A fate and transport ocean model for persistent organic pollutants and its application to the North Sea

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Abstract

An ocean model (FANTOM) has been developed to investigate the fate of selected persistent organic pollutants (POPs) in the North Sea. The main focus of the model is on quantifying the distribution of POPs and their aquatic pathways within the North Sea. Key processes are three-dimensional transport of POPs with ocean currents, diffusive air–sea exchange, wet and dry atmospheric depositions, phase partitioning, degradation, and net sedimentation in bottom sediments. This is the first time that a spatially resolved, measurements-based ocean transport model has been used to study POP-like substances, at least on the regional scale. The model was applied for the southern North Sea and tested by studying γ-HCH behaviour in sea water in the years 1995 to 2001. The model’s structure and processes are described in details. Concentrations of γ-HCH and its fluxes between upper sediment, sea and atmosphere were modelled, based on discharge and emission estimates available through various monitoring programmes. Model results are evaluated against measurements. Modelled concentrations of γ-HCH in sea water are in good agreement with the observations; the spatial distribution and the downward trend in the entire North Sea are reproduced during the simulation period. The correlation between the model results and measurements is better during warmer seasons suggesting the importance of the temperature dependency of the air–sea exchange.

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1. Introduction

Persistent organic pollutants (POPs) are synthetic organic chemical compounds which are environmentally persistent, bioaccumulative and toxic. They can be transported over long distances in the atmosphere and oceans. Included in the POPs are organochlorine compounds, e.g. hexachlorocyclohexane (HCH) which is the most abundant organochlorine pesticide in both the atmosphere and oceans. POPs are distributed throughout the oceans as a consequence of atmospheric deposition and direct introduction into aquatic systems. Already in the 1970s, it was being predicted that the oceans may be recipients of most of the persistent pesticides used globally (Goldberg, 1975). This was confirmed by observations (Bidleman et al., 1995) and global budget calculations (Strand and Hov, 1996) showing that the oceans are a major storage medium of HCH. Oceans are traditionally thought to be a global reservoir and ultimate sink of many POPs (Iwata et al., 1993; Dachs et al., 2002) and may be a slow but significant medium for their long-range transport (Wania and Mackay, 1999; UNEP, 2003). Upon long-term ongoing uptake of HCH the ocean may achieve equilibrium with respect to HCH partitioning between
air and sea, which has been observed for $\alpha$-HCH (Bidleman et al., 1995; Lakaschus et al., 2002).

The North Sea is surrounded by highly industrialised countries and receives large amounts of POPs from atmospheric deposition and river discharge. Monitoring campaigns show that nearly all known POP-like chemicals have been detected in the North Sea (OSPAR, 2000; Weigel et al., 2002) as a consequence of their persistence and continued input from contaminated sites and distant sources. Although concentrations of some POPs in the North Sea have been diminishing since the early 1990s, even the reduced levels can still be harmful to the environment (OSPAR, 2000). Concentrations of some POPs in sea water are often five orders of magnitude higher than those in the air (Wania and Mackay, 1999). This will contribute to the capacity of sea water to act as a source by releasing POPs to the atmosphere via the volatilisation process (Hornbuckle et al., 1993; Bidleman et al., 1995; Ridal et al., 1996; Sahsuvar et al., 2003). Furthermore, in shelf areas the sinking particles carry POPs down to the bottom sediments; they may then enter the water column again via re-suspension and return back to the sea surface. Therefore, as primary pollutant sources are reduced, remobilisation from previous repositories, such as water bodies, can act as secondary sources to the atmosphere.

A model to investigate the environmental fate of POPs is a unique tool for testing hypotheses about the processes affecting POPs cycling, especially those whose characteristics are not accessible by experimental approaches, e.g. for calculating single episodes of pollutant release and transport. With regard to availability of comprehensive data on POPs, the North Sea is comparatively well served. The datasets have been accumulated throughout national and international monitoring programmes (OSPAR, 2000) and research projects (Sündermann, 1994), though the data coverage is better for Lindane ($\gamma$-HCH) than for other compounds. The environmental fate of $\alpha$- and $\gamma$-HCH in the Baltic Sea has been studied using box models within the POPCYCLING-Baltic project during 1996–1999 (Pacyna, 1999). Besides that, there have been campaign-based studies, limited in both time and space, which addressed the occurrence and distribution of POPs in open ocean and shelf seas (Iwata et al., 1993; Schulz-Bull et al., 1998; Lakaschus et al., 2002; Jaward et al., 2004).

The fate of POPs in sea water depends on a number of mechanical (transport with moving flows), chemical (chemical decay, amalgamation with other chemicals, transfer to gaseous state, etc.), physical (transfer to another aggregative state, adsorption) and biological (pollutant accumulations and transport by biota) processes. These processes can only be fully taken into account with a three-dimensional, hydrodynamic ocean model. Therefore, the objective of this study was to design and evaluate such a model and use it to investigate the cycling of $\gamma$-HCH in the North Sea. It is a first study of this kind.

Section 2 describes the architecture of the fate and transport ocean model (FANTOM). Results from the 6.5 years simulations of the fate of $\gamma$-HCH in the North Sea, model evaluation and its sensitivity towards individual processes are presented in Section 3. Section 4 gives the conclusions and an outlook for future developments.

2. Model description

FANTOM is a three-dimensional Eulerian model designed for describing the long-term fate of POP-like contaminants in the coastal and shelf aquatic environment. FANTOM is aimed at tracing substances released from point or diffuse sources. The tracers can enter the model domain via rivers, adjacent seas or atmospheric deposition. The key processes are described in Fig. 1. They fall into four broad categories.

(a) Transport with ocean currents. In sea water the pollutant is transported by ocean currents via advection and turbulent diffusion (Section 2.1).

(b) Air–sea exchange. Air–sea exchange (Section 2.2) is represented by three mechanisms: reversible gaseous exchange (Appendix A), dry particle deposition (Appendix B) and wet deposition (Appendix C).

(c) Phase distribution. The pollutant in the model is either dissolved or bound to suspended particulate matter (SPM) present in sea water (Section 2.3). The particle-bound fraction of the pollutant (Appendix E) follows the SPM dynamics (Appendix D). It is subject to gravitational sinking and deposition to the bottom sediments. Redistribution of particles takes place in the sediment due to the disturbance of

![Fig. 1. Key processes included in FANTOM affecting the fate of POPs.](image-url)
sediment layers by biological activity (bioturbation). It can also be re-mobilised back to the water column when disturbed by erosion processes.

(d) Degradation in sea water: Both tracer fractions are subject to degradation in sea water (Section 2.4).

2.1. Transport with ocean currents

Evolution of the total (dissolved and particle-bound) concentration of the pollutant $C$ at a fixed location results from the sum of sources, sinks, and mechanical transport of a flow field. The latter has a key role in shaping the pollutant’s field in sea water. It has two components: transport governed by the averaged current velocity field (advection) and transport due to the presence of the random chaotic component in the velocity field (diffusion). Turbulence in the ocean is determined by the current velocity gradients, surface and deep perturbations, and sea water stratification. It plays an important role in the intensity of the diffusion processes and thus the pollutant’s spatial distribution (Baumert et al., 2005). Eulerian transport of tracers due to advection and turbulence is calculated in FANTOM in a similar way to that used by Pohlmann (1987) where only passive transport of conservative and dissolved tracers in the North Sea is considered. Additionally, tracers in FANTOM may undergo other processes in sea water (Fig. 1) acting as sources ($Q_C$) or sinks ($R_C$) in the model, leading to the following formulation:

$$
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( K_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_z \frac{\partial C}{\partial z} \right) - \left( u \frac{\partial C}{\partial x} + v \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} \right) + Q_C(t,x,y,z) - R_C(t,x,y,z)
$$

Horizontal flow field components in eastern and northern directions ($u$ and $v$) at every model grid point are input parameters required for calculating the horizontal advection of the tracer concentration. These parameters are provided by the ocean circulation model (Section 2.5.2), with the vertical component of the flow field $w$ being calculated from $u$, $v$ using the continuity equation. In addition the horizontal and vertical turbulent diffusion is calculated using the horizontal diffusion coefficients ($K_x$ and $K_y$) and the vertical diffusion coefficient ($K_z$) which are also provided by the ocean circulation model (Section 2.5.2).

2.2. Air–sea exchange

Air–sea exchange is believed to be the major pathway for atmospheric input to oceans and seas for many organochlorine contaminants (Iwata et al., 1993; Bidleman et al., 1995; Wania and Mackay, 1999; Lakaschus et al., 2002). Atmospheric deposition can occur as dry gaseous or dry particle deposition, or as wet deposition of gases and particles incorporated in rain droplets or snow. Hence, the net flux of a pollutant to the sea surface from the atmosphere $F_{surf}$ (ng m$^{-2}$ s$^{-1}$) is represented in FANTOM by the net gaseous air–sea flux $F_{a-w}$ (Appendix A), the dry particle deposition flux $F_{dry}$ (Appendix B) and the wet deposition flux $F_{wet}$ (Appendix C):

$$F_{surf} = F_{wet} + F_{dry} + F_{a-w}$$

Previous studies have shown that gaseous air–sea exchange dominates over wet and dry particle deposition of organochlorine compounds. Exceptions occur in regions and seasons with intensive precipitation and areas with a high concentration of atmospheric aerosol particles. The relative importance of the different mechanisms of the air–sea exchange is still in debate.

2.3. Phase distribution

Contaminants may be present in sea water either freely dissolved or bound to the suspended particulate matter (SPM). Redistribution between the dissolved and particulate phases essentially affects the dynamics of the tracer concentration distribution in the marine environment. The dissolved tracer fraction follows the path of the water masses, while the particles bound fraction quickly sedimentises and remains in areas where sedimentation is promoted.

Particulate organic carbon (POC), an organic carbon fraction of SPM, is calculated in FANTOM (Appendix D) and is used as a sorbing matrix for POPs. Such an approach is commonly used in modelling POPs accumulation in biota (Skoglund and Swackhamer, 1999) and their export to the deep sea (Scheringer et al., 2004).

The substance fraction bound to POC, $f_{POC}$ is calculated (Skoglund and Swackhamer, 1999; Scheringer et al., 2004) as:

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

The organic carbon–water equilibrium partition coefficient $K_{oc}$ (l kg$^{-1}$) is compound specific (Appendix E) and $C_{POC}$ (kg l$^{-1}$) is the concentration of POC in the solution (Appendix D).

Eq. (3) implies that the transfer of POPs from the particulate phase to the dissolved phase and thus also their transport behaviour are controlled by the abundance of
POC. This implies that increasing POC content will transfer the chemical from the dissolved to the particulate state. Higher POC concentrations result in lower concentrations of POPs (in ng kg\(^{-1}\)) in the particulate phase. Most of the POC present in sea water is in the form of particles (Appendix D), which sink to the sea bed by gravitational settling with a sinking velocity \(v_{\text{set}}\) (m s\(^{-1}\)). Correspondingly, the flux of chemicals bound to POC that is removed from the upper sea layers together with sinking particles \(F_{\text{set}}(\mu g \ m^{-2} \ s^{-1})\) is calculated as:

\[
F_{\text{set}} = v_{\text{set}} \cdot f_{\text{POC}} \cdot C
\]  

(4)

Many organic compounds are lipophilic (fat soluble) and hydrophobic. Lipophilic compounds are characterised by high values of octanol–water partitioning coefficient, \(K_{\text{ow}}\) (\(>10^3\)) (Appendix E). These are mostly bound to POC and tend to disperse and accumulate in the sediment rather than in the water column.

### 2.4. Degradation in sea water

Combined abiotic (due to photolysis and hydrolysis) and biotic degradation in sea water is represented in the model by a first order rate decay coefficient, \(k_{\text{deg}}\) (s\(^{-1}\)), with the higher order kinetics being neglected. It is assumed that degradation is linearly dependent on the compound total concentration \(dC/dt = -k_{\text{deg}} C\). No measurements of degradation in sea water exist. There is no experimental evidence suggesting that anthropogenic organic compounds bound to marine SPM are more resistant to degradation processes than those dissolved in sea water. Consequently the \(k_{\text{deg}}\) value for \(\gamma\)-HCH (Table 1) has been chosen on the basis of a thorough compilation of physical–chemical properties of selected POPs (Klöpffer and Schmidt, 2001; Lammel et al., 2001).

It is a recommended value for fresh water divided by a factor of 10 to account for reduced biotic degradation in sea water relative to fresh water. Following the expert estimates (EU TGD, 1996) the \(k_{\text{deg}}\) value is assumed to double per 10 K temperature increase. Degradation in the sediment is neglected.

### 2.5. Model setup

#### 2.5.1. Model area

The model covers the southern and central North Sea up to 57.1°N (Fig. 2), a shallow region with mean depth of 50 m and a maximum depth of 160 m. The horizontal resolution of the model is 1.5° by 2.5° (corresponding to 2.5–3 km) and there are 21 vertical layers of varying depth, i.e. 5 m in the upper 50 m, and 10 m in lower layers. The number of vertical layers is different from one grid point to another depending on the local depth.

In the North Sea the distribution and mixing of water masses is largely subject to tidal currents, meteorological conditions, and run-off from rivers and the Baltic Sea. Westerly winds prevail over the North Sea. The predominant circulation driven by winds and tides is anticlockwise along the North Sea coast causing short flushing times (time needed for the water mass to be exchanged). That means that the existing climate happens to be favourable for the North Sea ecosystem. However, this circulation pattern can regionally be reversed when transient prevailing easterly winds cause an extension of water mass flushing times (Sündermann et al., 2002).

The flushing time of water, calculated by the inflows and outflows, is estimated to be about 1 year in the entire North Sea (OSPAR, 2000). However the flushing time varies in different subregions of the North Sea: it ranges from 28 days in the northern part to 40 days in the central North Sea (Lenhart and Pohlmann, 1997). The

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept of the temperature dependent</td>
<td>(b)</td>
<td>10.14±0.55</td>
<td>–</td>
<td>Sahsuvar et al., 2003</td>
</tr>
<tr>
<td>Henry’s law constant</td>
<td>(K_{\text{ow}})</td>
<td>7.54±0.54</td>
<td>–</td>
<td>Kucklick et al., 1991</td>
</tr>
<tr>
<td>Slope of the temperature dependent</td>
<td>(m)</td>
<td>−3208±161</td>
<td>K</td>
<td>Sahsuvar et al., 2003</td>
</tr>
<tr>
<td>Henry’s law constant</td>
<td>(K_{\text{ow}})</td>
<td>−2382±160</td>
<td>K</td>
<td>Kucklick et al., 1991</td>
</tr>
<tr>
<td>Dry particle deposition velocity</td>
<td>(v_{\text{dep}})</td>
<td>(2 \times 10^{-5})</td>
<td>m s(^{-1})</td>
<td>McMahon and Denison, 1979; Slinn, 1983</td>
</tr>
<tr>
<td>Specific aerosol surface</td>
<td>(\theta)</td>
<td>(1.5 \times 10^{-4})</td>
<td>m(^2) m(^{-3})</td>
<td>Pekar et al., 1998</td>
</tr>
<tr>
<td>Adsorption constant</td>
<td>(s)</td>
<td>0.17</td>
<td>Pa m</td>
<td>Junge, 1977</td>
</tr>
<tr>
<td>Octanol–water partitioning coefficient</td>
<td>(K_{\text{ow}})</td>
<td>(3.98 \times 10^7)</td>
<td>–</td>
<td>Klöpffer and Schmidt, 2001</td>
</tr>
<tr>
<td>Settling velocity of SPM</td>
<td>(v_{\text{set}})</td>
<td>(3 \times 10^{-4})</td>
<td>m s(^{-1})</td>
<td>Pohlmann and Puls, 1994</td>
</tr>
<tr>
<td>Threshold shear velocity for erosion of SPM</td>
<td>(v_{\text{e}})</td>
<td>(0.28)</td>
<td>m s(^{-1})</td>
<td>Pohlmann and Puls, 1994</td>
</tr>
<tr>
<td>Threshold shear velocity for deposition of SPM</td>
<td>(v_{\text{d}})</td>
<td>(0.01)</td>
<td>m s(^{-1})</td>
<td>Pohlmann and Puls, 1994</td>
</tr>
<tr>
<td>Degradation rate in ocean water at 298 K</td>
<td>(k_{\text{deg}})</td>
<td>(2.3 \times 10^{-8})</td>
<td>s(^{-1})</td>
<td>Klöpffer and Schmidt, 2001</td>
</tr>
</tbody>
</table>
prevailing currents cause polluted coastal waters to have high residence time (time it takes for a substance to leave the water body, e.g. the North Sea) and be transferred along the coastline. This aspect is of key importance, because lying between land and sea coastal habitats are subject to a range of influences and are particularly sensitive to anthropogenic pressure.

2.5.2. Ocean circulation

The transport processes in FANTOM which are driven by ocean currents are calculated from the distributions of the flow field (Section 2.1) available from ocean circulation models. In this study the HAMburg Shelf Ocean Model (HAMSOM) was coupled with FANTOM (Fig. 3) for the entire simulation period. HAMSOM is a baroclinic, primitive equation circulation model based on a semi-implicit numerical scheme described elsewhere (Backhaus, 1985; Pohlmann, 1996). HAMSOM covers the same domain and uses the same spatial resolution of 1.5′ by 2.5′ as FANTOM (Fig. 2). Simulations were carried out with a time step of 10 min. Atmospheric forcing for HAMSOM is calculated using the ECMWF ERA-40 data at a 6 h time step and 1.125° spatial resolution (ECMWF, 2005). Boundary conditions for the open ocean are obtained from HAMSOM applied to the entire North Sea and a part of the north-eastern Atlantic (Pohlmann, 1996).

The results of the circulation model (e.g. flow fields and their variances, vertical diffusion coefficients, sea temperature and salinity distribution and sea surface height — see Fig. 3) are stored as daily means averaged over two periods of the predominant semidiurnal lunar tide $M_2$ (Bartels, 1957). Such a coupling approach has been used previously (Pohlmann, 1987; Luff and Pohlmann, 1995).

2.5.3. Compound selection

Lindane is one of the most widely used pesticides globally and it has been used for a long time. It was chosen for this study as it is a semi-volatile organic compound which is mostly observed in the dissolved phase in water. It possesses a relatively high water–air partitioning coefficient and a low octanol–water partitioning coefficient (Table 1).

Lindane consists of about 98% of $\gamma$-HCH, an isomer of the technical HCH which contains five stable isomers, namely $\alpha$ (60–70%), $\beta$ (10–12%), $\gamma$ (6–10%), $\delta$ (3–4%) and $\epsilon$ (3–4%) (Willet et al., 1998). The last two of these...
compounds are not routinely found in environmental samples. Technical HCH was banned in the 1980 because of its toxic effects in the environment. γ-HCH is still used in many countries as an insecticide in agriculture, as a wood and building preservative, and as a biocide to combat lice and scabies. Its use in the countries adjacent to the North Sea is restricted (SRU, 2004). But despite restrictions and bans, α- and γ-HCHs are still widely found in the North Sea. A large proportion enters the water through flooding, run-off from treated areas, and incorrect disposal of left-over mixtures into farm drains and sewage systems. Atmospheric depositions can also contain γ-HCH transported from remote regions (Semenen and Lammel, 2005).

Inventories and knowledge about HCH isomers in general and γ-HCH in particular are relatively complete. γ-HCH is subject to regular monitoring in the sea through national (Bund-Länder monitoring programme in Germany) and international monitoring programmes (OSPAR, HELCOM).

2.5.4. Initial and boundary conditions

Physical–chemical properties of a chemical, environmental parameters and release data are required input data for the model (Fig. 3). Initial and boundary conditions include initial distribution of the selected chemical and its values on the boundaries throughout the simulation period. For the studied domain (Fig. 2), the following boundaries are considered in the model: air–sea interface and boundaries with the neighbouring water bodies (i.e. Atlantic Ocean, Baltic Sea, English Channel) and the inflowing rivers that drain into the North Sea.

Daily mean distributions of flow components, their variances, sea surface height, diffusion coefficients, salinity and sea temperature were obtained from the corresponded HAMSOM simulations (Section 2.5.2).

The initial distribution of γ-HCH concentrations (Fig. 4) and its values on the sea boundaries were interpolated using measured non-filtered samples (Theobald et al., 1996) and therefore represent the total concentration. Initial conditions for the concentration are defined by the function $C_0$ as $C(x,y,z,0)=C^0(x,y,z)$. Boundary conditions for the water boundaries $B$ are prescribed:

$$C|_{(x,y,z)\in B} = C^B(x,y,z,t)$$

where $C^B$ is the concentration at the water boundary. The boundary condition at the coast is $\partial C / \partial n|_{(x,y,z)\in t=0} = 0$. At the bottom, with the bottom depth $D$, the tracer flux to the bottom is calculated according to Eq. (4) $F|_{z=D} = -F_{set}$.
When the re-suspension occurs (Appendix D) the tracer flux at the sea bottom is directed upwards.

Because the North Sea is a tidally influenced shelf sea, the inflowing rivers have estuarine characteristics, i.e. the tide and river flow interact. The phenomenon of mixing water masses is taken into account by using measurements at the last tide-free gauge station of each river (Lenhart and Pätsch, 2004). The river loads of the selected...
chemical in FANTOM from the European continental rivers including the Elbe, the Weser, the Ems, the Rhine and Meuse, and the Scheldt are calculated as a product of the daily fresh water discharge \( Q_{riv} \) (m\(^3\)/s\(^-1\)) (Lenhart and Pätzsch, 2004) and the concentrations of the compound \( C_{riv} \) (ng l\(^-1\)) (Fig. 5b). Data for \( C_{riv} \) from the German rivers were provided by the various Environmental Agencies (ARGE-ELBE, 2005; NLOE, 2005). The pollutant concentrations in the Dutch rivers are available from the Dutch online database Waterbase (DONAR, 2005). The loads of POPs reported to OSPAR (2000) were used for the Thames and the Humber (Fig. 2). Values of \( C_{riv} \) are available with different temporal resolutions (e.g. monthly means) and were interpolated using spline interpolation to fit the temporal resolution of the model.

Boundary conditions at the air–sea interface are based on measured monthly averaged total (gaseous and particle sorbed) concentration of \( \gamma \)-HCH in the air and its total concentration in precipitation \( C_{pr} \) (Fig. 5a) available from the EMEP online database (EMEP, 2005). The measured values from several EMEP stations (Fig. 2) were interpolated to the whole domain. The wind speed and direction, air temperature and precipitation rate \( P \) are calculated using the ECMWF 6 hourly ERA-40 data (ECMWF, 2005). The tracer’s flux on the sea surface is determined according to Eq. (2):

\[
F_{iz=0} = F_{surf} \]

Compound specific physical–chemical properties (e.g. \( K_{ow} \) and \( \delta_{iso} \)) are listed in Table 1. The Henry’s law constants were calculated as a function of temperature using values recently given by Sahsuvar et al. (2003) for all model simulations with the exception of the experiment where values reported by Kucklick et al. (1991) were used.

### 3. Results and discussion

The model simulations were carried out for the period from July 1995 to December 2001 with a time step of 10 min. Model results were stored as daily averaged values.

#### 3.1. Model evaluation

Model evaluation consisted of two stages.

(a) calculated \( \gamma \)-HCH concentrations in sea water were compared with the measured ones (Section 3.1.1).

(b) model sensitivity to input parameters was analysed (Section 3.1.2).

Time series for observed \( \gamma \)-HCH concentrations in sea water covering the simulation period were available in 16 locations (Fig. 2). Most of the data were provided by the German Oceanographic Data Centre (DOD, 2005) covering only the German exclusive economic zone of the North Sea. Time series at locations N, O and P are from Dutch database Waterbase (DONAR, 2005).

#### 3.1.1. Comparison between modelled and measured sea water concentrations

Daily averaged concentrations in the uppermost sea layer were compared with the individual measurements and plotted for six of these points (Fig. 6) located in different subregions of the North Sea and with sufficient number of measurements. A clear seasonal pattern with

<table>
<thead>
<tr>
<th>Symbol on the map</th>
<th>Lat.</th>
<th>Long.</th>
<th>Number of measurements</th>
<th>Months of sampling</th>
<th>Measurements: mean and range (ng l(^-1))</th>
<th>Model results: mean and range (ng l(^-1))</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>54.00° N</td>
<td>8.00° E</td>
<td>36</td>
<td>5–9</td>
<td>1.50 (0.37 – 3.00)</td>
<td>1.48 (0.58 – 3.03)</td>
<td>0.94</td>
</tr>
<tr>
<td>B</td>
<td>53.72° N</td>
<td>7.45° E</td>
<td>14</td>
<td>11–2</td>
<td>0.70 (0.10 – 3.00)</td>
<td>1.41 (0.81 – 2.24)</td>
<td>0.35</td>
</tr>
<tr>
<td>C</td>
<td>53.85° N</td>
<td>8.06° E</td>
<td>14</td>
<td>11–2</td>
<td>0.83 (0.10 – 3.00)</td>
<td>1.27 (0.68 – 1.88)</td>
<td>0.40</td>
</tr>
<tr>
<td>D</td>
<td>53.86° N</td>
<td>8.13° E</td>
<td>14</td>
<td>11–2</td>
<td>0.80 (0.10 – 2.00)</td>
<td>1.32 (0.69 – 1.32)</td>
<td>0.30</td>
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<tr>
<td>E</td>
<td>53.98° N</td>
<td>8.22° E</td>
<td>26</td>
<td>11–3, 5, 7–9</td>
<td>1.86 (0.10 – 3.00)</td>
<td>1.32 (0.67 – 2.47)</td>
<td>0.74</td>
</tr>
<tr>
<td>F</td>
<td>54.05° N</td>
<td>7.86° E</td>
<td>13</td>
<td>11–2</td>
<td>0.82 (0.10 – 2.00)</td>
<td>1.08 (0.62 – 1.52)</td>
<td>0.23</td>
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<tr>
<td>G</td>
<td>54.22° N</td>
<td>8.38° E</td>
<td>41</td>
<td>1, 2, 5–9</td>
<td>1.65 (0.43 – 3.95)</td>
<td>1.77 (0.86 – 3.00)</td>
<td>0.77</td>
</tr>
<tr>
<td>H</td>
<td>54.25° N</td>
<td>7.50° E</td>
<td>25</td>
<td>5–9</td>
<td>1.63 (0.42 – 2.55)</td>
<td>1.19 (0.68 – 1.76)</td>
<td>0.93</td>
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<tr>
<td>I</td>
<td>54.67° N</td>
<td>6.33° E</td>
<td>20</td>
<td>5–9</td>
<td>1.45 (0.30 – 3.49)</td>
<td>0.95 (0.38 – 1.31)</td>
<td>0.77</td>
</tr>
<tr>
<td>J</td>
<td>55.00° N</td>
<td>6.25° E</td>
<td>12</td>
<td>5–8</td>
<td>0.71 (0.23 – 1.32)</td>
<td>0.67 (0.35 – 1.23)</td>
<td>0.84</td>
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<tr>
<td>K</td>
<td>55.00° N</td>
<td>8.25° E</td>
<td>21</td>
<td>5–9</td>
<td>1.25 (0.42 – 2.75)</td>
<td>1.50 (0.74 – 2.33)</td>
<td>0.86</td>
</tr>
<tr>
<td>L</td>
<td>55.50° N</td>
<td>4.17° E</td>
<td>18</td>
<td>5, 9, 12</td>
<td>0.58 (0.17 – 0.95)</td>
<td>0.58 (0.22 – 0.91)</td>
<td>0.84</td>
</tr>
<tr>
<td>M</td>
<td>56.00° N</td>
<td>3.00° E</td>
<td>4</td>
<td>7</td>
<td>0.42 (0.28 – 0.70)</td>
<td>0.49 (0.38 – 0.59)</td>
<td>0.45</td>
</tr>
<tr>
<td>N</td>
<td>52.58° N</td>
<td>3.53° E</td>
<td>21</td>
<td>2, 3, 5, 8, 11, 12</td>
<td>0.79 (0.20 – 1.80)</td>
<td>1.00 (0.63 – 1.51)</td>
<td>0.83</td>
</tr>
<tr>
<td>O</td>
<td>51.96° N</td>
<td>2.68° E</td>
<td>6</td>
<td>2, 5, 8, 11</td>
<td>1.25 (0.50 – 0.70)</td>
<td>1.08 (0.96 – 1.15)</td>
<td>0.68</td>
</tr>
<tr>
<td>P</td>
<td>54.42° N</td>
<td>4.04° E</td>
<td>6</td>
<td>8</td>
<td>0.72 (0.10 – 1.20)</td>
<td>0.67 (0.32 – 1.07)</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Fig. 6. Observed (dots) and FANTOM (solid line) γ-HCH concentrations (ng l\(^{-1}\)) in the surface layer at the locations A, G, K, L, N, P. Geographical locations of points are given in Table 2 and are shown in Fig. 2.
higher concentrations in summer is predicted for most years in all locations. Similar patterns are also found in the atmospheric concentrations (Fig. 5a) and in the continental river loads of $\gamma$-HCH (Fig. 5b). The highest concentrations, up to 3.95 ng/l (Table 2), were found at locations near the coast, e.g. A (Fig. 6a), G and K (Fig. 6b and c); the lowest ones, of less than 0.2 ng/l (Table 2), were found in the open North Sea at locations L and P (Fig. 6d and f). Concentration of $\gamma$-HCH had decreased in all locations throughout the simulation period. The biggest drop in $\gamma$-HCH concentrations, 6–12 times, was found in the German Bight and near the southern North Sea coast, with the smallest, 4–5 times, in the central North Sea. Both observed and modelled concentrations in sea water at all locations increased during the first half of the simulation period, with highest concentrations in 1997–1998. During the second half of the simulation, in the years 1998–2001, there are negative trends in concentrations at all locations, both in observations and predictions by FANTOM. Also atmospheric concentrations of $\gamma$-HCH reflect such pattern with the highest concentrations of $\gamma$-HCH detected in precipitation during spring.
and summer of 1997 and decreased concentrations during 1998–2001 (Fig. 5a).

At most of the locations, namely at A, E, G to P, measurements were made during warm seasons (May–September) corresponding to the predicted maxima. At locations B, C, D and F measurements were conducted between December and March.

In order to evaluate the model results, measured \( \gamma \)-HCH concentrations are plotted against calculated ones in scatter plots (Fig. 7) for the same locations as in Fig. 6. Correlation coefficients for all locations where time series were available are presented in Table 2. Good correlation was found for locations A, H and P with correlation coefficients of 0.94, 0.93 and 0.94 respectively. Lower correlation coefficients between 0.23 and 0.40 were found for the locations F, D and B where the time series consist of the measurements conducted between December and March. The number of measurements and their temporal resolution, in particular at the locations P, O and M, make further statistical analysis inappropriate.

Time series of \( \gamma \)-HCH concentration in the southern North Sea surface water reported elsewhere (SRU, 2004) show a gradual decrease since the 1980s due to the restriction in technical HCH application in the countries adjacent the North Sea. This decrease is captured by the model during the studied period. Furthermore, model results suggest that \( \gamma \)-HCH concentrations declined in the entire modelling domain.

3.1.2. Uncertainty and sensitivity analysis

Although \( \gamma \)-HCH is a rather well studied contaminant and subject to national and international monitoring programmes, data availability remains an important constraint for constructing an observation based, spatially resolved model. Unlike regular monitoring in the atmosphere, where monthly or even weekly measurements of \( \gamma \)-HCH are available for the European region (e.g. EMEP, 2005), observations of sea water concentrations are discrete in time and space due to operational constraints. Many model input parameters are of limited availability and have to be estimated by extrapolation and interpolation methods. Those values that are available for a given parameter often exhibit large variability and uncertainties. Also there are uncertainties introduced by the poor temporal and spatial resolution in measured data, both in the sea water and in the atmosphere.

Experiments aimed at explaining the deviations in modelled and observed \( \gamma \)-HCH concentrations were performed (Fig. 8). In the first experiment it was assumed that the concentration of \( \gamma \)-HCH in water flowing into the North Sea from the English Channel and from the northern boundary of the modelling domain is zero,
i.e. $C^B = 0$ (Eq. (5)). The resulting time series of the concentration was plotted for location A in the German Bight where the impact of inflow from these boundaries was expected to be less pronounced than elsewhere. In the second experiment the Henry’s law constant temperature dependency was calculated using the values obtained by Kucklick et al. (1991) instead of those by Sahsuvar et al. (2003) used in other model runs (Table 1). Daily averaged concentrations in the uppermost sea layer resulting from the main simulation and both experiments were compared with the individual measurements at the location A (Fig. 8).

No regular measurements of $\gamma$-HCH concentrations in the English Channel and on the northern sea boundary were available for this study. Since concentrations in the whole North Sea decreased they have probably also decreased in the English Channel and on the northern sea boundary without being captured by the model. This offers an explanation for the overestimation in calculated concentrations during the years 2000–2001. The

Fig. 9. Vertically averaged annual mean concentrations of $\gamma$-HCH (ng l$^{-1}$) in the North Sea calculated by FANTOM for each year from 1996 to 2001.
overestimation is most pronounced at location N, lying in the passage of the English Channel water (Fig. 6e).

Correlation coefficients calculated for locations B, C, D and F (Table 2) are lower, even though they are situated only within a few model grid points from locations A, E, G and H, where correlations are much better. Calculated concentrations at locations B, C, D and F are higher than observed (Table 2). One explanation for this discrepancy could be that during winter the stronger winds which occur over the North Sea induce higher current speeds enhancing stronger water mass flushing. Consequently there is an increase in the amount of less polluted waters from the open lateral boundaries being transported into the German Bight. As mentioned above the decrease in γ-HCH concentrations in the English Channel and on the northern boundary might not be correctly captured by the model leading to overestimated winter concentrations. This hypothesis is verified by the modelling experiment when γ-HCH concentrations in the English Channel and on the northern boundary of the modelling domain were set to zero for the entire simulation period. Fig. 8 indicates that concentration without inflow from the lateral boundaries was a significant component of the γ-HCH burden until the second half of the year 2000. Furthermore, ongoing cycling of earlier emitted γ-HCH leakages from inappropriate disposal may play a role.

Atmospheric concentrations of γ-HCH used for this study were measured at coastal stations. Therefore there is no information on possible concentration gradients over the whole North Sea and in the subregions remote from the polluted coastal areas. Concentrations of γ-HCH in precipitation measured in Lista, Westerland and Kollumerwaard exhibit significant differences (Fig. 5a). For some pollutants, e.g. for polychlorinated biphenyls (PCBs), air concentrations over the coastal waters are expected to be higher than those over the open ocean waters because of their vicinity to sources. However, there are indications that air measured in Lista originate from the North Sea about 2/3 of the time (Haugen et al., 1998). Since the measured air concentrations were available only from Lista they were used for the whole modelling domain.

The seasonal pattern predicted by the model with higher γ-HCH concentrations during summer than during winter emphasises the importance of temperature dependency of the air–sea exchange. For the Great Lakes of North America and for the Arctic Ocean it has been found that during summer, the air–sea gas transfer is net volatilisational, whereas during colder period it is depositional (Ridal et al., 1996; Jantunen and Bidleman, 1996). Measurements suggest (Sahsuvar et al., 2003) that temperature dependency of $H_c$ has a profound effect on gas exchange predictions. This hypothesis is illustrated by Fig. 8 where γ-HCH concentrations resulting from model calculations using two different temperature dependency coefficients of $H_c$ are shown. Recent experimental data (Sahsuvar et al., 2003) used in this study lead to higher (10–50%) sea water concentrations. Therefore as parameterisation of the air–sea exchange seems to play a key role, its uncertainty should be reduced. Discrepancies in the experimentally determined values of $H_c$ and possibly physical processes not included in the model (see Appendix A) contribute to this uncertainty.

3.2. Horizontal and vertical distributions in sea water

Measurements in the North Sea’s uppermost layer of 5 m thickness compiled during summer 1995 and interpolated on the modelling domain of FANTOM (Fig. 4) show clear gradients of γ-HCH with the highest concentrations in the southern regions of the North Sea, in the estuaries of rivers and in the English Channel. The highest concentration of 8 ng l$^{-1}$ was found close to the mouth of the River Elbe.

Annual mean γ-HCH concentrations averaged vertically for the whole modelling domain in the years 1996–2001 were calculated (Fig. 9). These results show positive gradients of concentration towards the coasts; a similar pattern was found in the initial distribution (Fig. 4). During 1995–1997 total concentration of γ-HCH in the continental coastal water was above 1 ng l$^{-1}$ with a concentration of more than 25 ng l$^{-1}$ in the River Elbe estuary. As with the γ-HCH concentration at the selected locations (Fig. 6), concentrations in the whole modelling domain decreased. This effect is more pronounced in the southern regions of the North Sea where initial concentrations had been highest.

Observed spatial distribution of γ-HCH total concentration with decreasing concentrations towards the north-western part of the North Sea, similar to those showed by this modelling study (Fig. 9), have been reported in the scientific literature (Gaul, 1988; Theobald et al., 1996; Hühnerfuss et al., 1997, Lakachus et al., 2002) and by the OSPAR Commission (OSPAR, 2000). Low concentrations in the north-western North Sea (Fig. 9) are due to the inflow of cleaner Atlantic water. Along the coastline from southern Britain to Denmark close to the estuaries there are high concentrations; this indicates the importance of the river inflow which modulates the local circulation. In fact, measurements in coastal waters close to large estuaries suggest that river input is a significant source for γ-HCH in the North Sea (Sündermann, 1994; Hühnerfuss et al., 1997).
Another indication for that is the jagged pattern in the concentration’s time series in the German Bight (Figs. 6a, b and 8) which is due to variability of the fresh water inflow (Fig. 5b). As opposed to the German Bight, in the open North Sea (Fig. 6d, f) remote from the polluted estuaries, time series are smoother and sea water concentrations seem to be balanced by the volatilisation–deposition process. This offers an explanation for the slower decrease in γ-HCH concentrations in the central North Sea than in the southern German Bight. This also implies that in coastal areas, waterborne inputs of γ-HCH may be dominant, whereas atmospheric deposition is more important in the open sea and can exhibit the same order of the magnitude as river inputs (Hühnerfuss et al., 1997). A correlation between γ-HCH concentrations in water (Fig. 6) and its concentration in precipitation and in the air (Fig. 5a) is found.

The mean anti-clockwise currents pattern commonly observed in the North Sea (Section 2.5.1) favours short flushing times (stronger transport) of water mass along the south eastern coast of about 11 days and longer ones of about 40 days in the central North Sea (Lenhart and Pohlmann, 1997; OSPAR, 2000). Weaker transports (or longer flushing times) in some subregions of the North Sea suggest that the concentrations of semi-volatile compounds, such as γ-HCH, should be more sensitive to vertical exchange rates and less dependent on the horizontal circulation. This also implies that a relatively water soluble compound, e.g. γ-HCH, which ends up in these areas of the North Sea may not be subject to transport with sea currents to any significant extent. On the other hand, γ-HCH in the subregions with stronger transports, e.g. in the German Bight where the concentrations are also higher, will be transported northwards within the coastal current. Typical speeds of sea currents are 0.01 m s\(^{-1}\) which are 2–3 orders of magnitude slower than in the atmosphere. This, together with the variations in the water mass flushing times (see Section 2.5.1), implies that only those substances with a residence time in sea water of up to a year or longer may undergo transport with sea currents over long distances in the North Sea.

Vertical distribution of sea temperature and salinity in January and August 1997 and corresponded γ-HCH distribution from south to north along the 3° E are plotted in Fig. 10. In winter the southern North Sea is in general well mixed to the bottom (Fig. 10a). This is also reflected in
the distribution of γ-HCH total concentrations (Fig. 10b). During warm seasons a stable thermal stratification is formed by summer heating (Fig. 10c) enhancing vertical gradients in γ-HCH total concentrations in the northern part of the domain (Fig. 10d). High values of about 0.6 ng l⁻¹ are found near the sea surface, and low values of less than 0.2 ng l⁻¹ below, where the Atlantic water inflows. The high γ-HCH concentrations of more than 1.2 ng l⁻¹ were found in the continental river estuaries both in January and August. As already illustrated by the time series (Fig. 6), γ-HCH concentrations in August were higher than in January. Concentrations beneath the thermocline, if present, do not show seasonal variations. There were no measurements available on the vertical distribution of γ-HCH concentrations in the North Sea. Model results suggest that the vertical structure of total γ-HCH concentration (Fig. 10b, d) seems to be shaped by water column stratification and its seasonal variability (Fig. 10a, c).

4. Conclusions and outlook

The fate and transport ocean model FANTOM was developed to describe the oceanic fate of POPs in the North Sea. The processes considered are transport with sea currents, air–sea exchange, partitioning of particulate organic carbon, net sedimentation and degradation in the sea.

The model was applied to study the aquatic fate of the insecticide Lindane (γ-HCH) in the years 1995–2001. This is the first time that such model has been applied on the regional scale. Predicted γ-HCH concentrations in the surface water were compared with measured ones. The model is able to reproduce the spatial distribution of γ-HCH concentrations and capture its decrease during the simulation period. While there is excellent agreement for warm seasons, FANTOM overestimates winter concentrations of γ-HCH.

Model uncertainties and sensitivities were explored. From these it is concluded that particular data needs exist with regard to off-shore atmospheric environment and the description of the air–sea exchange. Concentrations in the atmosphere correlate with concentrations in sea water, indicating the significance of the atmospheric input of γ-HCH in the North Sea. Overestimations in the modelled concentrations in 2000–2001 seem to be due to the lacking data for the open sea boundaries. There were no measurements on the vertical concentration structure. Therefore model performance with regard to sediment-water exchange cannot be assessed.

Although FANTOM is capable of reproducing the spatial and temporal distribution of a fairly water soluble contaminant such as γ-HCH, it remains a future task to investigate the fate of compounds with different physical–chemical properties and hence environmental behaviour. FANTOM can be used to study the contribution of different sources and sinks to the mass budget. Also the sensitivity of POPs behaviour in the aquatic environment to the ambient processes under present and future climate conditions can be studied.

Acknowledgements

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Appendix A. Gaseous air–sea exchange

The gaseous air–sea transfer of organochlorines can be treated as a diffusion of the trace gases through spatially and temporally varying thin boundary layers in both media whose thicknesses are a function of near-surface turbulence and molecular diffusivity (Schwarzenbach et al., 1993). The kinetics of air–sea exchange in the open ocean is driven by near-surface turbulence with wind stress being the major controlling factor. In a wind driven ocean-atmosphere system, turbulence is generated due to shear, buoyancy, and large- and micro-scale wave breaking. The gas transfer dependency on wind speed over the ocean is often non-linear (Wanninkhof, 1992). In low wind speeds, when buoyancy may dominate in generating the turbulence and there are organic films, this dependency is weaker. Additionally, variability is introduced by the presence of small-scale waves and rain. Furthermore, many organochlorines are semi-volatile so they can occur in the atmosphere in both gaseous and condensed states under ambient temperatures. Therefore temperature may also play a central role in the air–sea transfer of POPs.

FANTOM uses a description of the gaseous air–sea gas exchange based on the stagnant two-film theory formulated by Whitman (1923) and restated by Liss and Slater (1974), with the adoption of the fugacity formulation as described in Mackay (2001). Accordingly, the net mass transfer across the air–sea interface is expressed as a product of a kinetic parameter representing the resistance to interfacial transfer and a term representing the deviation from the chemical equilibrium between air and water as a driving force for interfacial transfer. The chemical equilibrium between the two compartments is controlled by the ambient
parameters (e.g. temperature and wind speed), physical–chemical properties of the compound and its abundance in the environment.

The two mass transfer coefficients, \( u_1 \) and \( u_2 \) (m s\(^{-1}\)) for the stagnant (unstirred) atmospheric boundary layer and for the stagnant water layer close to the air–water interface respectively are calculated as a function of wind speed \( WS \) (m s\(^{-1}\)) at 10 m above the surface using relationships (according to Schwarzenbach et al., 1993)

\[
u_1 = 6.5 \cdot 10^{-4} \cdot (6.1 + 0.63 \cdot WS) 0.5 \cdot WS \\
u_2 = 1.75 \cdot 10^{-6} \cdot (6.1 + 0.63 \cdot WS) 0.5 \cdot WS
\]

Fugacity capacities of air and water \( Z_a \) and \( Z_w \) (mol m\(^{-3}\) Pa\(^{-1}\)) at air temperature \( T_a \) (K) and sea surface temperature \( T_w \) (K) are calculated as \( Z_a = 1/R \cdot T_a \) and \( Z_w = 1/H_c(T_w) \) respectively. The ideal gas constant \( R \) (R = 8.314, Pa m\(^3\) mol\(^{-1}\) K\(^{-1}\)) and the Henry’s law constant \( H_c \) (Pa m\(^3\) mol\(^{-1}\)) at \( T_w \) are used to describe the equilibrium partitioning of trace gases between air and water. Experimentally derived relationships for \( H_c \) are calculated from the temperature dependent equation (Kucklick et al., 1991; Paasivirta et al., 1999; Sahsuvar et al., 2003) using slope \( m \) (K) and intercept \( b \):

\[
\log H_c = b + m/T_w
\]

The overall exchange rate constant \( D_{sea} \) for volatisation from sea water (mol Pa\(^{-1}\) s\(^{-1}\)) is calculated according to Mackay (2001) and Wania et al. (2000) \( D_{wa} = A_w/(1/\nu_1 \cdot Z_a + 1/\nu_2 \cdot Z_w) \), where \( A_w \) (m\(^2\)) is the surface area of the water compartment. The gaseous exchange rate constant for the dry gaseous deposition is calculated similar to volatilisation one. Transfers from the atmosphere to the sea surface by dry particle and wet depositions are calculated separately (Appendix B and Appendix C).

The net mass transfer rate (mol s\(^{-1}\)) is calculated for the tracer gaseous concentrations in the air \( C_a \) and dissolved in sea water \( C_w \) expressed in mol m\(^{-3}\):

\[
\frac{dC_{a-w}}{dt} = D_{wa} \cdot (C_a/Z_a - C_w/Z_w) \\
\quad = D_{wa} \cdot (C_a \cdot R \cdot T_a - C_w \cdot H_c(T_w))
\]

The air–sea flux \( F_{a-w} \) (ng m\(^{-2}\) s\(^{-1}\)) to the surface is then re-calculated from Eq. (A2) using the tracer’s molar mass \( M \) (g mol\(^{-1}\)). The direction of the flux \( F_{a-w} \) is determined by its sign (i.e. positive values of \( F_{a-w} \) indicate gaseous deposition, and negative values indicate volatilisation from the sea surface).

**Appendix B. Dry particle deposition**

Organic contaminants sorbed to atmospheric aerosol particles can settle to the sea surface by dry particle deposition. The dry deposition flux from the atmosphere to the sea surface \( F_{dry} \) (ng m\(^{-2}\) s\(^{-1}\)) is expressed as a product of the contaminant particle-bound concentration in air \( C_{ap} \) (ng m\(^{-3}\)) and a dry deposition velocity \( v_{dep} \) (m s\(^{-1}\)):

\[
F_{dry} = C_{ap} \cdot v_{dep}
\]

Dry deposition velocities depend on particle size, underlying surface properties, and meteorological parameters (e.g. wind speed). For this study a uniform value of \( v_{dep} = 2 \cdot 10^{-5} \text{ m s}^{-1} \) was used. This was based on an empirical relationship between \( v_{dep} \) and the mass median diameter (an average value used to describe aerosols particles) for oceanic conditions (McMahon and Denison, 1979; Slinn, 1983) and the assumption that the \( \gamma \)-HCH distribution follows the air particles size distribution which peaks in the accumulation mode.

Atmospheric concentrations reported by the monitoring programmes often represent the total (gaseous and particle sorbed) compound concentration in air. The fraction \( f_{ap} \) of the total tracer concentration in air sorbed by aerosol particles is needed to estimate the dry particle deposition flux. It can be calculated based on an empiric relation which assumes that the equilibrium between the gaseous and aerosol particles bound fractions is determined by the substance vapour pressure and is independent of the particles chemical properties (Junge, 1977; Pankow, 1987) \( f_{ap} = s \cdot \theta / (P_{ol} \cdot \theta + s \cdot \theta) \), where \( P_{ol} \) is the temperature dependent saturated vapour pressure for supercooled liquid (Pa), calculated in a way similar to Eq. (A1). The specific aerosol surface \( \theta \) (m\(^2\) m\(^{-3}\)) and adsorption constant \( s \) (Pa m) used in this study (Table 1) are constants and represent the North Sea conditions (Pekar et al., 1998).

**Appendix C. Wet deposition**

Due to their semi-volatility POPs are episodically scavenged from the atmosphere by precipitation in both the gas and particulate phases (Pankow, 1987, Bidleman, 1988). During wet periods the removal of gaseous and particle sorbed compounds dominate other depositional processes. Because precipitation is intermittent and a local phenomenon, it is crucial to consider its spatial and temporal variability.

The wet deposition flux \( F_{wet} \) (ng m\(^{-2}\) s\(^{-1}\)) is calculated in FANTOM as a product of the tracer concentration in precipitation \( C_{pr} \) (ng l\(^{-1}\)) which includes both the dissolved and particulate phases and precipitation rate \( P \) (m s\(^{-1}\)):

\[
F_{wet} = C_{pr} \cdot P
\]

Spatial and temporal distributions of \( C_{pr} \) and \( P \) are based on measurements as described in Section 2.5.4. In the present model configuration no distinction is made between precipitation scavenging of vapours and particles.
Appendix D. Particulate organic carbon content

The total SPM in sea water consists of inorganic and organic portions, namely microflocs of mineral particles and organic matter. The fine sediment (mud) or particles smaller than 20 μm make up to 85% of SPM in the North Sea (Eisma and Kalf, 1987). The composition of SPM in sea water is controlled by a number of factors such as the rate of primary productivity, the amount of lithogenous input to the sea, and the sinking rate. Biogeochemical processes leading to release and/or uptake of elements from sea water during the horizontal or vertical fluxes of SPM are also responsible for its composition. The shelf seas are normally more productive than the open ocean. SPM are also responsible for its composition. The shelf processes leading to release and/or uptake of elements input to the sea, and the sinking rate. Biogeochemical rate of primary productivity, the amount of lithogenous sea water is controlled by a number of factors such as the smaller than 20 μm and organic matter. The fine sediment (mud) or particles organic portions, namely microflocs of mineral particles (Eisma and Kalf, 1987). In winter the fraction of organic matter is about 20% of the total SPM, whereas in other seasons the appearance of SPM may be dominated by phytoplankton (Puls et al., 1994).

The concentration of POC $C_{\text{POC}}$ (kg l$^{-1}$) in FANTOM is the composite of the concentrations of biogenic organic carbon $C_{\text{bio}}$ (kg l$^{-1}$) and sediment organic carbon $C_{\text{sed}}$ (kg l$^{-1}$): $C_{\text{POC}} = C_{\text{bio}} + C_{\text{sed}}$. The biogenic concentration $C_{\text{bio}}$ represents the POC of phytoplankton, zooplankton, bacteria, and small and large detritus suspended in the water column. These concentrations are calculated by an ecosystem model, described elsewhere (Pätsch et al., 2002).

Sediment organic carbon concentration $C_{\text{sed}}$ is derived from plant and animal detritus, bacteria or plankton formed in situ, or derived from natural and anthropogenic sources in river catchments. In the shallow regions under stormy conditions the bottom sediment can reach back to the sea surface. Measurements (Van der Zee and Chou, 2005) suggest that this sediment is an important contribution to the POC burden in the North Sea, especially in winter when sea currents are stronger and storm events are more frequent.

The sediment organic carbon is calculated in FANTOM as a portion of the total fine sediment distributed in the upper 2 cm of the sediment bed, a layer where nearly all the benthic biomass is found (Pohlmann and Puls, 1994). The POC content $p_{\text{POC}}$ of the bottom fine sediment $p_{\text{mud}}$ (in % of dry mass) is calculated based on the measurements reported by Wiesner et al. (1990) as $p_{\text{POC}} = \begin{cases} 5-1.4 \log(p_{\text{mud}}), & p_{\text{mud}} < 50 \% \\ 2.6, & p_{\text{mud}} > 50 \% \end{cases}$

The bottom sediment enters the near-bottom water layer of the model due to erosion. It is diffused to the upper water layers and may be returned to the bottom sediment via deposition by settling. In FANTOM deposition of SPM and erosion of bottom sediment are controlled by the bed shear velocity. The latter is a characteristic of the bed shear stress that depends on the wind and density driven currents, tidal currents and waves. The shear stress is calculated according to the formulation given by Soulsby (1997). Wave induced shear stress is dominant in shallow waters, such as the North Sea (Puls et al., 1994). Therefore, only bed shear velocity due to waves $v_{s}$ is considered in the model. The threshold shear velocity for erosion $v_{s,\text{cr}}$ is 0.028 m s$^{-1}$ and the one for deposition $v_{s,\text{de}}$ is 0.01 m s$^{-1}$ (Pohlmann and Puls, 1994). Thus, if $v_{s} > v_{s,\text{cr}}$, sediments from the disturbed sea bottom enter the water column and are distributed uniformly in the bottom water layer (Sündermann and Puls, 1990). The amount of eroded SPM depends on the fraction of fine sediment at the bottom. Eroded SPM is then diffused through the water column. SPM in the water column is subject to gravitational sinking with the uniform settling velocity $v_{\text{set}}$ of about 25 m day$^{-1}$. Further, if $v_{s} < v_{s,\text{de}}$, a portion of SPM in the bottom water layer is deposited back to the bottom sediments.

In the sediment the deposited SPM is re-distributed vertically by benthic organisms constantly disturbing the sediment by burrowing and feeding. Vertical bioturbation is described in the model as a diffusive transport process (Pohlmann and Puls, 1994).

In the water column SPM settles due to gravitational sinking. In the deep sea this process is the ultimate sink for SPM, whereas in the shallow regions re-suspension (erosion of previously deposited SPM) caused by currents and waves carries it back to the water column.

Finally, knowing the mass of the bottom sediment in the water column at a specific time and its density allows $C_{\text{sed}}$ is calculated.

The approach described here provides first order realistic spatial and temporal POC distributions. The full SPM dynamics calculations are described elsewhere (Sündermann and Puls, 1990; Pohlmann and Puls, 1994; Puls et al., 1994).

Appendix E. Fraction bound to particulate organic carbon present in sea water

The calculation of the particle-bound fraction of POPs is based on the assumption that the equilibrium between the tracer’s concentrations in dissolved and particulate phase is established instantaneously (Skoglund et al., 1996; Skoglund and Swackhamer, 1999). As equilibration time is neglected the following relationship is fulfilled $C_{p}/C_{w} = K_{\text{eq}} C_{\text{POC}}$, where $C_{p}$ (ng l$^{-1}$) and $C_{w}$ (ng l$^{-1}$) are the concentrations of POPs associated with POC and in the dissolved phase respectively; and $C_{\text{POC}}$ (kg l$^{-1}$) is the concentration of POC in solution.
(Appendix D). The organic carbon–water equilibrium partition coefficient $K_{oc}$ (l kg$^{-1}$) is commonly employed in modelling organic chemicals (Koziol and Pudykiewicz, 2001; Malanichev et al., 2004) to calculate their partitioning in different aquatic particulate matrices. The $K_{oc}$ value is compound specific and related to the dimensionless octanol–water partition coefficient $K_{ow}$ according to Karickhoff (1981) as $K_{oc} = 0.411 \cdot K_{ow}$. The octanol–water partition coefficient is the ratio of the concentration of a chemical in octanol and in water at equilibrium at a specified temperature (Karickhoff, 1981). Octanol is an organic solvent that is used as a surrogate for natural organic matter. This approach to describe the phase partitioning in water is appropriate for the fast uptake into the organic matrix. The uptake process may be far from the equilibrium during higher biological activity (i.e. during fast phytoplankton growth). Then a kinetic description would be more adequate (Skoglund et al., 1996; Axelman et al., 1997).

References


