Altered CB congener composition in Baltic herring indicates ongoing pollution

Anders Bignert, Mats Olsson, Lillemor Asplund*, Ulla Eriksson* and Lisbeth Häggberg*

Contaminant Research Group, Swedish Museum of Natural History, Box 50007
SE-104 05 Stockholm, Sweden

*Laboratory for Analytical Environmental Chemistry, Institute of Applied Environmental Research
Stockholm University. SE-106 91 Stockholm, Sweden

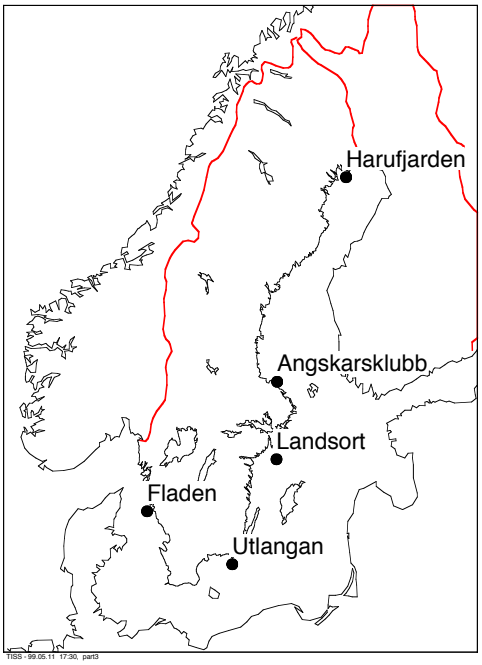

Figure 1. Five sampling sites where herring is sampled each year

Introduction

Since the middle of the seventies the concentrations of PCB in various biota samples from the entire Baltic has decreased significantly by about 85% (1). However, during last 10 years this decrease seems to have ceased in the southern part, the Baltic Proper. In the Gulf of Bothnia and at the Swedish West Coast the concentrations continue to decrease. An earlier study based on temporal variations in relative concentrations of various CBs in Baltic herring during the last 10 years indicated a more rapid decrease over time in concentrations for less chlorinated congeners than for CB-153 (2). We discussed the importance of positions of the chlorines in the various CBs with respect to tentative degradation processes such as degradation by OH-radicals, UV light and biological degradation and stressed the probable importance of atmospheric degradation. In the present study the time trend series on herring in Swedish marine areas are used to study the rate of decrease and the change in the ratio CB-118/CB-153 during 1988 and 1997 during the most recent time period.

Material and methods

Within the Swedish Environmental Contaminant Monitoring Programme samples of herring are collected and analysed annually at five sampling sites during the fall (Fig. 1) since the beginning of the 1980s and at two of these sites sampling in spring has also been running since the early 1970s. The monitoring program follows a guideline specifying used methods. As far as possible, the sampling locations have been selected to represent a locally unpolluted environment in various parts of Sweden so that the data will represent the background condition of the studied time

period. Ten to twenty specimens of young herring have been analysed individually and the annual geometric mean values have been calculated. Methods used for sampling, preparation and chemical analysis have been presented elsewhere as well as a method to allow comparison of total PCB concentrations using both capillary and packed column gas chromatography (1). Since 1988 capillary column has been used providing congener specific analysis.

On basis of the geometric mean values, log-linear regression analysis, have been applied for the studied period. The calculated annual change in concentrations (percent) has been calculated from the regression line for both the entire period and the last 10-year period (Fig. 2). Although significant decreases over time is achieved by using a log-linear regression line, this model gives a rather poor description of the development at the end of several time series, which seems to contain non-linear trend components. Hence, a simple 3-point running mean smoother fitted to the annual geometric mean values was applied and was found to be more appropriate (Fig. 4). The significance of this line was tested by means of an Analysis of Variance where the variance explained by the smoother and by the regression line is compared with the total variance (3).

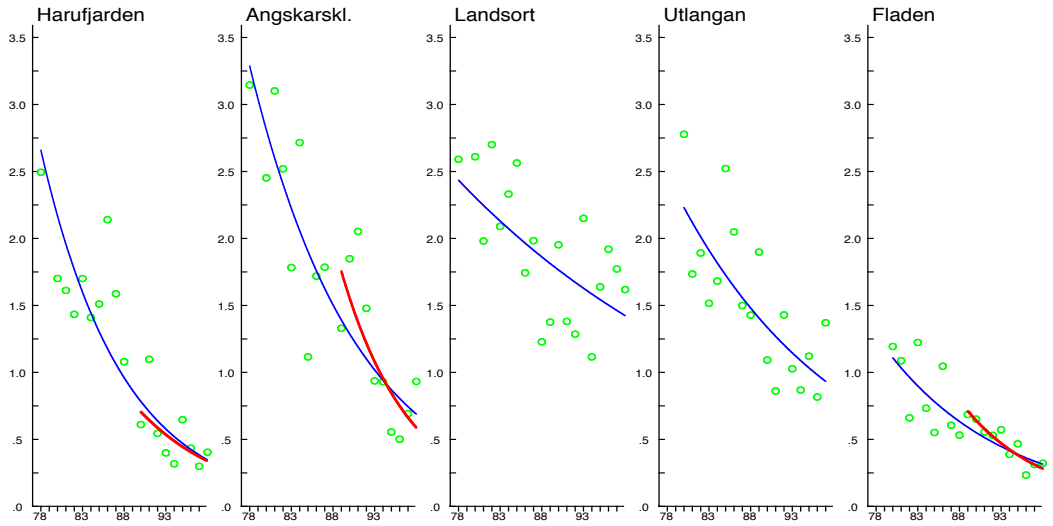

Figure 2. Total PCB in ug/g fat from herring muscle tissue from various sites along the Swedish coast during the period 1978/80 – 1997/98. A solid line indicates a significant ($P<0.05$) decreasing log-linear trend for the entire period. If significant ($P< 0.05$), a second line is plotted indicating a decreasing trend for the last ten years.

Results and Discussion

The time trends in concentrations of total PCB in herring samples collected during the fall are presented in Fig 2. After years of decreasing concentrations of PCB during the s70s and the 80s, the decrease seems to have ceased in the most recent 10-year period at the two locations representing the Baltic Proper (Landsort and Utlängan). However, it continuous both at the southern sampling site at the Swedish West Coast (Fladen) and in the two sampling sites in the north in the Gulf of Bothnia Harufjärden and Ängskärsklubb). The temporal trend for

concentrations of CB-153 during the last 10 years is presented for herring collected during the fall (Fig. 3). CB-153 is a major congener in herring and is regarded as highly persistent. In the two series from the Baltic proper the concentrations of CB-153 are constant over the time period and a similar condition is also indicated in southern Gulf of Bothnia. At the Swedish West Coast and in the most remote northern sampling sites the concentrations continuous to decrease.

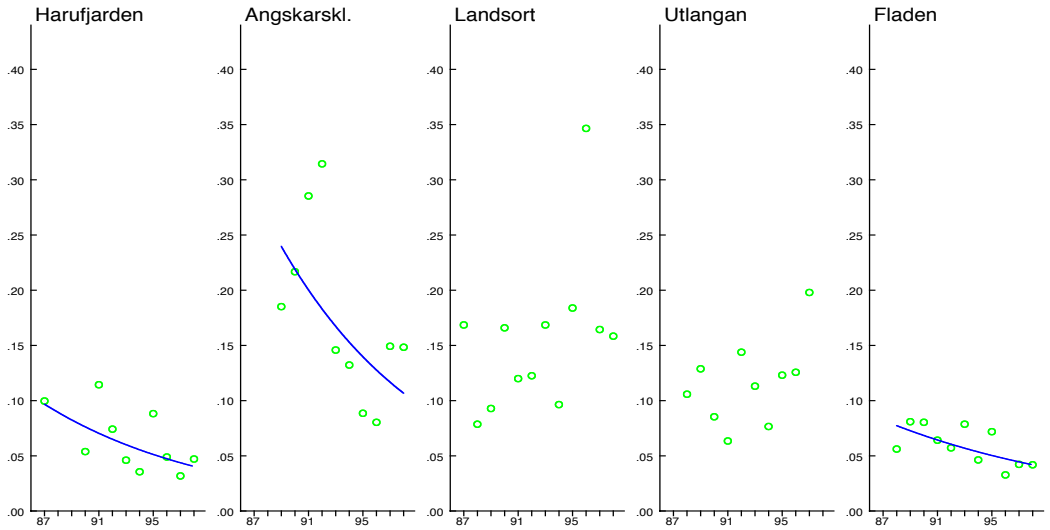

Figure 3. CB-153 in ug/g fat from herring muscle tissue from various sites along the Swedish coast during 1987/89 – 1997/98. A solid line indicates a significant ($P<0.05$) decreasing log-linear trend.

According to the model for global transport of semi-volatile compounds (Global chromatography) by Wania and Mackay (4, 5), environmental concentrations of heavier and less volatile congeners like CB-153 should decrease more slowly in cold areas than in warmer and they should decrease more slowly than more volatile congeners. In our trends the decrease seem faster both in the colder northern waters of the Baltic and in the warmer waters of the West Coast which indicate that temperature can not explain the altered trend.

Of congeners analysed (CB-28, -52, -101, -118, -138, -153 and CB-180) we have calculated the annual ratio for the various congeners and CB-153 to investigate whether lighter more volatile congeners decrease faster than the more heavy and in Fig. 4 the ratio CB118/CB-153 is presented. We have difficulties with CB-28 since the concentrations of these compounds in some of the samples are below the detection level of the method used making the time trends of these congeners fairly uncertain in some of the investigated locations.

If global chromatography explains the altered congener composition the more volatile congener would evaporate faster from an area than the less volatile CB-153 and the ratio CB-118/CB-153 would decrease over time. However, as was pointed out in our earlier report the lower number of chlorine will also make the congener more susceptible to environmental degradation (2). A faster decrease of CBs with lower numbers of chlorines (exemplified by CB-118/CB-153) is also true for the entire period in our herring series but the ratios increase or stabilise during the last 5 years.

This is found in all series except the herring samples from Utlängan (Fig. 4). Interestingly, also the series of spring collected herring from both Ängskärsklubb and Utlängan show a stabilised or slightly increased ratio CB-118/CB-153. A similar change in the development of the ratios CB-52/CB-153, CB-101/CB-153 and CB-138/CB-153 is also found during the most recent time period. Thus, the increasing ratios or stabilised ratios does not indicate that global chromatography explains that total PCB concentrations fail to decrease in recent time. Neither it seems probable that continuous environmental degradation processes by OH-radicals and UV light in the atmosphere or biological degradation in the biosphere would give a sudden change in the ratio between various CB-congeners. The most probably explanation is that new PCB is discharged to the Baltic environment. This could either be from PCB recently produced somewhere by the industry or from old PCB memories in the technosphere.

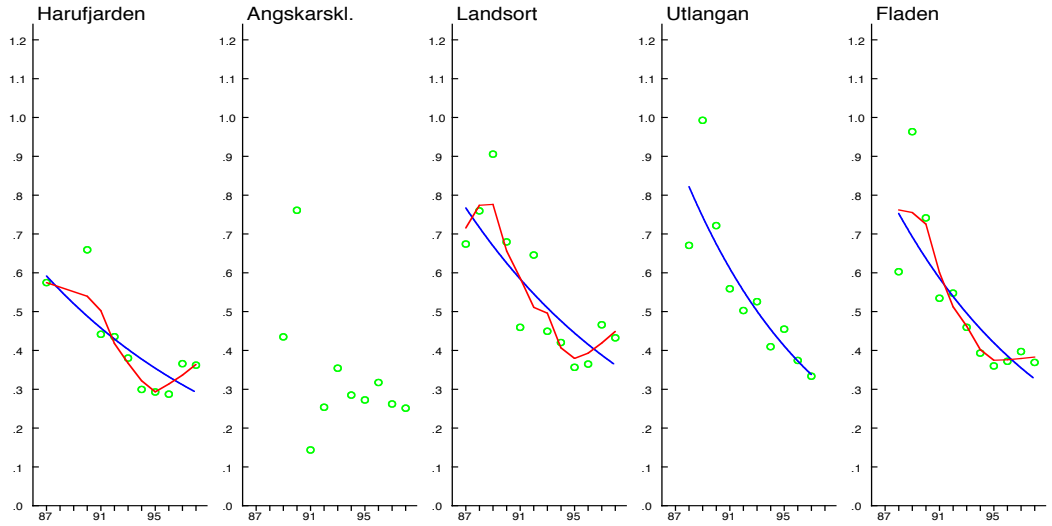

Figure 4. The ratio of CB-118/CB-153 in herring muscle from various sites along the Swedish coast during 1978/80 – 1997/98. A solid line indicates a significant ($P<0.05$) decreasing log-linear trend. The smoothed line at Harufjärden, Landsort and Fladen indicates a significant ($P< 0.05$) non-linear trend showing a stagnant or even increasing pattern at the end of the three time series.

Acknowledgement

This study was financed by the Swedish EPA.

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