SPATIAL AND TEMPORAL TRENDS AND PATTERNS OF PBDE:S AND HBCDD IN FISH FROM SWEDISH FRESH WATER AND MARIN ENVIRONMENT

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Introduction

One of the first findings of polybrominated diphenyl ethers (PBDEs) in environmental samples occurred in 1981. It was tri- to hexa-BDEs that were detected in fish from the Swedish river Viskan[1]. PBDEs have since then even been found in biological samples from remote areas[2]. Penta- and okta-BDEs were banned within the EU in 2004 and this drastically lowered the use of these substances in Europe. Hexabromocyklododecane (HBCDD) on the other hand is still in use, but it is nominated to be included in the Stockholm Convention. This study shows examples of temporal trends and spatial patterns of PBDEs and HBCDD in marine and freshwater fish.

Materials and methods

Fish of different species are annually sampled within the Swedish National Monitoring programmes, from sites without known local sources of contaminants, both in marine and freshwater. Results from a study of contaminants in perch, performed in cooperation with the costal county boards in northern Sweden in 2009, is also included in the analysis as well as results from a study of contaminants in arctic char from L. Vättern. The sampling sites within these studies are selected for examination of local differences and are not necessarily unaffected by local sources. The collection and sample preparation, both within these studies follows internationally agreed guidelines[3, 4]. The fish samples were analyzed for BDE-47, BDE-99, BDE-100, BDE-153, BDE-154 and HBCDD.

The samples were extracted with a mixture of n-hexane and acetone and the lipid content was determined gravimetrically. The lipids were re-dissolved in n-hexane and treated with concentrated sulphuric acid according to Jensen *et al.* [5]. The samples were analysed by GC connected to a mass spectrometer operating in the electron capture negative ionization mode. The bromine ions (m/z 79 and 81) were monitored. [6]

Principal component analysis (PCA) was performed on the proportions of single PBDE-concentrations to the sum of PBDEs to study differences in PBDE pattern. The percentage of each PBDE-congener relative to the sum was log-transformed prior to the PCA analysis. Before the PCA-scores were plotted they were centered and scaled to 100%. The eigenvector loadings were added to the PCA plot as vectors (biplot). Log-linear analysis was carried out to show possible significant temporal trends.

Results and discussion:

Temporal trends:

Since the beginning of 1980s, the concentrations of BDE-47, 99 and 100 in cod from southern Baltic Proper show decreasing trends of 6-11% per year, illustrated by BDE-47 in Fig. 1. Earlier studies have reported similar results with decreasing trends of PBDEs since the mid 1980s for pike in a southern Swedish lake[7] and in beginning of 1990s in guillemot egg from the Baltic Proper[8]. During the last decade, these substances also show decreasing concentrations in herring along the Swedish coast, and at a higher rate at the Swedish west coast. The concentrations BDE-153 and 154 do not seem to decrease over time in the Baltic Sea Fig. 1 but at the Swedish west coast concentration of these congeners in herring show a downward trend (not shown). The concentrations in arctic char from L. Abiskojaure in the northern part of Sweden show a somewhat different development over time. The analysed PBDE congeners show similar trends with increasing concentrations since the beginning of 80s with the highest concentrations in the beginning of 2000s, except for a high value in 1989. HBCDD show an increasing trend over time, this is in coherence with the results reported by Sellström *et al.*[8] in guillemot egg. In L. Abiskojaure the concentrations of HBCDD are close to, or at levels of quantification.

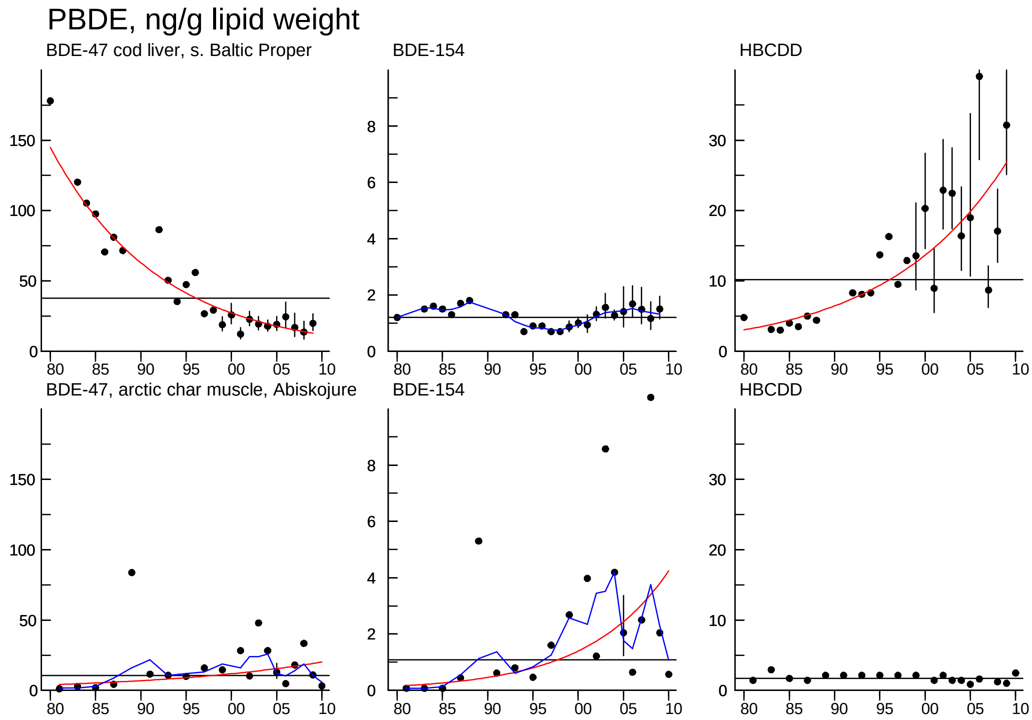

Figure 1. Log-linear trends of BDE-47, BDE-154 and HBCDD (ng/g lipid weight) in cod liver from southern Baltic Proper and in arctic char muscle from L. Abiskojaure in the arctic region (time series starting in 1980 and 1981 respectively). The red line shows a significant trend over the whole time period, the blue line a non linear trend and the black line the mean concentration over the whole period.

The ratios between BDE-47 and BDE-100 in cod from the southern Baltic Proper and in arctic char from L. Abiskojaure shown in Fig. 2, are decreasing over the whole time period for both the freshwater and the marine sampling site. This may be expected due to higher degree of degradation in lower brominated BDEs.

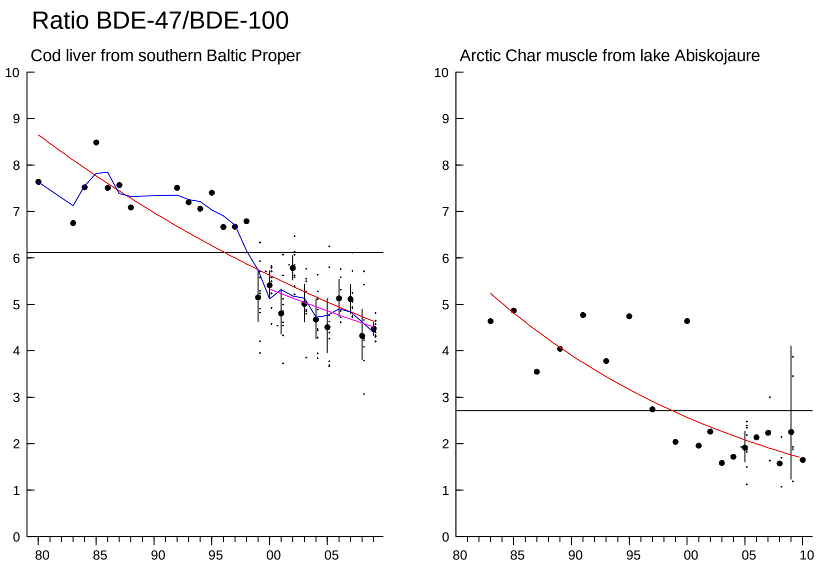

Figure 2. Log-linear trends of the BDE-47/BDE-100 ratio in cod liver from southern Baltic Proper and in arctic char muscle from L. Abiskojaure in the arctic region (time series starting in 1980 and 1981 respectively). The red line shows a significant trend over the whole time period, the blue line a non linear trend and the black line the mean ratio over the whole period.

The various lakes and stations along the coast showed a high between-site variation in PBDE- and HBCDD-concentrations, exemplified for BDE-47 in Fig. 3. The concentrations seem to agree with potential sources e.g. higher population density and textile production and lower concentration in remote lakes in or close to the mountain region in north-west of Sweden. Perch along the north Swedish coast show generally higher concentrations of PBDEs than perch from lakes at the same latitude.

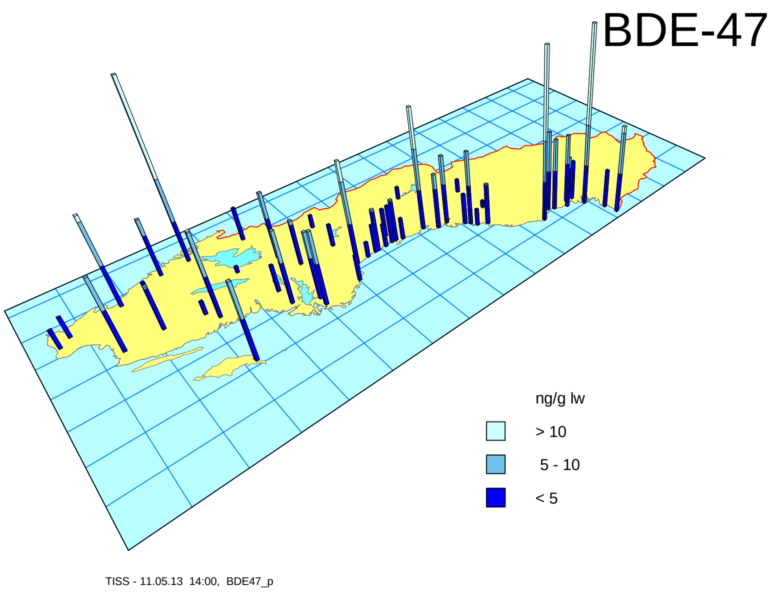

Figure 3. Spatial variation in concentration (ng/g lipid weight) of BDE-47 in marine and freshwater perch muscle. Arithmetic mean values 2007-2009 for freshwater and values from 2009 for the marine sites.

PCA showed that differences in HBCDD explain the largest variation between the various sites (not shown). The relative concentrations of various PBDE congeners show a different pattern in fresh water perch compared to coastal perch with relatively higher concentrations of BDE-153 in fresh water (Fig. 4A). Interesting patterns were also observed in different lakes of Arctic char. The relative concentrations of various PBDE congeners in arctic char show different patterns between lakes. Samples from Lake Vättern, the second largest lake in Sweden, where the highest concentrations are found, show a higher relative concentration of BDE-154 compared to the other lakes (Fig. 4B).

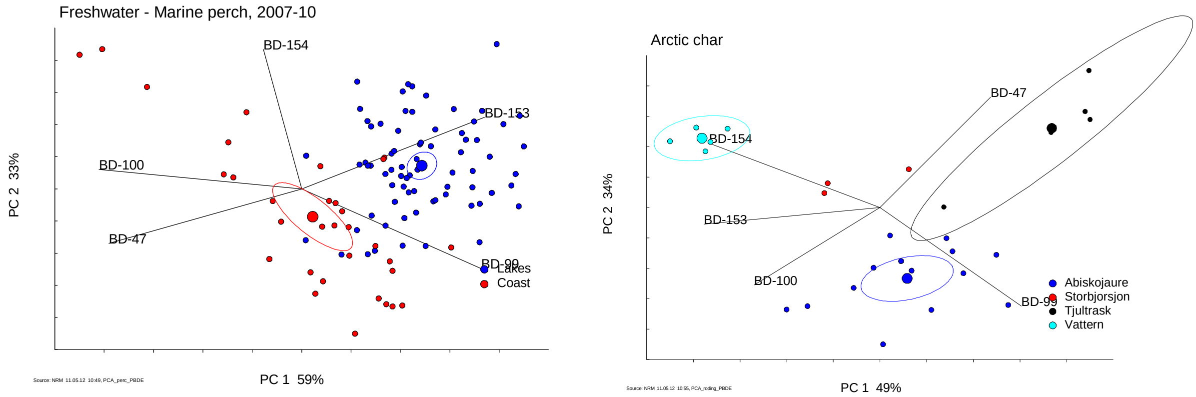

Figure 4 A) PCA analysis, biplot and Hotelling's 95% confidence ellipses for centre of gravity for the groups. The figure on the left show marine and freshwater perch and the figure on the right show arctic char and pike from the northern parts of Sweden.

B) PCA analysis, biplot and Hotelling's 95% confidence ellipses for centre of gravity for various lakes with arctic char samples

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