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Research Article

Decreasing trend of persistent organic pollutants (POPs) in herring from the southern Baltic Sea

GRAŻYNA SAPOTA

[1]*Institute of Meteorology and Water Management, Maritime Branch*
ul. Waszyngtona 42, 81-342 Gdynia, Poland
✉*Grazyna.Sapota@imgw.pl*

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Abstract

The aim of this work was to examine the level of POPs (DDT and its metabolites, isomers of HCH, HCB and PCBs) in pelagic herring (*Clupea harengus*) caught in the southern Baltic Sea once a year during the period 1998-2003. Historical time trends of POPs from the 1970s to the year 1998 were calculated on the basis of the HELCOM Database. The measurements executed within Integrated Monitoring Programme of the Baltic Sea Environment HELCOM/COMBINE confirm that declines in the levels of PCBs and DDT have occurred in some fish from the Baltic Sea over the past 30 years. In herring muscle PCBs have decreased to about 15% of levels of the early 1970s and DDT to 5% of 1970s levels.

INTRODUCTION

Persistent organic pollutants (POPs) are a group of chemicals which are very resistant to natural breakdown processes and therefore extremely stable and long-lived. POPs are not only persistent in the environment but many are also highly toxic and bioaccumulate in the tissues of animals and humans. Most do not occur in nature but are synthetic chemicals released as a result of anthropogenic activities. A vast amount of POPs have been released into the environment and due to long-distance transport by air POPs have become widespread pollutants and now represent a global contamination problem. The marine environment of the Baltic Sea, a semi-enclosed coastal sea with a water residence time of approximately 20 years (Reiheimer 1995), is contaminated with many POPs. There have been substantial inputs of POPs into the Baltic, from numerous sources, over the past 50 years. The sources include industrial discharges, such as the organochlorines in effluent from pulp and paper mills, runoff from farmland and dumped wastes. Currently, the use of DDT is banned for this area, but it is still used by tropical and sub-tropical countries in great amounts. The long-range transport of DDT from lower to higher latitudes is supported by the general atmospheric circulation pattern and by the temperature gradients, which facilitate evaporation in the tropics, and condensation and precipitation in the colder regions (Bignert *et al*. 1998, HELCOM 1996, Koziol and Pudykiewicz 2001). The measurements executed within the Integrated Monitoring Programme of the Baltic Sea Environment HELCOM/COMBINE confirm that declines in the levels of PCBs and DDT have occurred in some fish from the Baltic Sea over the past 30 years. Now it is very important to answer the question: is it possible and when to reduce the level of POP contamination to the concentrations *e.g*. in the North Sea?

MATERIAL AND METHODS

Study Site Description

The herring samples were taken once a year in September from Władysławowo fishing ground (southern Baltic Proper) (Fig. 1) during the period 1998-2003. The two or three year old females (n = 20) were selected for further analysis (HELCOM 1978, 1983, 1988, 1998).

Capillary Gas Chromatography

Freeze-dried fish muscle was Soxhlet-extracted in a mixture of hexane and acetone (1:2 vol.). Prior to the extraction internal standards (CB 65 and CB 207) were added to the solvent (Dannenberger and Lertz 1996). The extracts were purified on a column containing two layers (with K_2CO_3 and H_2SO_4) of silica gel, eluted with dichloromethane/hexane (5:95). The elute was then evaporated

and dissolved in isooctane and analysed by capillary gas chromatography with electron capture detector (GC – ECD) (Bremle *et al*. 1995, Sapota 1997, 2002). Multilevel calibration was applied for quantification. The concentrations of seven PCBs (IUPAC No 28, 52, 101, 118, 138, 156, 180), DDT and its metabolites, HCH isomers (α, β, γ) and HCB were determined in muscle tissue of fish. The values were expressed in ng g^{-1} on a lipid weight (l.w.) basis. The QUASIMEME test material was used as a reference material. The recovery value varied between 71-80% of HCH isomers and HCB, 87-94% of DDT and its metabolites, and 86-93% of PCB congeners. Limits of detection (LoD) were calculated as a concentration of analysed substances in carrier gas, which give a signal twice as large as noise level (Rödel and Wölm 1982). LoD of HCH isomers and HCB was 10^{-4} ng s^{-1}. LoD of DDT and its metabolites and PCBs was 10^{-3} ng s^{-1}. In the analysed material, only some concentrations of α-HCH were below LoD (in 1998 – 4 results; in 1999 – 5 results; in 2002 – 9 results).

Fig. 1. Sampling location.

The results were calculated using commercial software EXCEL and STATISTICA. The data from the HELCOM Database used for calculation were from the same region of the Baltic Sea as in the own analysis. The month of sampling, sex, age, number of fish and methods used were the same for all analysis and exactly defined in monitoring manuals (HELCOM 1978, 1983, 1988, 1998).

RESULTS AND DISCUSSION

The temporal trend for ΣDDT in herring was decreasing over the entire period. The applied time series analysis (exponential smoothing) shows a significant damping effect ($\phi = 0.933$) of DDT in herring muscle from the southern Baltic Proper (Fig. 2).

The longest time series, going back to the late 1960s and early1970s, reveals an annual decrease of about 7% in herring from the southern Bothnian Sea and of 11-12% in herring from the southern Baltic Proper (Olsson *et al*.

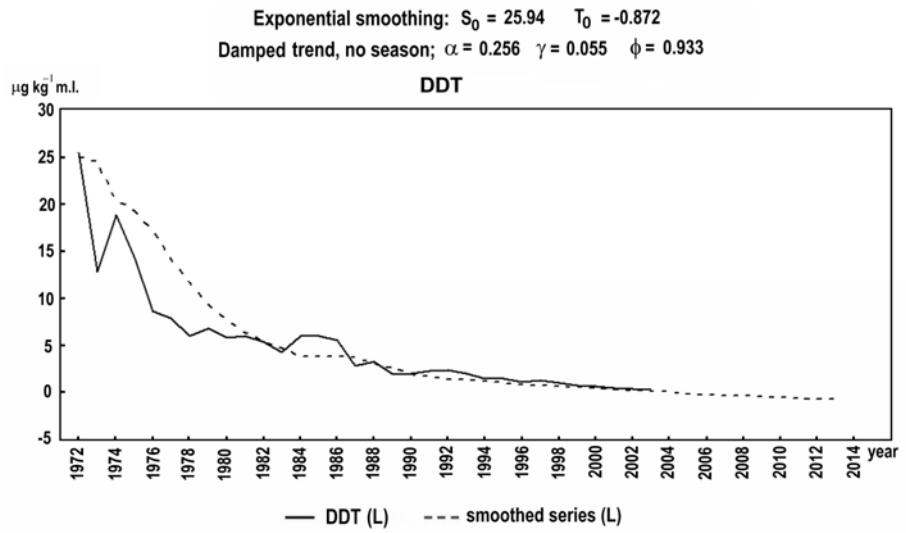

Fig. 2. The temporal trends of ΣDDT concentrations in the muscle tissue of herring from the southern Baltic Proper.

2002). All time series starting in the early 1980s or later show a similar decrease in the range of 9-14% in the Bothnian Bay and Bothnian Sea and 5-11% in the Baltic Proper. The decrease in concentration is statistically significant during the last 10 years for pelagic biota, like herring. The ΣDDT concentration also decreases at a similar rate in long-term monitoring studies going back to the late 1960s in Swedish fresh waters from the south up to the northern-most Subarctic regions of Sweden (Olsson *et al*. 2002). This indicates that decreases in atmospheric deposition probably also play an important role in explaining the processes in the Baltic (Bignert *et al*. 1998, Olsson and Reutergårdh 1986). Concentrations of DDT and its metabolites in herring caught in the Polish part of the southern Baltic Proper over the period 1998-2002 consequently showed a downward trend. However, the DDT concentrations in the Baltic Sea are more than five times higher than in the open ocean (HELCOM 1996).

The exponential smoothing applied to the time series analysis shows a fairly low damping effect ($\phi = 0.633$) and initial trend (T_0) of HCH in herring muscle from the southern Baltic Proper (Fig. 3). The annual decrease in α-HCH concentration ranges from 12 to 22 % in herring during the 1980s and 1990s. With lindane the annual decrease is more varied, ranging from 6 to 8% for herring from the Kattegat and 8 to 24% for herring from the Bothnian Bay and the Baltic Proper (Olsson *et al*. 2002).

The used time series analysis (exponential smoothing) shows the rather low

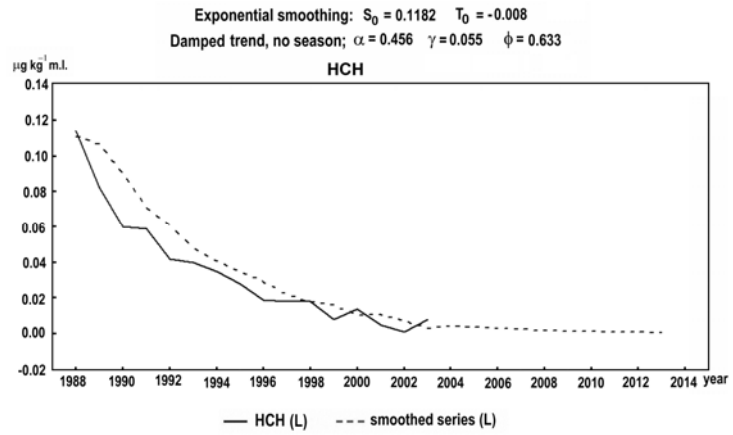

Fig. 3. The temporal trends of α-HCH concentrations in the muscle tissue of herring from the southern Baltic Proper.

damping effect (ϕ = 0.536) of HCB in herring muscle from the southern Baltic Proper (Fig. 4). This is probably an effect of fluctuation in HCB content. The annual rates at which the concentration of HCB in the Baltic Sea is decreasing range from 6 to 18% and the decrease is generally lower in the southern Baltic Proper (Olsson *et al*. 2002).

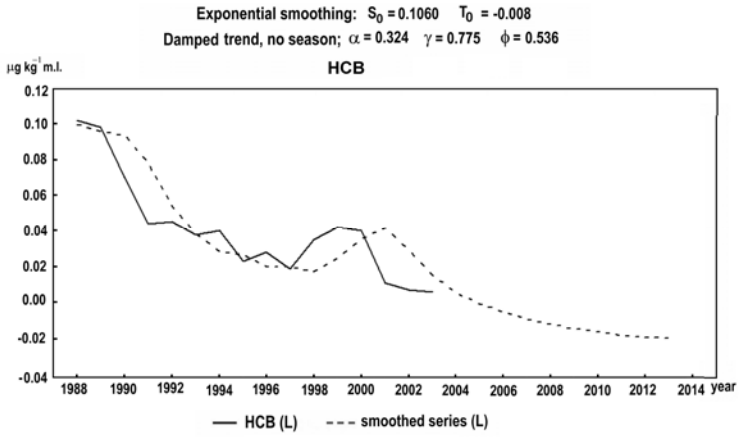

Fig. 4. The temporal trends of HCB concentrations in the muscle tissue of herring from the southern Baltic Proper.

PCB concentrations in biota have been decreasing over the past 30 years. The exponential smoothing used for the calculation shows the rather low damping

effect (ϕ = 0.610) of PCBs in herring muscle from the southern Baltic Proper (Fig. 5). The longest time series, going back to the late 1960s and early 1970s, thus reveals an annual decrease of about 4% in herring from the southern

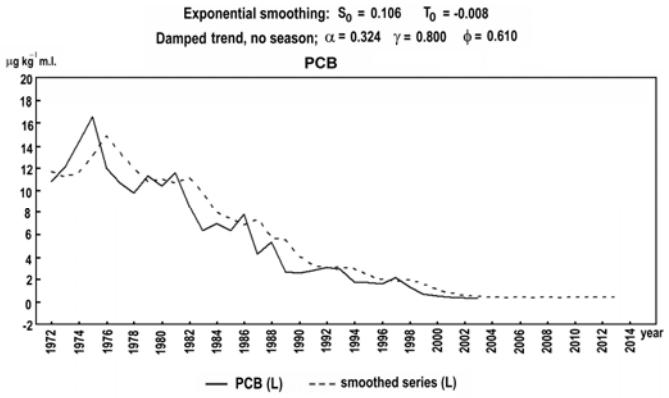

Fig. 5. The temporal trends of PCB concentrations in the muscle tissue of herring from the southern Baltic Proper.

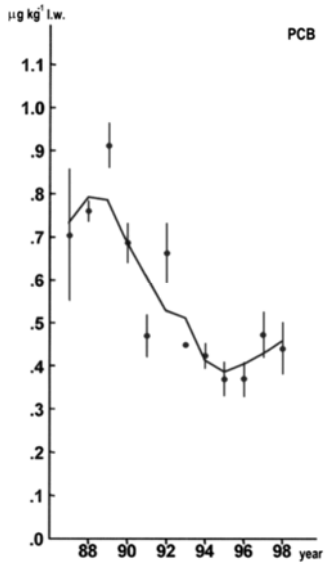

Fig. 6. Statistical analysis using the smoother technique reveals a significant increase in the less persistent PCB congener in herring muscle in the Baltic Proper (Olsson *et al.* 2002).

Bothnian Sea and about 9% in herring from the southern Baltic Proper. Shorter time series for the herring, starting in the early 1980s or later, also reveal an annual decrease ranging from about 10% in the Bothnian Bay to only about 3% in the Baltic Proper (Olsson *et al.* 2002). The relative amount of less chlorinated and less persistent PCB congeners increased in Baltic herring samples during 1990s, thus indicating recent discharge of less persistent and more volatile congeners to the Baltic environment (Bignert *et al.* 1999, Olsson *et al.* 2002) (Fig. 6).

In herring from the Polish part of the southern Baltic Proper no significant changes in concentrations of PCBs were observed during the period 1998-2002. Despite a decline,

the PCB content in herring muscle samples from the Baltic Proper is about twice that in the Bothnian Bay and still several times higher than in similar samples from the open North Sea and open ocean (HELCOM 1996). The answer to the question: "When will a total reduction of contaminants be possible?" is very difficult. We should take into account that the transport of POPs to the Baltic Sea is still present. At present a really significant damped trend is visible only for DDT and its metabolites; other analysed POPs indicate trends decreasing at a rather low rate.

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