terrestrial species and in some freshwater fish from Sweden (pike from Lake Bolmen included), where the ratio of BDE47 and 99 more resembles the technical product Bromkal 70-5DE (2).
For MeO-BDE47 in pike, the temporal trend shows significantly decreasing concentrations (Fig. 3a). The initial concentrations of MeO-BDE47 exceed the highest BDE47 levels by a factor of three (490 ng/g lpw). In the 1990s, although the concentrations show variations, there are indications of a reversed trend. Assuming biogenic sources of MeO-BDE one may expect a corresponding negative trend for the primary production during the time period. However, there is a weak, but opposite eutrophication trend in this lake from 1966 to 1997 (17). Furthermore, MeO-BDE47 was not detected in the roach samples, although Lake Krankesjön is eutrophied.

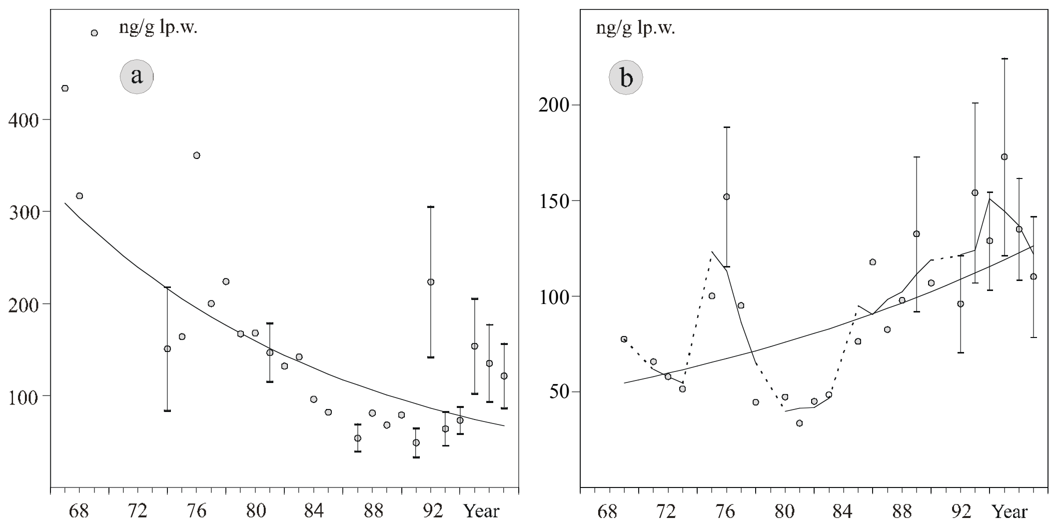

Figure 3. Temporal trends of a) MeO-BDE47 in pike from Lake Bolmen and b) HBCD in guillemot eggs from Stora Karlsö. The line represents a three-point running mean smoother ($p<0.002$) and the dots the arithmetic means with 95 % confidence intervals indicated. The curve represents the log-linear regression line ($p<0.001$ for MeO-BDE47 and $p<0.005$ for HBCD).

The concentrations of HBCD in guillemot eggs show a significant increase over the entire time period (Fig. 3b). Traces of HBCD were also detected in both pike and roach muscle but the concentrations were below the quantification limit so no time trends could be determined. The higher levels of HBCD in guillemot eggs may be due to biomagnification.

Brominated flame retardants are not produced in Sweden but are imported in finished products and goods. The annual amounts of penta-, octa-, decabrominated BDE products imported to Sweden between 1993-1997 were 40, 90, 20, 79, 123 tons for each respective year (18). The corresponding figures for HBCD were 50, 80, 90, 83 and 125 tons. PBDE have been found on air particulates in rooms containing computers and electrical equipment (19). The different appearance of the time trend of PBDE in human milk compared to trends reported in biota, may reflect differences in exposure routes. Unlike wildlife, humans may also be exposed through the increasing prevalence of flame-retarded products in the home and workplace.

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