Modelling the cycling of persistent organic pollutants (POPs) in the North Sea system: Fluxes, loading, seasonality, trends

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A B S T R A C T

The fate and cycling of two selected POPs is investigated for the North Sea system with an improved version of a fate and transport ocean model (FANTOM). The model uses atmospheric data from the EMEP MSC East POP model (Gusev et al., 2009), giving reasonable concentrations and seasonal distributions for the entire region, as opposed to the three observation stations that Ilyina et al. (2006) were limited to. Other model improvements include changes in the calculation of POP exchange between the water column and sediment. We chose to simulate the fate of two POPs with very different properties, γ-HCH and PCB 153. Since the fate and cycling of POPs are strongly affected by hydrodynamic processes, a high resolution version of the Hamburg Shelf Ocean Model (HAMSOM) was developed and utilised. Simulations were made for the period 1996–2005. Both models were validated by comparing results with available data, which showed that the simulations were of very satisfactory quality.

Model results show that the North Sea is a net sink for γ-HCH and a net source to the atmosphere of PCB 153. Total masses of γ-HCH and PCB 153 in 2005 are reduced to 30% and 50%, respectively, of 1996 values. Storms resuspending bottom sediments into the water column mobilise POPs into the atmosphere and have the potential to deliver substantial loads of these POPs into Europe.

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1. Introduction

Persistent organic pollutants (POPs) are eco-toxic artificial substances. In productive ocean waters, such as shallow water and shelf seas, POPs are bio-accumulative, thus entering the food web and being hazardous to living organisms, including humans (AMAP (1998)). However, our current understanding of processes affecting the cycling and fate of POPs in the ocean environment leaves a lot to be desired.

POPs enter the North Sea system from the surrounding highly populated, industrialised and agricultural countries. Major entrance pathways of POPs in the open ocean are via air–sea exchange processes that are dominated by dry gas deposition, wet deposition and dry particle deposition. In a semi-enclosed basin such as the North Sea, these atmospheric deposition processes are supplemented by input through rivers, with additional contributions coming from the adjacent seas, in this case, the North Atlantic Ocean, the English Channel and the Baltic Sea.

A number of studies investigating the fate of POPs in shallow and in open seas have been conducted. These include Breivik and Wania (2002a, 2002b) and Pacyna et al. (1999) for the Baltic Sea, and Iwata et al. (1993), Lakaschus et al. (2002) and Schulz-Bull et al. (1998) for open seas, all of which were limited temporally or spatially due to practical or analytical constraints. Ilyina et al. (2006, 2008) investigated the fate of POPs with a high resolution Fate and Transport Ocean Model (FANTOM), the first of its type, for the southern and central part of the North Sea.

It has been hypothesized that the oceans act as ultimate sinks of POPs. For example, Dachs et al. (2002) have suggested that oceans act as a global reservoir but ultimate sink for PCBs. What about shelf seas? Here, we investigate the fate and cycling of POPs in the North Sea system with the goal of determining whether it acts as a sink or source of these POPs to the atmosphere and the open ocean, while assessing the importance and roles of the various processes involved.

Our approach is to model the cycling of selected POPs in the North Sea system using an updated and improved version of the FANTOM model originally described in Ilyina et al. (2006). The fate of POPs depends on many processes in the ocean environment. Since these processes include, for example, advection and mixing, and can be strong functions of physical properties of water, such as temperature, a hydrodynamic model is a prerequisite tool for conducting such an investigation. For this purpose, a high resolution version of the Hamburg Shelf Ocean Model (HAMSOM, see Pohlmann (2006), was developed for use with the FANTOM.

The simulations are for the 10 year period 1996–2005.

Among the most common and well known POPs are PCBs (polychlorinated biphenyls, widely used in industry) and HCHs (hexachlorocyclohexane, widely used in agriculture). In this study,
we have selected two very different POPs for the simulations. Lindane, γ-HCH, is a legacy POP that is not hydrophobic and mostly dissolves in water, and has half lives of about 1.7 and 1.8 years in water and sediment, respectively, Ngabe et al. (1993) and Hornsby et al. (1996). PCB 153 is very hydrophobic, so it does not readily dissolve in water and mostly sorbs to organic material in aquatic environments, and has half-lives of about 13.7 and 18.8 years in water and sediment, respectively, Sinkkonen and Paasivirta (2000), and 1.7 and 1.8 years for γ-HCH in water and sediment, respectively, Ngabe et al. (1993).

The fate of POPs in the ocean is influenced by a wide range of interacting processes, including mechanical, e.g., transformation with moving flows; chemical, e.g., chemical decay and phase change; physical, e.g., adsorption; and biological processes, e.g., pollutant accumulations and transport by biota; and exchange between different compartments, including land–ocean, atmosphere–ocean and water–sediment exchange, see Fig. 1. POP processes simulated by the FANTOM are discussed in more detail in Section 3.1.1.

3. Model description

Comprehensive descriptions of both the FANTOM (Ilyina et al. (2006)) and HAMSOM (Backhaus (1985), Pohlmann (1996, 2006)) models have previously been given in the literature, so we give here only a brief overview while adding recent updates to both models. The model domain, both models, Fig. 2, covers the entire North Sea system, extending northwards as far as the Shetland Islands (60.3458 N), westward to the west of the Orkney Islands, situated to the north of the Scottish coast, (4.0625 W), southward to the English Channel (50.8708 N), and eastward to include the Skagerrak, Kattegat, the Danish Belts, and the westernmost part of the Baltic Sea (13.1458 E).

This configuration infers that there are 4 open boundaries; one each in the west, north, east, and south.

Model horizontal resolution is 1.5 ‘lat ×2.5’ lon, which is everywhere less than 3 km. There are 30 z-levels in the vertical as follows: 10 ×5 m layers in the upper 50 m where the depth of the uppermost layer changes in time and space with varying sea surface height; 5 ×10 m layers from 50 to 100 m; 5 ×20 m layers from 100 to 200 m; and 10 ×50 m layers from 200 to 700 m. Additionally, the FANTOM has 20 sediment layers, representative of the upper 2 cm of the sediment bed. Time steps of 5 and 10 min are used with the HAMSOM and the FANTOM, respectively. Model topography has been interpolated from the improved DYNOCS topography, Larsen and She (2001) resolution of 1 nautical mile (1.852 km), onto the model grid.

3.1. FANTOM model

The FANTOM is a 3-dimensional Eulerian model which was developed to simulate and study the fate of POPs and other pollutants in coastal regions and shelf seas. Model processes fall into five main categories: transport with ocean currents; air–sea exchange processes; phase distribution processes; degradation processes; and exchange between the water column and sediment (deposition and resuspension). The processes are summarised in Section 3.1.1 below.

The FANTOM model is continuously undergoing improvement. Recent changes include improved open boundary and initial conditions, and corrections to flux and conservation equation calculations. These improvements together with the use of reasonable spatial and temporal distributions of POPs in the atmosphere, have led to a set of interesting new results not anticipated in previous FANTOM simulations.

3.1.1. FANTOM: simulated POP processes

POP processes simulated by the FANTOM are shown in Fig. 1. For completeness of outline, we present here a brief description of the processes with equations. For a complete discussion see Ilyina et al. (2006).

3.1.1.1. Transport with ocean currents. The total concentration of a pollutant, C, at a fixed point is calculated with a simple Eulerian, advective–diffusive model (1) with sources and sinks, Qc and Re, respectively, as follows:

\[ \frac{\partial C}{\partial t} = - \boldsymbol{u} \cdot \nabla C + K_h \nabla^2 C + Q_C(t, x, y, z) - R_C(t, x, y, z) \]
where the left-hand-side is the local rate of change of concentration, $\vec{u}$ is the velocity vector and $K_{HV}$ is the scalar diffusivity coefficient (turbulent mixing coefficient) in the horizontal and vertical directions, and $\vec{u}$ and $K_{HV}$ are calculated with the HAMSOM. Sources of POPs to North Sea water are due to: deposition from the atmosphere; input through rivers; outward flux at open boundaries; and resuspension from sediment into the water column. Sinks are due to: volatilisation to the atmosphere; output at the open boundaries; sinking out of the water column into sediment; and degradation in water.

3.1.1.2. Air–sea exchange. The net flux of a pollutant from the atmosphere to seawater, $F_{surf}$, with units $[\text{ng m}^{-2} \text{s}^{-1}]$, is calculated as the net value of gaseous air–sea flux, $F_{a-w}$, dry particle deposition flux, $F_{dry}$, and wet deposition flux (due to precipitation), $F_{wet}$: $\begin{align*} F_{surf} &= F_{a-w} + F_{dry} + F_{wet}. \end{align*}$

Gas exchange at the air–sea interface is based on the stagnant two-film theory formulated by Whitman (1923) and Liss and Slater (1977) with the inclusion of a fugacity formulation as described by Mackay (2001). The chemical equilibrium of the POP between the two compartments is controlled by temperature, wind speed, physical–chemical properties of the compound and its abundance in the environment.

Fig. 1. Cartoon presenting the most important processes connected to the fate and transport of highly water-soluble and highly POC-attached persistent organic pollutants in the oceanic environment simulated by the FANTOM model. Uptake and transport through the food web is not included.

Fig. 2. Model domain with topography (metres). River sources of freshwater are shown by magenta dots and the four locations of the different time series used in Figs. 4 and 10, respectively, are shown by solid colour circles.
where the organic carbon $f_{POC}$ either freely dissolved or bound to suspended particulate matter SPM respectively. $R$ is the ideal gas constant, $T_a$ and $T_w$ are temperature in air and water, respectively, and $H_c$ is Henry's law constant at $T_a$. The volatilisational exchange rate, (5), is calculated according to Mackay (2001) and Wania et al. (2003):

$$D_{wa} = \frac{A_w}{\pi r^2} \cdot u,$$

where $A_w$ is water surface area and $u1$ and $u2$ are mass transfer coefficients which are functions of wind speed Schwarzenbach et al. (1993). The exchange rate for gas deposition is similarly calculated.

### 3.1.1.3. Phase distribution and flux from water into sediment. POPs are either freely dissolved or bound to suspended particulate matter SPM in seawater. The organic carbon fraction of SPM, POC, is calculated and used as a sorbing matrix for POPs. The fraction of a P00 bound to POC, $f_{POC}$, is calculated as:

$$f_{POC} = \frac{K_{OC} \cdot C_{POC}}{K_{OC} \cdot C_{POC} + 1},$$

where the organic carbon–water equilibrium partition coefficient, $K_{OC}$ [L/kg], is compound specific and $C_{POC}$ [kg/L] is the concentration of POC in solution. Since most POC in seawater is in particle form, it sinks to the bottom with sinking velocity, $v_{set}$, implying a downward settling flux of POPs with sinking particles, $F_{set}$ [$\mu g \ m^{-2} \ s^{-1}$]:

$$F_{set} = v_{set} \cdot f_{POC} \cdot C.$$

### 3.1.1.4. Degradation in water and sediment. Combined abiotic and biotic degradation in seawater and sediment are represented by 1st order rate decay coefficients, $k_{deg}$ [s$^{-1}$], where higher order kinetics have been neglected. Assuming that degradation is linearly dependent on the compound total concentration gives:

$$\frac{dC}{dt} = -k_{deg} \cdot C.$$

### 3.1.1.5. Water–sediment exchange. POPs sorbed to POC settle to the bottom, (Eq. (7)), becoming part of the sediment, and are thus subject to the laws of sediment dynamics. Resuspension of bottom sediment occurs when strong friction velocities are found close to the bottom. In a shallow sea, such as the North Sea, bottom friction is influenced by storms, tidal dynamics, and residual currents, so we can expect to see resuspension of sorbed POPs, especially during winter storms and at spring tide, and particularly in shallower coastal and southern regions of the North Sea, see Fig. 2 for model topography. We have chosen a critical bottom friction velocity of $\sqrt{\frac{g}{\alpha}} = 2.8 \text{ cm/s}$, but we can expect the amount of resuspended particulate matter to increase during stronger and more sustained events.

Upon resuspension, the sorbed and dissolved POPs undergo continuous equilibrium partitioning. So for a lipophilic POP, like PCB 153, where most of the POP is contained in sediment, we can expect a transfer of the POP from the sorbed to the dissolved state during storm and tidal events. The increase in dissolved concentration leads to increased volatilisation and, thus, a change in the net air–sea flux. Following an event, the remaining suspended sorbed POP sinks out of the water column and back into the sediment.

### 3.1.2. FANTOM: initial conditions, forcing and boundary data

For air–sea exchange processes, near surface POP concentrations in precipitation, gas and particulate phases from the EMEP MSCE-POP multi-compartment model, Gusev et al. (2009), are used. Monthly values from the 50 km EMEP grid have been interpolated into the FANTOM timestep and grid. MSCE-POP model values are in reasonable agreement with available observations within the FANTOM model domain (OSPAR (2008), Gusev et al. (2009) and Alexey Gusev pers. comm.).

At the open boundaries, POPs are advected into or out of the model domain with the local HAMSOM horizontal velocity perpendicular to the boundary. When velocities are inward, POP concentrations from available observations and model results are used, see Malanichev et al. (2004), Wodarg et al. (2003), Schulz-Bull et al. (1998, 2009), Iwata et al. (1993), Lakaschus et al. (2002), Ilyina et al. (2006), and Dirk Wodarg pers. comm.

POPs also enter the model domain through rivers, where the total flux of a POP at a point source (same as HAMSOM) into the model domain is calculated as the concentration times the freshwater flux at any given time. POP concentrations entering the model domain through rivers are calculated from available data. OSPAR data (www.ospar.org/) is used for British and Norwegian rivers, Helpdesk Water data (www.helpdeskwater.nl) in Dutch rivers, VMM in Belgian (Scheldt) rivers (www.vmm.be), and Arge-Elbe (fgg-elbe.de), Flussgebietsgemeinschaft Weser (fgg-weser.de) and the Lower Saxony Administration, Germany (www.nlwkn.de) data in the German rivers Elbe, Weser and Ems, respectively. γ-HCH data were available for every river. However, PCB 153 data were directly available for German, Dutch and Belgian rivers only, and for British and Norwegian rivers (OSPAR data) had to be extracted from combined PCB data sets (combined concs. of PCBs 28, 52, 101, 118, 153, 138, 180). This was accomplished by assuming constant ratios of these seven PCBs in all rivers entering the North Sea (Michael Bergemann Arge Elbe pers. comm.). Calculated concentrations of PCB 153 in British and Norwegian rivers have been verified (Richard Moxon, OSPAR, British rivers, and Ian Allan, Norsk Institutt for Vannforskning (NIVA), Norwegian rivers, pers. comm.).

The total concentration of POC is the sum of concentrations of biogenic and sediment organic carbon. Biogenic POC is composed of plankton, bacteria and detritus suspended in the water column, while sediment POC sources are derived from plant and animal detritus, natural and anthropogenic river inputs, and in situ formed plankton and bacteria. Daily values of biogenic POC concentrations have been interpolated from the ecosystem model of Lorkowski et al. (2012) and sediment POC is calculated in the FANTOM.

The FANTOM initial condition was chosen by spinning the model up from a cold start for a number of years. First, the model was run for three years beginning in 1996 with zero POP concentration in the water column and sediment. The model was rerun for three year spin up periods (1996–1998, since river and atmospheric concentrations were generally greatest at this time), using the solution of the previous 3-year run as the initial condition. This process was repeated until water column and sediment concentrations were in reasonable agreement with available observations, over a period of a number of years, and the model appeared to have reached a state of equilibrium. Total spin up time amounted to 24 years for both POPs. The model run for the period 1996–2005 was then performed.
3.2. HAMSOM model

The HAMSOM is a baroclinic, shallow water equation, ocean circulation model based on a semi-implicit numerical scheme, which was first developed in the 1980s and has been successfully applied to study different regions of the world ocean, see, e.g., Mayer et al. (2010) and Pohlmann (1996). Surface forcing is provided by the NCEP/NCAR global atmospheric reanalysis (Kalnay et al. (1996), Kistler et al. (2001)), where six-hourly values of atmospheric parameters: air temperature; humidity; cloud cover; precipitation; sea level pressure; and near-surface wind speed and direction; have been interpolated into the model grid and timestep.

Open boundary conditions are provided by a larger scale (20 km grid) Northwest European Shelf version of the model (Pohlmann (1996)), where sea surface elevation is prescribed with a zero gradient condition. Temperature and salinity are calculated at the open boundaries utilizing a radiation condition (Orfanksi (1976)) and an additional relaxation term under inflow conditions to account for the possibility that outflow occurred before and has transported water properties from the model domain interior into the model domain’s vicinity. Initial conditions for temperature and salinity are interpolated into the model grid from Levitus climatology (WOA-01, Boyer et al. (2005)). The model was spun up for two years so that the solution is nor influenced by the initial conditions (the North Sea has flushing time of 1–2 years).

In the horizontal direction, subgridscale processes are parameterized using the Smagorinsky (1963) diffusivity which is proportional to the sum of the horizontal shear and the linear strain rate. In the vertical direction, turbulence is parameterized using a method developed by Kochergin (1987) where the vertical eddy diffusivity (momentum diffusivity or mixing coefficient) is dependent upon vertical shear and water column stability. At the bottom boundary, a semi-implicit formulation for the quadratic bottom stress is introduced to account for bottom friction (Backhaus (1985)). A friction velocity due to the effect of wind waves and swell is calculated at the bottom, and has important consequences for sediment erosion and deposition, as discussed in Section 3.1.1.

Locations of freshwater runoff into the model domain are shown in Fig. 2. Monthly climatological river runoff data for major Continental and British rivers were taken from Damm (1997). The River Spey, see Lewin and Weir (1977), has been added to this set. Norwegian freshwater runoffs were also taken from Damm (1997) but have been subdivided from his 7 subregions to 28 point sources, including the Glomma and Numedalslågen rivers. These monthly runoffs have been interpolated into each time step in the model.

4. Model validation

4.1. HAMSOM model validation

Our goal here is to show that the model is capable of reproducing the basic and detailed structure of the North Sea hydrodynamics. Therefore, we do not wish to compare model results with individual observations but, rather, to show that the salient features seen in the observations are reproduced by the model. The model is validated by comparing model surface maps of temperature and salinity with available observational data.

For temperature, we compare model results with monthly SST data provided by the Bundesamt für Seeschifffahrt, which have been combined with station data to reduce absolute error of the satellite measurements (Becker et al. (1986)), Fig. 3. In winter the signature of North Atlantic water is given by T > 5 °C and this water is also seen to enter the model domain from the north and the south. The location of the 7.5 °C isotherm in both model results and observations are in good agreement. Water cools as one moves away from the northern boundary and the English Channel into the North Sea proper. Temperatures less than 6 °C extend from the Ijssel Meer to the German Bight, to westward of the Jutland Peninsula and into the Skagerrak. A tongue of water warmer than 6 °C extends into the Skagerrak but temperatures get cooler in the Kattegat and towards the Baltic Sea (not shown in figure). Values are in good agreement offshore of the Norwegian and British coasts. In summer, the situation is reversed with warmer water nearer the coasts, particularly the Dutch and German coasts and around the Danish Belts in the east (not shown). The 15 °C isotherm can be taken as a rough estimate for the signature of North Atlantic water and agreement between model and observations is satisfactory. Model temperatures are ~1–2 °C warmer near southern coasts, however, the general agreement is quite good, and we conclude that the model is capable of reproducing realistic temperature conditions.

For salinity, model results are compared with the data sets of Loewe et al. (2003) who estimated surface salinity throughout the North Sea from cruise data collected in January-February and July 2002, see Fig. 4. The model is validated using HAMSOM results averaged over the same periods as the observations. In winter, a broad tongue of salty water with S>35.0, representative of Atlantic inflow, extends from the north of the model domain southward to approximately 57 N in both data sets. This salty water is also seen in the southernmost region of the model domain where it enters through the English Channel. The S = 34.0 isohaline extends from offshore of the Dutch coast, eastward to north of the East Frisian Islands, then west of the German Bight and northward to the Skagerrak, then offshore to the west of the Skagerrak and along the Norwegian coast. Also, along the British coast, the S = 34.0 isohaline is seen offshore around the Firth of Forth in the north and around the Humber and Wash region. Low salinity is due to freshwater input from rivers in coastal regions and, in the Skagerrak region, from the Baltic Sea. Summer distributions reflect increased late spring freshwater runoff from rivers and the Baltic; the S > 35.0 isohaline has retreated northwards; the S = 34.0 isohaline has moved northward and westward, and further off the Dutch, German and Danish coasts, the Skagerrak, and Norwegian coast, respectively; water is generally fresher in the western North Sea off the British coast; and there is less input of salty water through the English Channel. All features are clearly seen in both model and observational data.

Although we have discussed only temperature and salinity results here, the fact that model results stay true to observations shows that all aspects of the model are functioning well. In particular, salinity acts mainly as a passive tracer, thus reflecting current patterns to a high degree. Therefore, we can say with some level of confidence that the model responds well to forcing at the surface and the open boundaries and that calculated processes such as advection and diffusion are reasonable. See Pohlmann (2006) for further discussion on validation of the model for the southern North Sea.

4.2. FANTOM model validation

Since observations of γ-HCH and PCB 153 are limited to a few points in space and occasional measurement in time, the FANTOM model is validated by comparing time series of model results with available observations at discrete locations in both water and sediment and are given in Fig. 5.

Fig. 5(a) shows time series of upper water column concentrations of γ-HCH to the west of the North Frisian Island of Sylt and the Jutland Peninsula, see Fig. 2 for location. Model values start out, 1996–1997, with maximum concentrations of ~4 ng/L in summer and ~3 ng/L in winter. Values start to decrease in 1998, when maximum concentrations of ~2 ng/L are seen, and continue to decrease to the end of the time series when concentrations drop to less than 1 ng/L. Observations are limited to a few measurements per year, mostly made during the summer months. Maximum observed concentrations of ~3 ng/L are seen in 1997, after which they decrease to less than 2 ng/L in 1999, and decrease further to much less than 1 ng/L towards the end of the
time series. In general, model values are somewhat greater than those observed. Nevertheless, both sets of data follow a similar pattern with values decreasing substantially towards the end of the time series.

Time series of $\gamma$-HCH concentration in sediment to the north of the East Frisian Islands, between the mouths of the Weser and Ems rivers, are plotted in Fig. 5(b), see Fig. 2 for location. Model values start out with concentrations of less than ~0.1 ng/g d.w., remaining generally constant up to the end of 1999. Values begin to decrease in 2000, continuing to do so to the end of the time series. Although the few observations from 1998 to 1999 exceeded 0.2 ng/g d.w., model results are generally in very good agreement with observations.

In Fig. 5(c) time series of upper water column concentrations of PCB 153 at the same point as a) above, are shown. Model values start out with concentrations of ~0.01 ng/L and generally decrease slowly to minimum values at the end of the time series. The limited number of observations also show concentrations decreasing in time, and the model results are in excellent agreement with observations.

Finally, Fig. 5(d) shows time series of PCB 153 concentrations in sediment to the north of the West Frisian Islands, see Fig. 2. Model values are generally ~0.5 ng/g d.w. throughout the time series and in very good agreement with observations.

We mention very briefly here the occasional very rapid increases in concentration seen in the model PCB 153 water column time series, c), and also the events seen in the model PCB 153 sediment time series, d). We return to these features in the discussion section.

In summary, we think that the general agreement between model results and observations is quite good and generally acceptable.

5. Results and discussion
5.1. Distributions of $\gamma$-HCH and PCB 153 in water and sediment

Model concentrations of total $\gamma$-HCH and PCB 153 in near surface waters are plotted in Fig. 6. Looking first at $\gamma$-HCH for February (winter) 1997, top left panel, it is seen that concentrations increase from north to south and are generally greatest off the southern British, Dutch and German coasts, particularly around river sources. Because of the predominantly cyclonic North Sea circulation, see for example Sündermann and Pohlmann (2011) and references therein, large quantities of $\gamma$-HCH are advected along the continental coast resulting in high concentrations extending from west of the Jutland Peninsula, into the Skagerrak and off the Norwegian coast. This pattern is repeated throughout the year,
however, highest concentrations are found in the summer months, see panel for August top right. For 2004, second panel, the patterns and seasonality of 1997 are repeated. However, it is apparent that concentrations are reduced by a factor of ~3–5 from 1997 values.

Looking at PCB 153 for 1997, third panel, beginning in February (winter), concentrations generally increase from north to south and are greatest in areas around Continental and British river sources. The cyclonic circulation again leads to higher concentrations to the west of Jutland, up into the Skagerrak and offshore of the Norwegian coast. The pattern repeats itself throughout the year but, in contrast with γ-HCH, concentrations are highest in winter and least in summer, particularly near river sources, see map for August third panel right. In 2004, bottom panel, the patterns and seasonal variability of 1997 are clearly reproduced but concentrations are reduced by up to 5 times relative to 1997. Note that concentrations of PCB 153 are about two orders of magnitude less than those of γ-HCH.

Maps of distributions of γ-HCH and PCB 153 in sediment are plotted in Fig. 7. The top panel shows γ-HCH in February, left, and August 1997, right. High values are found throughout the southern North Sea and are somewhat higher in summer. In 2004, second panel, concentrations have been substantially reduced away from southern North Sea river sources and also in the Skagerrak, Kattegat and Scottish coastal regions, which is apparent from the notable reduction in red shaded areas in the southern North Sea. Highest concentrations of PCB 153 in 1997, third panel, are found close to British and Continental river sources with little seasonal variability observed. Similar distribution patterns are found in 2004, bottom panel, with concentrations somewhat reduced from 1997 values. We stress here the greater reduction in sediment concentrations of γ-HCH in 2004 relative to PCB 153 is due to relatively short half-life (Section 2) and reduced availability for sedimentation. Recall, that PCB 153 is lipophilic, is mostly sorbed to POC and is thus available for deposition and sedimentation, while γ-HCH is hydrophilic and is practically all dissolved in water.

5.2. Surface fluxes of γ-HCH and PCB 153

5.2.1. Seasonalities and trends of surface fluxes

Time series of surface fluxes of γ-HCH and PCB 153 for the period 1996–2005 are plotted in Fig. 8, top and third panels, respectively. Daily cumulative values with a running average of 11 days are given for gas deposition, volatilisation, wet deposition, dry particle deposition, and river input.
Fig. 5. Time series, 1996–2005, of concentrations of, a), \(\gamma\)-HCH in the upper water column (5 m), b), \(\gamma\)-HCH in sediment, c), PCB 153 in the upper water column (5 m), and, d), PCB 153 in sediment. Model results are given by solid lines, observations are shown as points. The coloured circles show locations of the respective model times series and observations, see Fig. 1. Tick marks on the x-axis show February and August for each year.

Fig. 6. Near surface (upper 5 m) distributions of concentrations in ng/L of \(\gamma\)-HCH for 1997, upper row, 2004, 2nd row, and PCB 153 for 1997, 3rd row, and 2004, bottom row. Values are daily averaged at the end of Feb and Aug. Note the different scales on different rows.
Fig. 7. Same as Fig. 6 but in sediment. Concentrations are in ng/g dry weight.

Fig. 8. Time series, 1996–2005, of daily surface mass fluxes and river mass inputs of γ-HCH, top panel, and PCB 153, third panel, for the entire model domain, and total mass contained in the water column and sediment of γ-HCH, second panel, and PCB 153, bottom panel. Tick marks on the x-axis are for Feb and Aug of each year. Surface fluxes plotted are volatilisation, wet deposition, dry gas deposition, and dry particle deposition.
For γ-HCH, top panel, gas deposition is the major contributor to air–sea exchange, followed by a substantial contribution through volatilisation, and minor contributions through wet and particle deposition, and flux through river input. Gas deposition exhibits a clear annual cycle, with highest fluxes occurring between February/March and August/September and peak values found in May/June. Values decrease around September and minimum values are found around the first half of December, after which values increase through January–February, thus completing the annual cycle. A clear downward trend is seen with maximum fluxes in 1996 of about 250–300 kg/day decreasing to 50 kg/day in 2005. Minimum flux values also show a downward trend, decreasing from about 15 kg/day in 1996 and 1997 down to 3 kg/day in 2003–2005. Volatilisation of γ-HCH also exhibits a clear annual cycle with highest values in August–October and lowest values in February–April. A clear downward trend in values is seen, with maximum fluxes down from about 90–100 kg/day in 1996 down to less than 20 kg/day in 2005 and minimum fluxes down from 20 kg/day in 1996 to less than 10 kg/day in 2005. Wet deposition also exhibits an annual cycle and downward trend with highest values in July/August and lowest values in December, down from 15 kg/day and 0.5 kg/day in 1996 to about 2 kg/day and 0.1 kg/day in 2005, respectively. River inputs display the same patterns with maximum values in April–June down from about 4 kg/day in 1996 to 1 kg/day in 2004–2005 and minimum values around December down from 2 kg/day in 1996 to 0.5 kg/day in 2005. Particle deposition is very little relative to the other contributions. Because gas deposition is generally greater than volatilisation, we say that, at the surface, the North Sea is not depositional for γ-HCH, or the atmosphere acts as a net source to the North Sea for γ-HCH. However, due to the phase shift in annual cycles, it is seen to be net volatilisation, i.e., a net sink to the atmosphere, between October and January.

For PCB 153, third panel, volatilisation is the largest contributor to air–sea exchange. Gas and wet deposition are each 3–4 times less than volatilisation, while particle deposition is more than an order of magnitude less. River input is about half as big as volatilisation, and is the major surface source of PCB 153 into the North Sea. Volatilisation exhibits a clear annual cycle with minimum values generally in May–August, increasing rapidly around September to maximum values in October–January, then decreasing in February/March, thus completing the annual cycle. We note also the strong peaks in volatilisation seen in winter. These peaks are due to storm events lasting about a week. POPs are resuspended from the sediment and into the water column, as shown in Fig. 8d, thus causing the increase in volatilisation. In 1996, minimum fluxes are about 0.7–0.8 kg/day, while maximum values are generally greater than 1.5 kg/day. These values increase somewhat until 1999 before dropping off in 2000, after which a clear downward trend is observed. River input displays a pattern in time very similar to that of volatilisation: a smooth annual cycle is observed, beginning with minimum and maximum fluxes of 0.3 kg/day in August 1996 and 0.7 kg/day in January 1997, respectively. Thereafter, an upward trend is observed until 2000 after which the trend is downwards, dropping off to minimum and maximum values of about 0.05 and 0.12 kg/day, respectively, by 2005. Gas deposition values are least in January, increase in February and remain constant for the period March–November before decreasing in December. A clear downward trend is seen for the entire period. Minimum and maximum fluxes begin at about 0.1 and 0.3 kg/day, respectively, in 1996, dropping to less than 0.05 and 0.15 kg/day, respectively, in 2005. The wet deposition time series generally follows an annual cycle and trend similar to that of volatilisation, while the contribution from particle deposition is small. Volatilisation at the surface is generally much greater than the sum of all depositions so that, at the surface, the North Sea is a net source to the atmosphere for PCB 153. However, in summer, the sum of the depositions can exceed volatilisation and the North Sea thus becomes net depositional for PCB 153 at that time.

Magnitudes of surface fluxes of PCB 153 are generally 1–2 orders less than those of γ-HCH.

5.2.2. Distributions of surface fluxes

Distributions of surface fluxes of γ-HCH and PCB 153 are plotted in Fig. 9. For γ-HCH in 1997, dry gas deposition, top row left two panels, is greatest offshore of the British coast, particularly in the south and near the Scottish coast, and also in the southwesternmost part of the Continental coast, near the Belgian and French coasts. Fluxes decrease to the north and east.

Volatilisation fluxes, second row left two panels, increase from north to south with greatest values seen in areas around Continental and British river sources, where highest concentrations in the water column are located (Fig. 6). A clear annual cycle is seen with highest values in the summer months, following the seasonal pattern of concentrations in the water column, which is modulated by the annual cycle in river input flux. Similar patterns are seen in 2004, top two rows right two panels, but fluxes have been greatly reduced, as has been discussed in the previous section.

Wet deposition, not shown, is generally greatest to the north and maximum values can be located either in coastal regions or in open water. Dry particle deposition, not shown, is greatest off the British coast, particularly off Scotland. Large values are also occasionally seen in Continental and Scandinavian coastal areas.

From these results, we conclude that most of the flux of γ-HCH across the surface into the North Sea occurs offshore of the British coast. Volatilisation occurs mostly between the southern British and Dutch coasts and near southern Continental and southern British rivers, where surface water concentrations are greatest, and follow an annual cycle, reflecting the cycle in upper water column concentrations.

For PCB 153 in 1997, dry gas deposition, third row left two panels, is greatest in the southernmost region of the North Sea, with substantial values extending further north off the English coast and out into the central North Sea.

Volatilisation of PCB 153, bottom row left two panels, is greatest off the British, Dutch and German coasts, especially near British and Dutch river sources where water column concentrations are greatest (Fig. 6). Large values extend throughout most of the North Sea in winter, including the Wadden Sea to the west of Jutland, the Skagerrak, and offshore of the Norwegian coast. An annual cycle with greatest concentrations in winter is seen, similar to the annual cycle of surface water concentrations (Fig. 6). In 2004, bottom two rows right two panels, distributions are similar to those seen in 1997, while flux rates have been reduced by several factors.

Wet deposition of PCB 153, not shown, is generally variable throughout the North Sea, with large values seen in different regions at different times of the year. Dry particle deposition of PCB 153, not shown, is generally greatest off the British coast, particularly in the south, and also along continental coasts. Large values in the open North Sea are also occasionally seen.

In summary, volatilisation of PCB 153 is greatest in the vicinity of British and Dutch rivers, where concentrations in the water column are greatest, and an annual cycle with highest volatilisation fluxes in winter is seen. For deposition, gas deposition is greatest in the southernmost region of the North Sea, wet deposition is generally variable throughout the North Sea, while particle deposition is generally greatest off the British coast.

5.3. Total annual fluxes of γ-HCH and PCB 153

Total annual mass fluxes of γ-HCH and PCB 153 for 1997 and 2004 are given in Fig. 10 on a log₁₀ scale. For γ-HCH, in 1997, dry gas deposition is the greatest source, followed by wet deposition which is almost twenty times less, river input which is half of the latter, and dry particle deposition which is nearly two orders magnitude less again. Degradation in water is the main sink, and is one third less
than the greatest source, followed by volatilisation, about a factor of 2 less, degradation in sediment, more than 2 orders of magnitude less again, and, finally, sinks at the open ocean boundaries, which are fairly negligible. In 2004 all sources and sinks have been substantially reduced from 1997 values. Dry gas deposition remains the greatest source and degradation in water the greatest sink, now exceeding even gas deposition by about 20%. In both years dry gas deposition is greater than volatilisation, therefore the North Sea acts as a net sink for γ-HCH, since the sinks at the open boundaries are negligible.

Comparing the sums of sources and sinks of γ-HCH, we see that they are almost equal in 1997, sinks being just 4% greater, reflecting the idea that the system was in a steady state at that time. In 2004 the sum of the sinks is clearly greater than the sources (by about 60%) because all inputs have been substantially reduced from 1997. Hence, we can anticipate that total concentrations in the North Sea will be reduced.

For PCB 153, input through rivers is the greatest source, followed by wet and dry gas deposition with half as much each, and dry particle deposition which is an order of magnitude less than input through rivers. Volatilisation is the greatest sink, followed by degradation in sediment, an order of magnitude less, degradation in water, an order of magnitude less again, and net flux outward through the open ocean boundaries, which is, like γ-HCH, fairly negligible. In 2004, all sources and sinks have been substantially reduced from 1997 values, except for degradation in sediment. In both years volatilisation is an order of magnitude greater than the sum of all deposition at the surface, therefore the North Sea acts as a net source to the atmosphere for PCB 153.

Next, comparing the sums of sources and sinks of PCB 153, we see that the sinks are a factor of six to seven greater for both years. This tells us that the system was never in a steady state, at least for the time period under consideration. Almost all of the hydrophobic PCB 153 sorbs to POC in the water column before sinking to the sediment where it is stored for long periods of time due to its long half-life. Thus, a steady input of PCB 153 over time results in increasing concentrations of the POP in the North Sea, while reduced inputs through rivers and the atmosphere will cause concentrations to reduce but on a much longer time scale.

5.4. Exchange of γ-HCH and PCB 153 between water and sediment

One interesting and important set of features worth discussing are the events of rapid increase in PCB 153 concentration in water seen in Fig. 5c). These events are due to storms, which occur mostly during the winter months, causing erosion of fine fraction of sediment and thus resuspension of POPs into the water column. The first event, in early winter 1996–1997, shows a rapid increase in PCB 153 water column concentration to the west of the North Frisian Islands, see location in Fig. 2, and a simultaneous decrease in sediment concentration to the north of the coast of Holland, Fig. 5d), indicating that this was a substantial storm that extended at least between these two points.

Concentration of PCB 153 in water decreases following the passing of the storm, indicating sinking of PCB 153 out of the water column, generally returning to pre-storm (or pre-winter) concentrations in spring. Recovery to pre-storm concentrations in sediment, however, takes a number of years, indicating that much of the POP has been advected out of the area by ocean currents or has been volatilised to the atmosphere (see discussion of Fig. 8).

The second event in water, in February 1999, Fig. 5c), shows a rapid increase and subsequent decrease in concentration to the west of Jutland. On this occasion, a slight increase in sediment concentration...
is observed at the point to the north of the Dutch coast, indicating an
advective flux of PCB 153 into the area followed by sinking out of
the water column. The third event, in late 1999, shows, again, a rapid
increase in water column concentrations to the west of Jutland. On
this occasion a rapid increase in concentration in sediment to the
north of the Dutch coast is also seen, indicating strong advection of
resuspended PCB 153 into this area, followed by local sinking. The
last major event in January 2005 makes a very slight impression on
concentration in the water column to the west of Jutland. On
153 subsequently sinks back down into the sediment, where almost
all of it is contained, and where it can remain for a relatively long time
due to its long half-life. Since relative to the water column, very little
γ-HCH is contained in sediment, storm events cannot greatly affect
total concentration in water. The point is reinforced by comparing ratios
of the two POPs in sediment to water; the ratio of PCB 153 being several
orders of magnitude greater.

To present direct ‘communication’ between sediment and water
column, model time series of concentrations of the two POPs in
water and sediment are plotted with daily mean bed shear velocity
at a single point in the German Bight, Fig. 11 (same location as in
Fig. 5c). Looking first at PCB 153, the same four events as in
Fig. 5c) are apparent, because of the proximity of the location to the
point shown in Fig. 5c). But now, we see the direct local exchange
between water column and sediment. A clear seasonal cycle is seen
in the bed shear velocity, with highest values in winter due to the
regular occurrence of storm events. The ‘wavy’ red line in Fig. 11b)
corresponds to this seasonality. The bed shear velocity often exceeds
the critical value of 2-8 cm/s in winter, black line, indicating that
erosion can occur during these storms.

Notable change of concentration in the water column generally
occurs when the bed shear velocity is generally greater than 6 cm/s
with higher values resulting in greater erosion, and a value 11 cm/s
would be necessary to empty the model sediment to its lowest
layer. Note that the displayed bed shear velocities are only daily aver-
gaes, and do not show the development of the velocity. A mean value
of 6 cm/s can come from large or small variations around this value.
In sediment dynamics, it is not the average but the peak values that
determine erosion events and the amount of resuspended mass. For
the case of an average of 6 cm/s, some really strong events, with,
e.g., 10 cm/s peaks, can be included, which would more or less
empty the model of sediment in the region of the storm, while within
other 24 h periods with the same average, you might have only
values between 5 and 7 cm/s, an erosion event that would only
scratch the sediment surface. Therefore, occasionally, high velocities
are not accompanied by clear erosion events.

5.5. Seasonality and trends of total mass of γ-HCH and PCB 153 in water
and sediment

Total mass of γ-HCH and PCB 153 for the entire model domain are
presented as time series for the period 1996–2005, Fig. 8 second and
bottom panels, respectively. Total mass of γ-HCH in the water column
drops from a maximum of ~7·10^5 kg at the beginning of the time
series to ~2·10^4 kg at the end, ~30% of the initial mass. An annual
cycle is seen with values increasing from minimum around February,
following increasing gas deposition (Fig. 8 top panel), reaching
maximum values around July/August, before decreasing in the fall,
now as a result of decreasing dry gas deposition, and completing the annual cycle in winter.

The total mass $\gamma$-HCH contained in sediment is over two orders of magnitude less than in the water column. Again, a clear annual cycle is seen with extrema appearing about two months after those in the water column due to settling in summer and resuspension in winter. Total mass in 2005 has also been reduced to ~30% of that in 1996.

For PCB 153, the total mass in sediment is more than an order of magnitude greater than that in water. Total mass in water starts out at around 50 kg, remains there until 2000, before dropping off to about 20 kg towards the end of the time series. Total mass in sediment in 1996 is ~1800 kg and decreases fairly linearly to ~900 kg in 2005. Strong winter storm events cause resuspension of PCB 153 from the sediment into the water column, resulting in a rapid decrease of mass in sediment accompanied by a simultaneous rapid increase of mass in water. These mobilised POPs are equilibrially partitioned, and result in increased volatilisation and, thus, potentially delivering substantial loads of POPs to Europe.

Typically, PCB 153 concentrations in water increase in the winter, especially so during strong storms, remaining high until the spring when they return to pre-winter values. Concentrations generally increase in summer, when the North Sea can be net depositional for PCB 153, before decreasing in September–October, thus completing the annual cycle. Although the trend in sediment is downward, an annual cycle is still apparent and concentrations increase in spring and summer when primary production is greatest and decrease somewhat in fall before the onset of winter storms.

The storm and resuspension events seen for PCB 153 are also found for $\gamma$-HCH. These events, however, make very little impact on the total amount of $\gamma$-HCH in the water column since, relatively speaking, so little of it is contained in the sediment. The events also result in rapid increases in volatilisation of, notably, PCB 153 and, to a lesser extent, $\gamma$-HCH.

6. Summary and conclusions

The cycling of two selected POPs with very different properties, $\gamma$-HCH and PCB 153, has been investigated with a fate and transport ocean model, FANTOM, for the North Sea system. Additionally, their seasonality and related trends have been discussed. Since the fate of POPs in the ocean are dependent upon hydrodynamic processes and variables, the FANTOM has been combined with a high resolution version of the HAMSOM hydrodynamic model. The model domain includes the entire North Sea system and model simulations are for the period 1996–2005.

The HAMSOM and FANTOM models have been validated by comparing simulated results with available observations. Since the results from both models are generally in good to excellent agreement with available observations, we concluded that all aspects of both models were functioning well.

The North Sea acts as a sink for $\gamma$-HCH. Gas deposition is the major contributor to air–sea exchange followed by volatilisation, and minor contributions from wet and particle deposition, and deposition through river input.

The North Sea acts as a source of PCB 153 to the atmosphere. Volatilisation is the largest contributor to air–sea exchange, while river input is the largest source, being about half as big. Gas and wet deposition are 3–4 times less, while particle deposition is more than an order of magnitude less. This finding is in contradiction to results of Ilyina et al. (2008). However, as mentioned already, in their study the northern part of the North Sea was neglected and, moreover, they used essentially constant atmospheric forcing fields, as opposed to our spatially and temporally resolved values.

For both POPs, exchange at the open boundaries with the North Atlantic Ocean, the English Channel and the Baltic Sea is negligible.

Concentrations and total mass of $\gamma$-HCH in the water column are greatest in summer, due to the large net depositional flux from the...
atmosphere in the spring and early summer months, and are least in winter. The annual cycle in sediment lags that in the water column by about two months. For PCB 153, concentrations in the water column are greatest in winter, when erosion due to storms causes resuspension of sediment fine fraction, the carrier of PCB 153. The resuspended PCB 153 settles out of the water column and back into the sediment in the spring.

A significant result is that POPs mobilised from bottom sediments into the atmosphere during storm events have the potential to deliver substantial loads of POPs into Europe.

The trends in both POPs is downward for the 10-year period of the simulations. The total mass of γ-HCH in 2005 is reduced 30% of what it was in 1996, in both the water column and in sediment. For PCB 153, the total mass is reduced 50% of what it was in 1996, in both the water column and in sediment. The reason for the downward trend is reduced concentrations in the atmosphere and river input.

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References


