



Mass budgets and contribution of individual sources and sinks to the abundance of γ -HCH, α -HCH and PCB 153 in the North Sea

Tatjana Ilyina^{a,*}, Gerhard Lammel^{b,c}, Thomas Pohlmann^a

^aCentre for Marine and Atmospheric Sciences (ZMAW), Institute of Oceanography, University of Hamburg, Bundesstr. 53, 20146 Hamburg, Germany

^bZMAW, Max Planck Institute for Meteorology, Bundesstr. 53, 20146 Hamburg, Germany

^cMasaryk University, Research Centre for Environmental Chemistry and Ecotoxicology, Kamenice 3, 62500 Brno, Czech Republic

ARTICLE INFO

Article history:

Received 4 December 2007

Received in revised form 11 March 2008

Accepted 4 April 2008

Available online 4 June 2008

Keywords:

Modeling

Fate

Transport

Marine environment

FANTOM

ABSTRACT

Mass budgets of hexachlorocyclohexanes (α -HCH and γ -HCH) and a polychlorinated biphenyl (PCB 153) for 1995–2001 were calculated based on model simulations and observations for the North Sea as a whole and the German Bight, a coastal shallow subregion. For the North Sea the air–sea fluxes of the three pollutants were net depositional and dominated by local sources (γ -HCH and PCB 153) or atmospheric deposition (α -HCH). The air–sea fluxes were net volatilizational in the German Bight. Unlike HCH, PCB 153 does not show a downward trend in the North Sea marine environment during the study period. Due to its physicochemical properties it is expected to readily enter the food chains. Model results suggest that during studied period, the North Sea was a sink for PCB 153 and a source of HCHs for the outer world.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

The fate and behavior of persistent organic pollutants (POPs), e.g. hexachlorocyclohexanes (HCHs) and polychlorinated biphenyls (PCBs) in the environment has attracted considerable scientific and political interest arising from concern of human and wildlife exposure to these chemicals and their discovery in pristine environments far from the sources. POPs are ubiquitously distributed in the global oceans as a consequence of atmospheric deposition and river inputs (e.g. Tanabe et al., 1983; Iwata et al., 1993; Bidleman et al., 1995; Lakaschus et al., 2002). The study of processes and pathways that POPs undergo in the aquatic environment is particularly important as the hydrosphere is where many POPs resist degradation (hence, accumulate) and are more prone to bioaccumulation (hence, enter the food chains). Oceans can be considered as a global reservoir and ultimate sink compartment of many POPs (e.g. Iwata et al., 1993). However, in response to long-term uptake of POPs coastal and even open ocean water bodies may turn into net volatilizational, i.e. act as sources to the atmosphere, seasonally or permanently (Bidleman et al., 1995; Bruhn et al., 2003). In shallow seas like the North Sea the sinking particles carrying POPs down to the bottom sediments may enter

the water column via resuspension. Therefore, even when primary pollutant sources are reduced, remobilization from water bodies could act as a secondary source for the atmosphere.

Mass budgets of POPs and POPs-like chemicals in the marine environment are required to evaluate both scientific knowledge and chemicals management options. For a south-eastern part of the North Sea (the German Bight), such budget calculations were already performed for several POPs based on measurements (Hühnerfuss et al., 1997). However, measurements of most POPs in seawater are too sparse to allow a comprehensive assessment of their pathways and fluxes in and out of the North Sea or its subregions. Furthermore, mass budgets of sea areas based on field data are uncertain as the variability of the concentrations in both time and space can be high in particular in shelf seas and coastal areas (e.g., Bruhn et al., 2003). A multimedia mass balance model was used to budget the fate of the sum of 6 PCBs (Wania et al., 2001) and HCH (Breivik and Wania, 2002) in the Baltic Sea based on constant water fluxes. Mass budgets of POPs-like contaminants in seas have not been assessed so far with a three-dimensional hydrodynamic model capable to resolve environmental conditions and processes. Many pollutants sources in the North Sea are land-based. Thus, finer spatial resolution of the model can improve the representation of distribution of POPs in the near-coastal areas and their transport with sea currents. For instance, by comparing the results of a meso-scale and a large-scale circulation model Pohlmann (2006), showed that especially in the coastal North Sea along the Dutch and German coast, a meso-scale model better captures the

* Corresponding author. Present address: School of Ocean and Earth Science and Technology, Department of Oceanography, University of Hawaii at Manoa, 1000 Pope Road, Honolulu, HI 96822, USA. Tel.: +1 808 956 3679; fax: +1 808 956 7112.
E-mail address: ilyina@soest.hawaii.edu (T. Ilyina).

observed patterns of temperature and salinity and more accurately quantifies the kinetic energy of residual flow. This study is the first attempt to estimate mass budgets and the contribution of individual key processes to the burdens of organic pollutants using a model with high spatial and temporal resolution. We address α -HCH, γ -HCH and PCB 153 in the North Sea. This choice of substances includes different physicochemical properties, i.e. lipophilicity (PCB) vs. water solubility (HCHs; Table 1), as well as different historical usage and emission trends, i.e. banned in Europe three decades ago (α -HCH, PCB 153) vs. usage restrictions introduced in the 1990s (γ -HCH).

2. Model description

FANTOM (Fate and Transport Ocean Model) is a three-dimensional numerical model designed for simulating the long-term fate of pollutants in the shelf and coastal aquatic environment. A full description of the model, its forcing and model validation is given by Ilyina et al. (2006) and Ilyina (2007). The pollutants can enter the model domain via rivers, adjacent seas or atmospheric deposition. In seawater they are transported with vertical and horizontal ocean currents and large-scale turbulent diffusion calculated by a circulation model (Pohlmann, 1996). A pollutant is either dissolved or bound to particulate organic carbon (POC) present in seawater. POC concentrations in the North Sea were calculated by an ecosystem model (Pätsch et al., 2002). The particle-bound fraction is a function of substance lipophilicity and is subject to gravitational sinking and deposition to the bottom sediments. Particles can also re-suspend back to the water column when sediments are disturbed by ocean currents and waves. Sediment compartment is represented by the upper 2 cm of the sediment bed, a layer where nearly all the benthic biomass is found. Degradation in seawater is described by a first order rate decay coefficient (Table 1). It is assumed to double per 10 K temperature increase. The reversible air–sea gaseous flux of pollutants is determined based on the two-film model in accordance with the fugacity concept formulation (Schwarzenbach et al., 1993). Henry's law constant H_c ($\text{Pa m}^3 \text{mol}^{-1}$) is used to describe the equilibrium partitioning of POPs between air and water. Experimentally derived relationships for H_c are calculated from a temperature dependant equation (Table 1; Paasivirta et al., 1999; Sahsuvar et al., 2003) using intercept b and slope m (K) at sea surface temperature T_w (K):

$$\log H_c = b + \frac{m}{T_w} \quad (1)$$

The dry atmospheric particle deposition flux is calculated as a product of the pollutants particle-bound concentration in air and dry deposition velocity. The wet deposition flux is calculated as a product of the pollutant concentration in precipitation based on measurements, which includes both the dissolved and particulate phases, and the precipitation rate.

Model calculations were initialized by measurements-based POPs seawater concentrations (DOD, 2005). Oceanic boundary conditions were extrapolated from the measured values used for the model initialization. Boundary conditions were based on monitoring data of POPs in air (Fig. 1; EMEP, 2005) and in the rivers (OSPAR, 2002; DOD, 2005; DONAR, 2005). Monthly mean concentrations of POPs in air and rain available from the few coastal stations (i.e. for PCB 153 only from Lista, for γ -HCH and α -HCH also from Westerland and Kollumerwaard) were interpolated on the entire model grid. River loads were calculated as a product of the daily fresh water discharge and the concentration of POPs at the last tidal gauge station of each river (Fig. 1). Measurements in the rivers were available as annual (for the British rivers), monthly (for the rivers Ems and Weser) or weekly and bi-weekly (for the other continental rivers) mean concentrations. Note that the seasonal and spatial variability of the atmospheric deposition fluxes are uncertain as only precipitation rates were available in gridded form. Pollutant concentrations in air and precipitation (Fig. 1) were only available at a few coastal monitoring stations and were extrapolated to the entire model domain (Ilyina et al., 2006). As air pollutants' concentrations show no or negative spatial trend from coastal areas to the open sea, the pollutant deposition fluxes might be somewhat overestimated.

The model was applied to the southern North Sea, a shallow region with the mean depth of 50 m and a maximum depth of 160 m (Fig. 2). The horizontal resolution of the model is 1.5' to 2.5' corresponding to 2.5–3 km. The model has 21 vertical layers of varying depth. The simulation period was from July 1995 to December 2001.

Mass budgets of γ -HCH, α -HCH and PCB 153 calculated by FANTOM include exchange fluxes between the air and seawater as well as between seawater and the upper sediment and the sinks and sources to the seawater burden. These calculations were performed for two regions further on named as the North Sea (entire model domain, i.e. south of 57 °N) and the German Bight (northern border at 55 °N and the western border at 6°25'E; Fig. 2). The total mass change (ΔM_{POP}) was integrated over a period of time (Δt) for these two sea regions. It is given as:

$$\frac{\Delta M_{\text{POP}}}{\Delta t} = \text{NetGas} + \text{Dep} - \text{Deg} + \text{NetFlow} + \text{Riv} - \text{NetSink} \quad (2)$$

with gaseous dry deposition flux minus the volatilization flux (NetGas), wet and dry particle depositions (Dep), degradation rate in seawater (Deg), net flows through the lateral boundaries into and out of the model domain (NetFlow), river input flow (Riv), the loss rate due to sinking minus rate of resuspension from the bottom sediments (NetSink). The annual mass change is obtained by integrating these fluxes over time, i.e. one year in this study. Inventories calculated that way demonstrate the contribution of an individual key process for the abundance of studied POPs in the North Sea.

Table 1

Physicochemical properties of γ -HCH, α -HCH and PCB 153 at 298 K and temperature dependencies of Henry's law constant used in FANTOM (cf. Eq. (1))

	γ -HCH	α -HCH	PCB 153
Saturation vapor pressure, p (Pa)	6.6×10^{-3a}	8.4×10^{-3a}	4.1×10^{-5c}
Water solubility, s (mg l^{-1})	7.4^a	2.0^a	8.8×10^{-4c}
Octanol-water partitioning coefficient, K_{ow} (-)	3.98×10^{3b}	5.89×10^{3b}	5.62×10^{6c}
Degradation rate in seawater, k_{deg} (s^{-1})	2.7×10^{-8b}	2.3×10^{-8b}	1.6×10^{-9c}
Intercept of the temperature dependent Henry's law constant, b (-)	10.14 ± 0.55^d	10.13 ± 0.29^d	14.05^e
Slope of the temperature dependent Henry's law constant, m (K)	-3208 ± 161^d	-3098 ± 84^d	-3662^e

^a Rippen (2000).

^b Klöpffer and Schmidt (2001).

^c Beyer et al. (2002).

^d Sahsuvar et al. (2003).

^e Paasivirta et al. (1999).

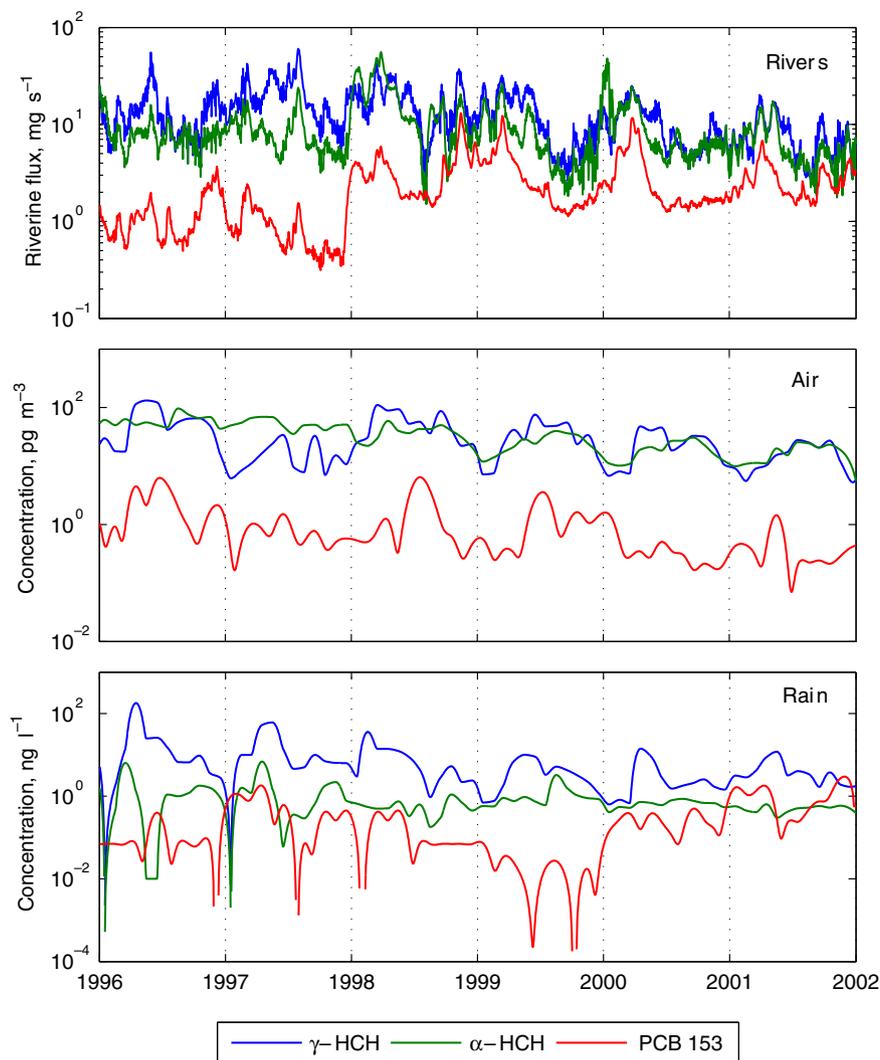


Fig. 1. Total riverine input flux of γ -HCH, α -HCH and PCB 153 (mg s^{-1} , sum of continental rivers Elbe, Weser, Ems, Rhine, Meuse and Scheldt and British rivers Thames, Welland, Humber, Tees, Tyne and Forth) and γ -HCH, α -HCH and PCB 153 concentrations in air (pg m^{-3}) and rain (ng l^{-1}) measured at the EMEP station Lista (58.1°N , 6.5°E). Geographical locations of rivers are shown in Fig. 2. Note that logarithmic scales are used.

3. Results and discussion

The spatial distributions of the vertically integrated annual mean concentrations of γ -HCH, α -HCH and PCB 153 (Fig. 2) show positive gradients towards the coasts with highest concentrations in the southern and south-eastern part of the North Sea. High concentrations close to the estuaries indicate the importance of riverine sources. In fact, river inflow influences the local circulation. In combination with wind and tidal induced residual currents it leads to a mean anti-clockwise pattern of sea currents commonly observed in the North Sea. This favors the accumulation of POPs in the German Bight located in the inner south-eastern corner of this circulation cell. Such pattern is calculated for all three pollutants. Low concentrations in the north-western North Sea are due to the inflow of cleaner Atlantic water.

In the case of γ -HCH, the largest input for the North Sea as a whole occurred through atmospheric deposition and lateral transport with ocean currents (Fig. 3). The total atmospheric deposition (76–95% of all sources) is much higher than the net inflow through the lateral boundaries (1–10%) and riverine inflow (<2% of all sources). The net air-sea gas exchange flux was depositional for the North Sea as a whole, but volatilizational for the German Bight.

Although the particle-bound mass fraction of γ -HCH was <2% the contribution of net sinking to the sea bottom is found among the most significant processes both for the North Sea and for the German Bight (Fig. 3). This is due to high POC content in the North Sea. The resuspension flux corresponded to about 10% of the sinking flux. The North Sea as a whole lost γ -HCH (Fig. 3) to adjacent seas (28% of all sinks), most through the northern boundary, and to the air above (60% of all sinks). Degradation and sinking with particles made up 5–12% of all sinks in the German Bight and the North Sea as a whole.

Similar to the North Sea, the German Bight also was exporting γ -HCH with the atmospheric input (65%, 1995–2001 mean) and rivers (10–30%) accounting for the main sources. Mass budgets calculations using concentration measurements in 1991 and 1992 together with mean water mass flows and annual atmospheric deposition averaged for the years 1991–1997 suggested that the outflow of γ -HCH from the German Bight was lower than the inflow (Hühnerfuss et al., 1997). This was attributed to degradation of γ -HCH and to partial isomerization of γ -HCH to α -HCH induced by marine microorganisms. The riverine sources were of similar magnitude but the atmospheric deposition flux was one order of magnitude lower than for 1996–2001 used in this study. Inherent

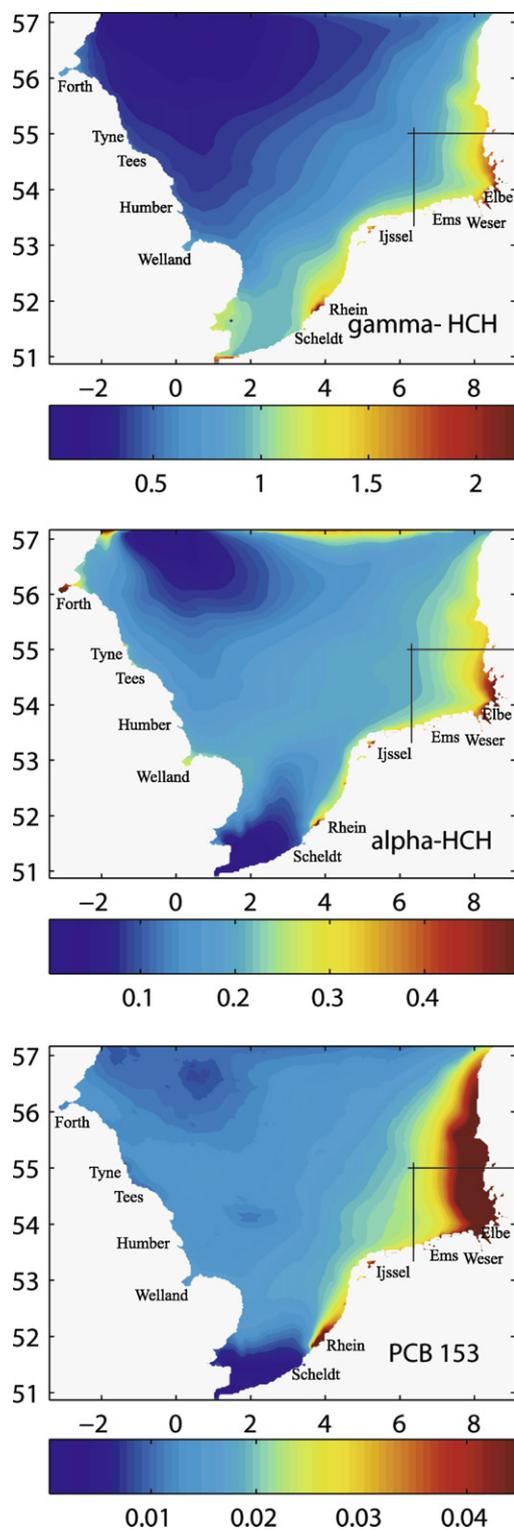


Fig. 2. Modeling domain, boundaries of the German Bight (lines) and mean vertically integrated concentrations of γ -HCH, α -HCH and PCB 153 (ng l^{-1}) in the North Sea calculated by FANTOM for the years 1996–2001. Rivers locations are indicated.

to the uncertainties of this semi-empirical approach the mass balance is an estimation of the order of magnitude. These uncertainties or the isomerization process, not considered in the model could explain the disagreement.

One of the major processes contributing to the α -HCH budgets in seawater is gaseous air-sea exchange (Fig. 3). The net gaseous transfer of α -HCH was depositional for the entire North Sea

throughout the simulation period. For the German Bight, analogous to γ -HCH a net volatilizational flux of α -HCH during the entire simulation period is found. Net volatilization from coastal waters had been observed in summer 1995 (Bethan et al., 2001). Following the ban of technical HCH in the 1980s α -HCH had not been used in Europe. However, this pollutant is still cycling in the region in consequence of remobilization from ground surfaces (including the sea). Model experiments with oceanic inflow of α -HCH at the lateral boundaries switched off showed only small effects on α -HCH North Sea concentrations (Ilyina, 2007). As in case of γ -HCH the flux into and from the bottom sediment layer is rather high.

Other significant processes for α -HCH in the German Bight were river inflow (<40% of all sources), net transfer through the lateral boundaries and degradation (both <5%, mean of 1995–2001). The total outflow flux through the lateral boundaries increased gradually during the 6 years of the model calculations. This, together with gradually decreasing α -HCH mass (Fig. 3) suggest that the North Sea region as a whole loses α -HCH mostly through the oceanic boundaries. Additionally, the ratio γ -HCH/ α -HCH calculated from the seawater concentrations of these isomers (Fig. 2) show offshore gradients in the North Sea with values of about 5 in the German Bight and <1 in the central North Sea. These ratios can indicate the different degradation rates and possibly isomerization (Hühnerfuss et al., 1992) of these two isomers. They also imply the significance of local sources for the levels of γ -HCH in the North Sea as compared to α -HCH, at least throughout the simulation period.

For PCB 153 in the North Sea, contribution of atmospheric deposition, sinking with particles and oceanic inflow is quite high, while contribution of the river inflow and degradation components is low. The wet deposition flux (30–40% of all sources) exceeds gaseous air-sea exchange. This reflects rather high concentrations of PCB 153 in rain measured at the EMEP station Lista used for model calculations (Fig. 1). The net gaseous flux is depositional in 1996, reversed in 2001 and close to equilibrium from 1998 to 2001. The net gaseous air-sea flux integrated for the German Bight similar to HCHs was very close to zero and volatilizational in 1997 and 2001 (Fig. 3), as a consequence of both higher seawater concentrations in the German Bight than in the whole North Sea. Note that the accuracy of volatilization flux quantification for PCB is limited by the uncertainty of the temperature dependency of the Henry's law constant (Bruhn et al., 2003) and is thought to be least certain under present model setup.

PCB 153 is the least water soluble and the most lipophilic chemical addressed in this study (Table 1). About 30–50% of PCB 153 is bound to particles in the open North Sea and about 90% in the German Bight (Ilyina, 2007). A simple equilibrium partitioning approach (i.e. partitioning ratio linear with K_{ow}) is used in the model, well justified by field observations (e.g. Sobek et al., 2004). The high particle-bound mass fraction provides an explanation for the large magnitudes of PCB 153 settling and resuspension fluxes both for the North Sea and for the German Bight. In fact, the model results indicate that the sinking flux can be high enough to dominate the mass budget in contrast to the budgets of the two HCH isomers.

Accordingly, the vertical distribution of PCB 153 in the water column follows the distribution of suspended particulate material with maxima at the surface in summer and in the bottom layers in winter shaped by sinking of POC and repeated resuspension due to frequent storm events (Ilyina, 2007). In comparison to PCB, more soluble HCH isomers follow water mass stratification with maximum at the surface throughout the year. Such vertical patterns are in agreement with observations in other shelf seas, i.e. the Baltic Sea and the Black Sea (Axelman et al., 2000; Maldonado and Bayona, 2002).

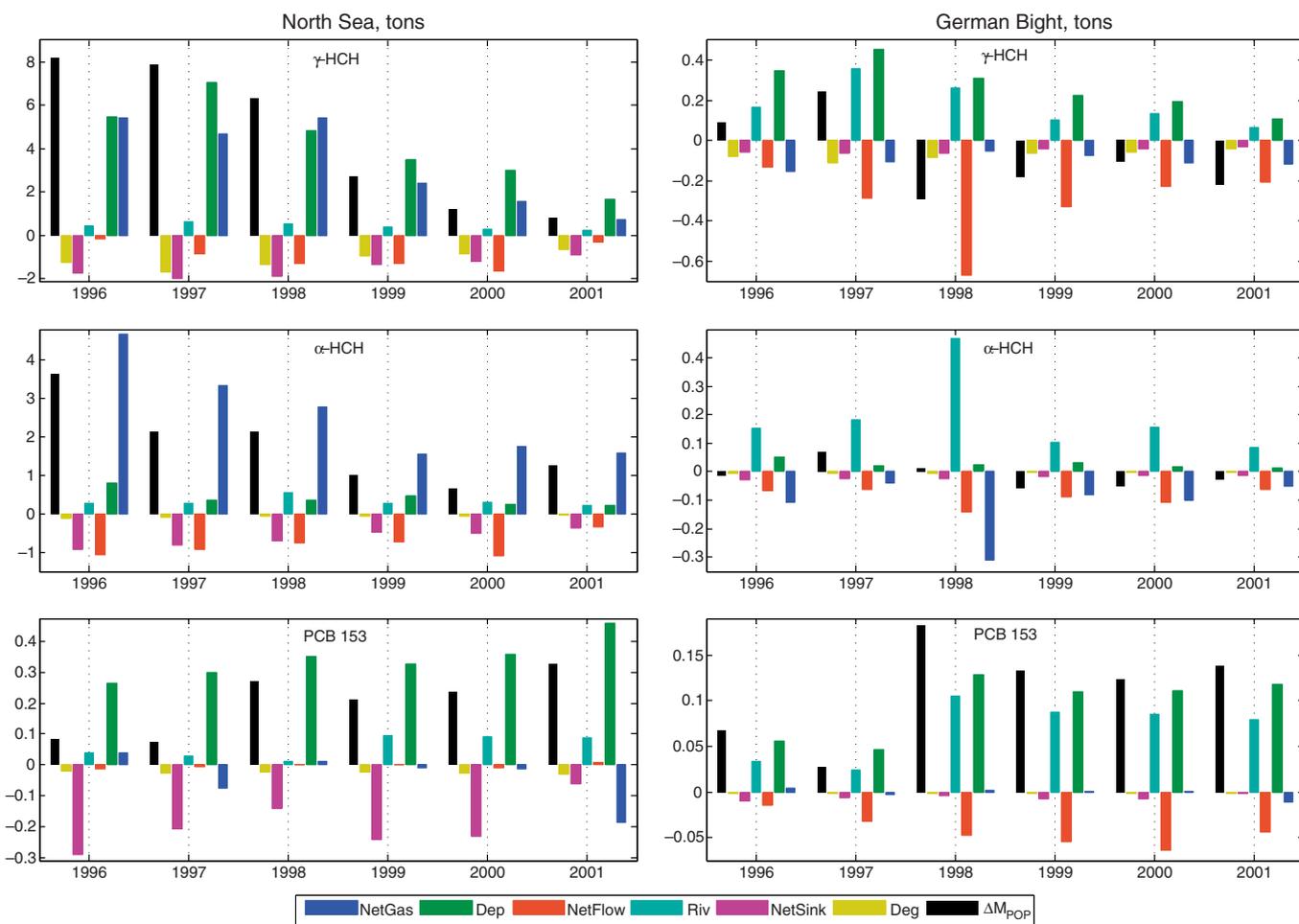


Fig. 3. Masses of γ -HCH, α -HCH and PCB 153 (tons) accumulated over a year due to different processes calculated for the North Sea and the German Bight. *NetGas* is the net gaseous air-sea flux (dry atmospheric deposition minus volatilization); *Dep* is wet (in dissolved and particulate phase) and dry atmospheric particle depositions; *NetFlow* is the net flow through the lateral model boundaries (inflow minus outflow); *Riv* is rivers input; *NetSink* is the flux between seawater and upper sediments (sinking minus resuspension); *Deg* is elimination due to degradation in seawater; the overall mass change of a compound in seawater over a year is given by ΔM_{POP} (cf. Eq. (2)).

The ratio between sinking and resuspension fluxes of PCB 153 is close to unity in the shallow and well mixed German Bight. The German Bight has high contributions from the riverine inflow which exceeded the gaseous deposition and the net sinking flux. This is attributed to the high PCB 153 loads in rivers (Fig. 1), mainly in the river Elbe, which were one order of magnitude higher than in other rivers. Because measured concentrations of PCB 153 in rivers were low and often lie at or below the detection limit, the river loads might have been overestimated. Nevertheless, measured and modeled PCB 153 seawater concentrations near the major rivers estuaries were in the same range throughout the simulation period (Ilyina, 2007). The inflow – outflow rates through the northern boundary provided the largest contribution to the PCB 153 inventory, but were very close in magnitude.

The results of this study indicate that PCB 153 seawater concentrations are still largely controlled by atmospheric depositions and primary discharges rather than by remobilization from the sediments, a major repository of PCBs in the aquatic environment (e.g. Palm et al., 2004). Remobilization may become a prominent source for the North Sea in the future. According to model calculations, a tendency for a slight increase of this contaminant in the North Sea is detected (Fig. 3). As degradation and river inflow played minor roles, the North Sea waters must have been a sink of PCB 153 for the outer world (including the air above). Measurements of PCB levels in precipitation and air from coastal and continental background sites in northern and central Europe (Aas and

Brevik, 2007) and in Baltic Sea sediments (data until 1998; Olsson et al., 2000) reveal no obvious trend for the study period. Downward trends are suggested in air on a longer time scale when the years after 2001 were included (Holoubek et al., 2007).

A comparison of PCB 153 concentration in flatfish (dab) liver (BFAFI, 2006) and seawater in the German Bight shows a parallel behavior ($r = 0.94$, $p > 0.99$; Fig. 4). Both measurements in fish liver and modeled concentrations in seawater indicate an increase of PCB 153 levels during 1999–2001. No long-term trend could be established so far, because the very low levels made quantification unreliable. In the Baltic Sea PCB levels in biota were declining (UNEP, 2002). Due to high lipophilicity of PCB 153 the concentrations in fish liver are high given low seawater concentrations. The levels of the HCH isomers in fish liver in the North Sea are lower despite higher concentrations in seawater as a consequence of the higher water solubility of HCHs. They decrease obviously following the emission trend (Fig. 4).

Overall, air-sea flux and transport with ocean currents are the major mechanisms which determine the cycling of the three POPs in the North Sea environment. Model test simulations with atmospheric deposition switched off (Ilyina, 2007) show that it is the main supplier of the studied POPs in the open North Sea. The model experiment results suggest that the atmospheric deposition is largely responsible for the annual cycle in seawater concentrations of these three pollutants. This is supported by calculated mass budgets and by the knowledge that the sea currents in this subregion

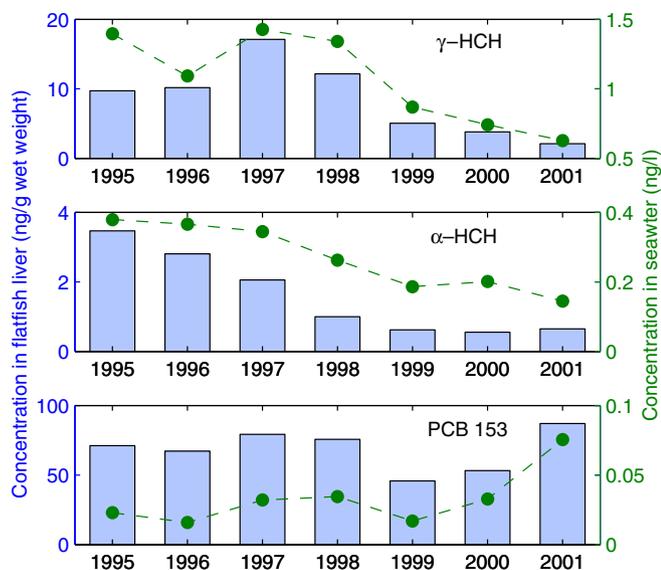


Fig. 4. Concentrations of γ -HCH, α -HCH and PCB 153 in flatfish (dab) liver (ng g^{-1} wet weight) measured (courtesy of BFAFI, 2006) in the German Bight (bars, left axis) and annual mean modeled seawater concentrations (ng l^{-1}) averaged for the German Bight area (dashed lines, right axis).

of the North Sea are weaker favoring weaker exchange and longer residence times of water masses. In the subregions close to the major estuaries model results suggest that the river inflow can be responsible for more than 50% increase in the studied pollutants concentrations, while volatilization causes decreases in the concentration values of γ -HCH, α -HCH and PCB 153 by a factor of 2, 4 and 6–20, respectively (Ilyina, 2007). This phenomenon is less pronounced in the open North Sea where seawater concentrations of the three pollutants are lower than in coastal zones (Fig. 2).

4. Conclusions

Model-based mass budgets of γ -HCH, α -HCH and PCB 153 in the North Sea were calculated for the first time. The southern North Sea was a sink for PCB 153 and a source of HCHs during 1996–2001 for the outer world (including the North Sea atmosphere). The results are strongly influenced by the spatially and temporally resolved characteristics of the ambient environment, e.g. the hydrographic conditions (ocean currents, water mass stratification), emphasizing the added value of comprehensive modeling. Obviously, the pathways of pollutants in a shelf sea, as well as the relative importance of their sources and sinks can significantly differ on a rather small spatial scale, i.e. in the North Sea and a coastal subregion. The spatial variability might even be higher as some insufficiently available input data was interpolated.

Acknowledgements

We thank the Federal Maritime and Hydrographic Agency (BSH) and the Federal Research Centre for Fisheries (BFAFI), Hamburg, for providing monitoring data. This work was supported by the Max Planck Society.

References

Aas, W., Breivik, K., 2007. Heavy metals and POP measurements, 2005. EMEP/CCC-Report 6/2007, Norwegian Institute for Air Research, Kjeller, Norway.
 Axelmann, J., Broman, D., Näf, C., 2000. Vertical flux and particulate/water dynamics of polychlorinated biphenyls (PCBs) in the open Baltic Sea. *Ambio* 29, 210–216.
 Bethan, B., Dannecker, W., Gerwig, H., Hühnerfuss, H., Schulz, M., 2001. Seasonal dependence of the chiral composition of α -HCH in coastal deposition at the North Sea. *Chemosphere* 44, 591–597.

Beyer, A., Wania, F., Gouin, T., Mackay, D., Matthies, M., 2002. Selecting internally consistent physical-chemical properties of organic compounds. *Environ. Toxicol. Chem.* 21 (5), 941–953.
 BFAFI 2006. Annual Report 2005. Federal Research Centre for Fisheries, Hamburg, p. 153.
 Bidleman, T., Jantunen, L., Falconer, R., Barrie, L., Fellin, P., 1995. Decline of hexachlorocyclohexane in the Arctic atmosphere and reversal of air-sea exchange. *Geophys. Res. Lett.* 22, 219–222.
 Breivik, K., Wania, F., 2002. Mass budgets, pathways and equilibrium states of two hexachlorocyclohexanes in the Baltic Sea environment. *Environ. Sci. Technol.* 36, 1024–1032.
 Bruhn, R., Lakaschus, S., McLachlan, M.S., 2003. Air/sea gas exchange of polychlorinated biphenyls in the Baltic Sea. *Atmos. Environ.* 37, 3445–3454.
 DOD 2005. German Oceanographic Data Centre, <<http://www.bsh.de/>>.
 DONAR 2005. Dutch Online Database Waterbase, <<http://www.waterbase.nl/>>.
 EMEP (2005). EMEP Data Online, <<http://www.emep.int/>>.
 Holoubek, I., Klánová, J., Jarkovský, J., Kohoutek, J., 2007. Assessment of the Central European trends in the background levels of persistent organic pollutants based on the results of the long-term integrated monitoring in Kosetice observatory, Czech Republic Part I. Ambient air and wet deposition 1988–2005. *J. Environ. Monitor.* 9, 557–563.
 Hühnerfuss, H., Faller, J., König, W.A., Ludwig, P., 1992. Gas chromatographic separation of the enantiomers of marine pollutants. Part 4: on the fate of hexachlorocyclohexane-isomers in the Baltic and North Sea. *Environ. Sci. Technol.* 26, 2127–2133.
 Hühnerfuss, H., Bester, K., Landgraff, O., Pohlmann, T., Selke, K., 1997. Annual balances of hexachlorocyclohexanes, polychlorinated biphenyls and triazines in the German Bight. *Mar. Pollut. Bull.* 34, 419–426.
 Ilyina, T., 2007. In: Basedow, J. et al. (Eds.), Fate of Persistent Organic Pollutants in the North Sea: Multiple Year Model Simulations of γ -HCH, α -HCH and PCB 153, Series: Hamburg Studies on Maritime Affairs, vol. 7. Springer, Berlin, Heidelberg, p. 132.
 Ilyina, T., Pohlmann, T., Lammel, G., Sündermann, J., 2006. A fate and transport ocean model for persistent organic pollutants and its application to the North Sea. *J. Mar. Syst.* 63, 1–19.
 Iwata, H., Tanabe, S., Sakai, N., Tatsukawa, T., 1993. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environ. Sci. Technol.* 27, 1080–1098.
 Klöpffer, W., Schmidt, E., 2001. A multimedia load model for the Baltic Sea. *Environ. Sci. Pollut. Res.* 8, 180–188.
 Lakaschus, S., Weber, K., Wania, F., Schrems, O., 2002. The air-sea equilibrium and time trends of hexachlorocyclohexane in the Atlantic Ocean between Arctic and Antarctic. *Environ. Sci. Technol.* 36, 138–145.
 Maldonado, C., Bayona, J.M., 2002. Organochlorine compounds in the northwest Black Sea water: distribution and water column processes. *Estuar. Coast. Shelf Sci.* 54, 527–540.
 Olsson, M., Bignert, A., Eckhéll, J., Jonsson, P., 2000. Comparison of temporal trends (1940s–1990s) of DDT and PCB in Baltic sediment and biota in relation to eutrophication. *Ambio* 29, 195–201.
 OSPAR (2002). OSPAR commission for the protection of the marine environment of the North-East Atlantic. Quality Status Report 2000. Region II – Greater North Sea, OSPAR Commission, London, p. 136.
 Palm, A., Cousins, I., Gustafsson, Ö., Axelmann, J., Grunderb, G., Broman, D., Brorström-Lundén, E., 2004. Evaluation of sequentially-coupled POP fluxes estimated from simultaneous measurements in multiple compartments of an air–water–sediment system. *Environ. Pollut.* 128, 85–97.
 Pätsch, J., Kühn, W., Radach, G., Casiano, S., Gonzalez, J.M., Davila, M., Neuer, S., Freudenthal, T., Llinas, O., 2002. Interannual variability of carbon fluxes at the North Atlantic station ESTOC. *Deep-Sea Res.* II 49, 253–288.
 Paasivirta, J., Sinkkonen, S., Mikkelsen, M., Raantio, T., Wania, F., 1999. Estimation of vapor pressures, solubilities and Henry's law constants of selected persistent organic pollutants as functions of temperature. *Chemosphere* 39, 811–832.
 Pohlmann, T., 1996. Predicting the thermocline in a circulation model of the North Sea – part I: model description, calibration and verification. *Cont. Shelf Res.* 16, 131–146.
 Pohlmann, T., 2006. A meso-scale model of the central and southern North Sea: consequences of an improved resolution. *Cont. Shelf Res.* 26, 2367–2385.
 Rippen, G., 2000. Umweltchemikalien. Ecomed Publisher, Landsberg, Germany.
 Sahsuvar, L., Helm, P., Jantunen, L., Bidleman, T.F., 2003. Henry's law constants for α -, β -, and γ -hexachlorocyclohexanes (HCHs) as a function of temperature and revised estimates of gas exchange in Arctic regions. *Atmos. Environ.* 37, 983–992.
 Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 1993. Environmental Organic Chemistry. Wiley, New York.
 Sobek, A., Gustafsson, Ö., Hajdu, S., Larsson, U., 2004. Particle-water partitioning of polychlorinated biphenyls in the photic zone: a 25-month study in the open Baltic Sea and the North Pole area. *Environ. Sci. Technol.* 38, 1375–1382.
 Tanabe, S., Hidaka, H., Tatsukawa, R., 1983. Polychlorinated biphenyls and chlorinated hydrocarbon pesticides in Antarctic atmosphere and hydrosphere. *Chemosphere* 12, 277–288.
 UNEP (2002). United Nations Environment Programme. Regionally based assessment of persistent toxic substances. Europe Regional Report, Geneva.
 Wania, F., Broman, D., Axelmann, J., Näf, C., Agrell, C., 2001. A multicompartment, multi-basin fugacity model describing the fate of PCBs in the Baltic Sea. In: Wulff, F.V., Rahm, L.A., Larsson, P. (Eds.), A systems analysis of the Baltic Sea. Springer-Verlag, Berlin Heidelberg, pp. 417–448.