Scenarios of Temporal and Spatial Evolution of Hexabromocyclododecane in the North Sea

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Spatial and temporal distribution of the flame retardant hexabromocyclododecane (HBCD) in the North Sea was examined for the period from 1995 to 2005 using a pollutant transport model FANTOM. Model calculations allow conclusions on relevant sinks and fluxes in and out of the North Sea and on the time needed to establish a steady state. Calculations were performed for two additional scenarios with different rates of primary degradation ranging from fast degrading to absolute persistency. Concentrations calculated in the scenarios with degradation are in line with the monitoring data available for HBCD. Concentrations calculated in the “persistent” scenario disagree with measured data. According to our model calculations, steady state is established within months for the water and the top layer sediment with no evidence for a temporal trend, except for the “persistent” scenario, in which concentrations increase continuously in the southeastern part of the North Sea, where hydrographic and circulation characteristics produce areas of converging currents. Our model study enables a better understanding of the fate of HBCD in the North Sea, its potential for transport and overall elimination. We discuss these findings in the light of different concerns for PBT substances.

Introduction

In recent years regulatory chemicals management has focused on substances that are persistent, bioaccumulative, and toxic (PBT) or very persistent and very bioaccumulative. Precautionary regulatory action for such substances is rationalized with the intrinsic potential for increasing exposure along the food chain due to bioaccumulation, and the uncertainty about potential effects of prolonged exposure together with the “irreversibility” of residues in the environment due to persistency. A different line of argument refers to persistency as a prerequisite for transport of the substance to areas distant from releases including pristine environments. The first line of argument is concerned about overall persistency, i.e., implying that only persistency in all relevant compartments causes the irreversibility. The second line of argument is concerned about persistency in mobile compartments (air or water) and the resulting potential for transport, regardless of whether the substance will persist in the receiving environment.

According to the assessment of the EU expert working group, the flame retardant HBCD is a substance showing PBT behavior although not being persistent in sediment (1). Based on this assessment, HBCD has been identified as a substance of very high concern under the EU chemicals management regulation (REACH) and is currently also under assessment for inclusion in the Stockholm Convention and in the UN-ECE Protocol on POPs. The North Sea is a receiving basin for a relevant portion of emissions in Europe. We assess the fate of HBCD in the North Sea to understand its potential for transport with ocean currents using the model FANTOM (2; see Supporting Information).

According to laboratory data, HBCD has a low overall persistence (3) and has limited potential for transport in the air (low calculated air–water partitioning constant). Thus, for comparison, we test scenarios with hypothetical substances which have the same properties as HBCD, but different potential for primary degradation, i.e., "fast degrading" and "persistent". In the course of the simulation period from 1995 to 2005, emissions from one significant point source ceased, thus our model results indicate the likely impact of this change on HBCD levels in the North Sea. Detectable levels of HBCD have been reported in blubber of harbor porpoise around the UK coast (4, 5), in environmental samples in areas near known sources (6, 7), and in wildlife in the Arctic (6, 8, 9). The prevalent diastereomer in biota is α-HBCD (whereas the technical product consists of α, β, and γ diastereomers) (10), and in top predators α-HBCD has been detected exclusively (11). Based on the model results, we quantify the relevant fluxes of HBCD through the model boundaries, i.e., the fraction of HBCD that is available for further transport. Although there is considerable uncertainty in the input data and boundary conditions, the response of the system, for instance to change in the emission regime, is considered independent from the absolute value.

Methodology

Model Description. The Fate and Transport Ocean Model (FANTOM; 2) is a three-dimensional model based on the equation of transport of fluid. The model domain covers the North Sea up to 57° N (Figure 1). Input of the substance occurs through inflow from the rivers and adjacent water bodies (i.e., Atlantic Ocean, Baltic Sea, English Channel), and wet and dry atmospheric depositions. Horizontal and vertical transport with sea currents is driven by the advective and turbulent flow calculated by an ocean circulation model (12).

In the water column, a substance exists in truly dissolved phase and as bound to particulate organic carbon. The particle-bound fraction is subject to settling to lower water layers and ultimately to the sediment layer. The dissolved fraction of the substance is involved in air–sea exchange in accordance with the fugacity concept (13). Degradation is described by a first order rate decay coefficient, which is assumed to double per 10° K temperature increase. More details on the model are given in Supporting Information.

Input Data. Annual emissions of HBCD are estimated for manufacturing sites and for HBCD processing sites like textiles or XPS and EPS. Site-specific emissions data are taken from the risk assessment for existing chemicals in the EU and corrected for changes in annual consumption over the modeling period (14–16; see Supporting Information). Concentrations of HBCD in the rivers (Figure 2) are estimated based on the climatological mean monthly values of fresh
water discharges of the rivers (17) and HBCD emissions to rivers from known point sources. Atmospheric concentration of 5.1 pg m$^{-3}$ was based on measurements from the Baltic island Gotland and is considered representative for the marine air (6).

Initial concentrations in the model compartments are derived from a spin-up run. In this way, initial distributions of HBCD concentrations (Figure 1) are shaped by the North Sea hydrodynamics. Concentrations in the English Channel are estimated from the mass flow of rivers ending in the English Channel area and an assumed dilution by a factor of 10. Table 1 summarizes input data used in this study; additional details are given in Supporting Information.

Model Uncertainties. Significant uncertainty is associated with the estimates taken for the initial and boundary conditions, as well as with some assumptions made in our modeling study. We discriminate four major sources of uncertainties.

(a) HBCD emission data refer to technical product; potentially different environmental behavior of the individual HBCD diastereomers are neglected. The water solubility used to calculate fugacity in seawater compartment is the sum of the solubilities of the diastereomers and is dominated by the solubility of the $\alpha$-diastereomer.

(b) No retention or elimination of HBCD is considered in rivers from source to the river mouth. This leads to a more dynamic change in the river concentration than anticipated in reality. Model grid points near the supplying rivers estuaries are most sensitive to this simplification. The calculation of the emission from consumption data using emission factors can only reveal orders of magnitude. It does not account for potential changes in the technology at a given site which may cause a change in the ratio of emission and consumption. This may cause a change in the ratio of emission and consumption. We evaluate the effect of this uncertainty on an absolute scale by comparing model results with available measurements. However, on a relative scale, the trend in HBCD emissions is captured in the river data, and the conclusions on the North Sea aqueous system’s response to changing emission pattern are not affected by the uncertainty in the absolute concentrations.

(c) Due to lack of measured data, uniform HBCD concentrations in air (5.1 pg m$^{-3}$) are prescribed in all model grid points. Higher atmospheric concentrations have been reported near point sources (8, 9), which could be leading to somewhat underestimated depositional fluxes in this modeling study. There are no data on the offshore gradients in HBCD atmospheric concentrations and net atmospheric deposition of HBCD is smaller (by about $10^{-3}$) than the rivers inflow.

(d) Partitioning between dissolved and particle-bound HBCD is described as an equilibrium and no kinetics is considered. In fact, the particle size and composition influences the equilibration time and concurrently its capacity to absorb and desorb HBCD. However, on longer time-scales, such as a decade as in this study, a kinetic approach is not needed (18).
Model Scenarios. We test three different model scenarios: a “best understanding” scenario which aims at describing the potential for degradation of HBCD to the best of our understanding, a “fast degrading” scenario with a high potential for degradation, and a “persistent” scenario without any degradation (see Table S1 in Supporting Information). Other parameters were kept the same in all three scenarios. In view of the uncertainties about the “true” half-life of HBCD in the North Sea, we discuss the relevance of the three scenarios.

The model uses different degradation rates to describe the degradation of the freely dissolved and the particle-bound fraction. Particles in the model are either suspended in the water column or settled in the sediment layer. However, experimental data can not distinguish rates for the two fractions. For HBCD, an overall half-life ranging from 11 to 32 days was determined in aerobic water–sediment microcosms (3). Degradation of the freely dissolved fraction is expected to be low and, in the absence of data, is assumed to be zero in the “best understanding” scenario. For the particle-bound fraction, the lower end of the range of reported aerobic degradation half-life is used (11 days at 20 °C). In the “fast degrading” scenario, the same degradation half-life was assumed for both the particle-bound and the freely dissolved phases. In the “persistent” scenario, elimination by degradation has been disregarded completely.

Results and Discussion

Spatial and Temporal Evolution of Concentrations. Concentration time series in water and sediments are presented at four selected locations and three scenarios (Figure 3). Chosen locations illustrate the concentration dynamics in the regions of the North Sea with different hydrodynamic properties, i.e., close to the rivers Tees and Scheldt estuaries (P3 and P4), in the German Bight (P1), and in a location (P2) remote from the coast (see Table S2 in Supporting Information for locations of P1–4). In line with rapid elimination, steady state concentrations are established within months in the water phase and the sediment layer of the entire modeling domain in the “best understanding” and the “fast degrading” scenarios (Figure 3). Yet, concentrations vary substantially across the model region.

<table>
<thead>
<tr>
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<tr>
<td>water solubility, [mg L⁻¹]</td>
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<td>octanol–water partitioning coefficient, log Kow [-]</td>
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<tr>
<td>vapor pressure, [Pa]</td>
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<tr>
<td>concentration in air, [pg m⁻³]</td>
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<td>14</td>
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<tr>
<td>concentration in rainwater, [ng L⁻¹]</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>concentration in sediments (mean and range), [ng L⁻¹]</td>
<td>50 (0–1208)</td>
<td>15</td>
</tr>
<tr>
<td>concentration in the English Channel (mean and range), [ng L⁻¹]</td>
<td>0.55 (0.2–1.2)</td>
<td>14</td>
</tr>
<tr>
<td>concentration at the northern boundary (mean and range), [ng L⁻¹]</td>
<td>6.9 × 10⁻⁴ (6.7 × 10⁻⁴ to 7.1 × 10⁻⁴)</td>
<td>model spin-up run</td>
</tr>
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</table>

* As sum of the solubility of the three isomers α-, β-, and γ-HBCD.
and in the coastal locations (P1, P3, and P4) they are determined by the discharge from adjacent rivers. Overall, analyzed time series indicate no time trend throughout the simulation period in the “best understanding” and the “fast degrading” scenarios. In the “persistent” scenario, concentrations show a gradual increase exceeding the measured concentrations for HBCD (see below) already in the first year of the simulation. The steady state is established in the entire modeling domain, except for the southeastern North Sea (at location P1). The southeastern coastal area of the North Sea is characterized by converging transport patterns, relative weakness of tidal currents with related stratification and/or sedimentation, and small residual currents. The proximity of riverine sources to this area, together with the mean anticlockwise pattern of sea currents commonly observed in the North Sea favors accumulation in the German Bight (southeastern North Sea), and in the estuarine areas. This phenomenon is illustrated by concentrations calculated under “persistent” scenario for location P1 (Figure 3).

Concentrations in seawater are similar in magnitudes for all scenarios in the locations close to sources, i.e., in the estuaries (cf. P4 and P3) where inflow from rivers dominates other processes. Offshore concentrations in the “best understanding” scenario are about a factor of 2 higher at the sea surface and up to an order of magnitude higher in the sediment compared to the “fast degrading” scenario. This phenomenon is illustrated in the locations P1 and P2, where both advection and vertical exchange processes are intensive. Seasonal cycles in concentrations, determined by fresh water discharge from the rivers, are more pronounced in the “best understanding” scenario (because more mass is available for transport) and less pronounced in the “fast degrading” scenario (due to rapid elimination). In addition, both fractions (particle-bound and

**FIGURE 3.** Time series of HBCD total concentrations in the surface water (particle-bound and freely dissolved) and in the upper sediments at locations P1, P2, P3, and P4 calculated in the three scenarios (Table S1). Note separate scales for the “best understanding” and “fast degrading” (left axis), and “persistent” (right axis) scenarios. Geographical locations are shown in Figure 1.
truly dissolved) degrade in the “fast degrading” scenario. Thus the export flux to the sediment by sinking particles is less.

Concentrations along the British coast shown for the location P3 are indicative of the potential effect of emissions reduction: Emissions to the river Tees stopped by the end of the year 2003 (cf. Figure 2). Following the emissions course, concentrations in seawater decreased in all scenarios. Depending on the degradation scenario, the time needed to establish a new steady state at P3 ranged from about a month (“fast degrading”), to 6 months (“best understanding”), and up to a year (“persistent” scenario). The same pattern is calculated for the sediment. Note that the exact values are artifacts of the assumption that the load discharged by the river immediately responds to changes in the emission pattern, i.e., retention and remobilization in the rivers are neglected. Nevertheless, model results indicate that HBCD near the British coast has a low residence time due to resuspension, transport with currents, and, depending on the scenario, degradation.

Calculated spatial distributions of concentrations in the surface water layer (ranging from $10^{-4}$ to $10^2$ ng L$^{-1}$) and in the sediment (ranging from $10^{-4}$ to $10^2$ ng g$^{-1}$ d.w.) in the “best understanding” scenario are shown in Figure 4 for the beginning, the middle, and the end of the simulation period. Modeled concentrations show steep offshore gradients along the British coast and in the southeastern part of the North Sea, particularly along the continental coastal zone. Hydrographic and circulation characteristics are essential constraints for the spatial distribution of concentrations in the North Sea. They are responsible for the concentration gradients with high values near the contributing river mouths and low values in the central part of the North Sea remote from the sources.

As rivers are major sources of HBCD in this study, the horizontal distribution in the upper sediment generally follows the seawater distribution. Slightly higher concentrations in the sediment compartment are calculated in the central North Sea (off the east coast of England; Figure 4), a location known for high content and deposition rates of suspended particulate matter (19). A high-concentration zone off the UK coast (around P3) stretches along the coastline northward from the source in the beginning of the simulation period and southward in the middle of the simulation.

Oceanic flows are quite intensive in this area; accordingly, they modulate the path of this high-concentration zone. This zone disappears completely after emissions from the river Tees declined (cf. Figure 2). Spatial distributions calculated in other scenarios are consistent with the “best understanding” scenario, differing in the absolute values and the presence of an accumulation area in the southeastern North Sea discussed previously (P1 in Figure 3).

**Comparison with Measured Concentrations.** Large offshore gradients in the calculated concentrations make a comparison with available measurements difficult. No monitoring data are reported for HBCD for the North Sea water and a direct comparison with calculated concentrations is not possible. A significant amount of data are available for the blubber of harbor porpoise stranded off the UK coast. Assuming a biocenontration of approximately $10^6$ and a biomagnification of 3 (20), the concentrations range calculated for the North Sea water ($10^{-4}$ to $10^2$ ng L$^{-1}$; Figure 4) converts to concentration in predators (whole body) between $3 \times 10^{-3}$ and $3 \times 10^{-4}$ µg kg$^{-1}$ w.wt. Assuming a lipid content in this organism of 10% and that HBCD will prevail in the lipid, the estimated concentration in the lipid ranges from $3 \times 10^{-3}$ to $3 \times 10^4$ µg kg$^{-1}$ lipid wt. Morris et al. report concentration of $4.4 \times 10^2$ to $68 \times 10^2$ µg kg$^{-1}$ lipid wt in the blubber of harbor porpoises (lipid content of the blubber ca. 90%) for the year 1998 (7). Law et al. report concentration from 64 to $19.2 \times 10^2$ µg kg$^{-1}$ w.wt. for the period from 1994 to 2003 with a pronounced increase in the concentrations after the year 2000 (4) and a decrease in concentrations after 2003 (5). Based on this calculation, our modeled concentrations in seawater could be leading to levels reported for harbor porpoises from areas off the UK coast. However, our concentrations do not show any pronounced temporal trend for the UK coast, nor for other regions of the North Sea (Figure 3) as was suggested by the data by Law et al (4). Measured concentrations of HBCD in marine sediments in the southeastern part of the North Sea for the period from 2002 to 2005 ranged from $3 \times 10^{-2}$ to 6.5 ng g$^{-1}$ d.w (21). These measurements display an offshore gradient supporting our model results. No temporal trend has been reported in these observations. Thus, these findings are best represented by the “best understanding” and “fast degrading” scenarios (Figures 4 and 3). Concurrently, temporal increase in concentration for the southeastern part

![Figure 4](image-url)
of the North Sea calculated under “persistent” scenario is not confirmed by observations.

Distribution and Fluxes in the North Sea. To compare the relevance of the processes that act as sources or sinks in the model, the fluxes in and out of the North Sea were integrated for the entire modeling domain over each year (22; and see Supporting Information) for all scenarios and are presented for the beginning and the end of the simulation period (Figure 5). Inflow from the rivers is the major and dominant source (Figure 5a) and degradation is the dominant elimination process (Figure 5b), except for the “persistent” scenario. Another important removal mechanism is the sinking to the bottom. Net sinking flux calculated under the “best understanding” scenario is up to a factor of 2 higher than in the “fast degrading” scenario (Figure 5c).

Due to effective elimination under the “fast degrading” scenario, the air to sea flux was always positive (Figure 5d). In the “persistent” and the “best understanding” scenarios volatilization exceeded deposition and declined proportionally to the decrease in the rivers’ discharge. Note that volatilization, wet, and dry atmospheric deposition fluxes are calculated based on the constant concentration in air; hence they are affected by this uncertainty.

The exchange fluxes through the open oceanic boundaries (outflow and inflow) are relatively small compared to the magnitude of other processes (Figure 5e and f). This indicates that most of the released mass is eliminated near sources (i.e., the rivers’ mouth). The net oceanic flow to the North Atlantic through the northern boundary (NetFlowAo), and (f) at the southern boundary (NetFlowEc) is calculated as the difference between the Inflow and Outflow fluxes. The total mass change over a specific year in the water compartment is ∆Mwater (g), and in the sediment is ∆Msed (h).

FIGURE 5. Fluxes of HBCD (kg/year) out of and into the modeling domain due to different processes (see eqs S1 and S2 in Supporting Information) calculated for the beginning (1995) and the end (2005) of the simulation period under three model scenarios (Table S1): “Riv” is the rivers inflow (a). Elimination by degradation (Degwater + Degsed) is the sum of the degradation fluxes in the water and the sediment compartments (b). The net flux into the sediments (NetSink) is the difference between the sinking and the resuspension fluxes (c). Net air to sea flux (Dep−Vol) is the sum of wet and dry depositions minus the volatilization flux (d). HBCD transported by ocean currents through open oceanic boundaries in and out of the model domain, (e) at the northern boundary (NetFlowAo), and (f) at the southern boundary (NetFlowEc) is calculated as the difference between the Inflow and Outflow fluxes. The total mass change over a specific year in the water compartment is ∆Mwater (g), and in the sediment is ∆Msed (h).
Figure 5g and h show the change in mass over a year for seawater and the sediment. In the “persistent” scenario, the mass increases gradually in the beginning and the end of the simulation period. In the “fast degrading” scenario, the mass in both model compartments declines, except for the first year, when a small increase in the sediment mass occurred (see Supporting Information). In the “best understanding” scenario, the model suggests a continuous build-up in the sediment, while the seawater mass decreased following the reduced inflow from the rivers (Figure 5a).

Implications. The three scenarios tested in this study provide a helpful basis for discussing the two lines of concern for PBT substances referring to either potential for unknown effects combined with irreversibility or to transport to pristine environments (see Introduction). Predicted concentrations and responsiveness to changes in emission are very similar in the “fast degrading” and “best understanding” scenarios. Concentrations decline steeply with increasing distance from point sources and respond immediately to changes in emission. However, as long as emissions occur, the substance will be detectable in sediments and biota but monitoring data will not allow distinction between the two scenarios. Neither the presence nor a temporal trend observed in monitoring data can reveal information on persistency of the chemical in the system. Concentrations in both scenarios are reversible and a comparison of environmental concentrations near point sources with predicted safe concentrations (i.e., predicted no-effect concentrations), based on today’s known hazard data seem an adequate measure of the environmental risk caused by the emissions.

In terms of elimination from the system, the “best understanding” scenario falls between the two other scenarios. At the end of the simulation period, the most relevant elimination is sinking to the sediment (60% of the discharged mass), followed by degradation (30%), and despite the low potential for volatilization a relevant portion (10%) outgases to the atmosphere.

As for the two lines of arguments regarding regulation of PBT substances, the “fast degrading” scenario suggests that a product should not pose a concern provided that environmental concentrations are below derived safe concentrations for parent and potential breakdown products. Nevertheless, it will likely be detectable in biota while emissions occur. The “best understanding” scenario indicates that a product might be transported to remote environments (depending on its half-life in the atmosphere) but concentrations will respond promptly to changes in emission. The “persistent” scenario shows both a potential for further transport (depending on the half-life in the air) and a delay in the decrease of concentrations or even a continuous build-up after a decline in emissions, thereby falling within both lines of arguments about PBT substances.

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Supporting Information Available
This information is available free of charge via the Internet at http://pubs.acs.org/.

Literature Cited


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