ASSESSMENT OF TEMPORAL TREND AND SPATIAL DISTRIBUTION OF HEXABROMOCYCLODODECANE IN THE NORTH SEA USING A NUMERIC MODEL (FANTOM)

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Abstract

The flame retardant hexabromocyclododecane (HBCD) has recently been categorized as a PBT substance in the EU with reference to published monitoring data. HBCD has been chosen for this case study to better understand its fate, potential for transport and overall elimination in the marine environment. Model calculations were performed using a three-dimensional transport model for the North Sea (FANTOM) to allow conclusions on relevant sinks and fluxes in and out of the system and on the time needed to establish a steady state in the water and sediment compartments. Temporal trends and spatial distributions of HBCD in the North Sea were calculated for the period of 1995 to 2005. Results were complemented with scenarios with both extremes for biodegradation. Calculated concentrations for sediment were comparable to measured data. According to model calculations, steady state is established within months for the water and the top layer sediment with no evidence for a temporal trend.

Introduction

In recent years regulatory chemicals management has focused on substances that were both persistent and bioaccumulative. Precautionary regulatory action for such substances is rationalized with the intrinsic potential for exposure along the food chain, due to bioaccumulation, 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 release. The first line of argument is concerned about overall persistency, i.e. only persistency in *all* relevant compartments causes the irreversibility. The second line of argument is concerned by persistency in mobile compartments (air or water) and the resulting potential for transport, irrespective of whether or not the substance will persist at the receiving remote environment. With the introduction of the new chemicals legislation in Europe (REACH), the regulatory focus has been expanded to substances that are of 'equivalent concern' to substances that are persistent and bioaccumulative and makes reference to findings from data form environmental monitoring to conclude on the equivalency for concern. Hexabromocyclododecane (HBCD) has recently been categorized by the technical committee in the EU as not meeting the criteria for persistency but as a PBT substance based on other evidences (data from environmental monitoring programs). It has been chosen for this modeling study to better understand the underlying mechanisms in the distribution of HBCD and the potential for temporal trends in the environmental levels.

HBCD is used as a flame retardant in polystyrene building insulation panels. Another use is in flame retardant back-coats for instance for upholstery textiles. The commercial product of HBCD consists mainly of the 3 dia-stereomers α, ß, and γ; with fractions of 8, 15 and 75%, respectively.[1] HBCD has a low water solubility (65.6 µg/L, sum of the individual solubilities of the three diastereomers, a low vapor pressure (6.3 x 10-5 Pa) and is very hydrophobic (Log Kow=5.62).[2,3] In line with the high hydrophobicity, considerable bioconcentration has been reported for HBCD (log BCF=4).[4] Degradation occurs predominantly under anaerobic conditions with half-lifes ranging from approximately two days to two months for primary degradation by dehaloelimination forming cyclododecatriene.[1] Subsequent mineralization has been proven in a recent study. Results from monitoring studies performed until 2003 reveal detectable levels of HBCD in environmental samples (river and estuarine sediments) predominantly in areas with known point sources or in river basins.[5,6] In wildlife, detectable levels are more dispersive and low levels of HBCD have also been reported in fat tissues of top predators in the Arctic.[5,6,7,8] Unlike the technical product, the prevalent diastereomer in biota is α-HBCD, and in top predators α-HBCD has been detected exclusively.[9] With a half-life of 11 days in aerobic sediments HBCD has low overall persistency.[1] Degradation of the freely dissolved fraction is expected to be slower and in the absence of data assumed to be zero for this study. With this assumption the modeling study describes a case where there is an intrinsic potential for transport but also for

efficient overall elimination in the environment. For comparison two additional scenarios were calculated. In one scenario, a degradation half-life of 11 days is assumed also for the freely dissolved phase, in the other elimination by degradation has been disregarded completely. Other parameters were kept the same.

The North Sea has been chosen as a modeling domain because it is a receiving basin for a relevant portion of emissions in Europe. In the course of the simulation period of 1995 to 2005 emissions from one significant point source have been discontinued which resulted in a decrease of about one third of the total emission considered in the beginning of the calculations. This allows conclusions on the relevance of emission reduction programs. Of specific interest is the North Sea also because recently published data indicates an increase in the concentration of HBCD in the blubber of stranded harbour porpoise around the UK cost.[10] This study has been performed with a recently developed three-dimensional transport model for the North Sea (FANTOM). The model provides information on relevant sinks and fluxes in and out of the North Sea and on the time needed for establishing steady state concentrations in the different compartments. The FANTOM model has been applied and validated for a series of tracers like HCH isomers and a PCB congener.[11,12] In the following temporal and spatial distribution of HBCD is presented. These results will be further evaluated to quantify the relevant fluxes and specifically the net flux of HBCD through the model boundaries i.e. HBCD that is available for further transport. The uncertainties in the rivers concentrations, are carried forward to the calculated concentrations at a given model grid point. Nevertheless, the response of the system, specifically to change in the emission regime is independent from the absolute number and provides helpful basis in the discussion on the use of monitoring data in the identification of PBT substances.
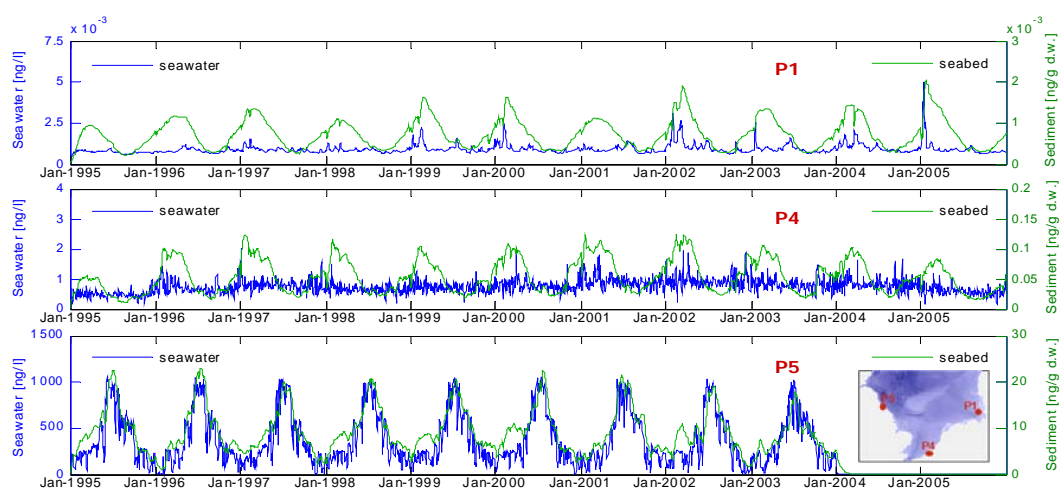

Figure 1. Time series of calculated HBCD concentrations in seawater (left axis) and marine sediments (right axis) at locations P1, P4 and P5 shown on the map. P5 reflects the decrease in concentration after the closing of a relevant point source.

Materials and Methods

The Fate and Transport Ocean Model (FANTOM) is a three-dimensional model based on the equation of transport of fluid.[11] The model has a horizontal resolution of 1.5' to 2.5' corresponding to 2.5-3 km and 21 vertical layers of varying depth. Input of the substance to the North Sea occurs through inflow from the rivers and adjacent water bodies (i.e. Atlantic Ocean, Baltic Sea, English Channel), and wet and dry atmospheric depositions. Transport with sea currents is driven by the advective and turbulent flow calculated by an ocean circulation model. In the water column a substance exists in truly dissolved phase and as bound to particulate organic carbon (POC). Distribution between dissolved and particulate phases is calculated using an equilibrium carbon-water partition coefficient. The particle bound fraction is subject to settling to lower water layers and ultimately to the sediment layer. The sediment compartment in the model is restricted to a layer of 2 cm of the upper sediment bed, where nearly all the benthic biomass is found. The bottom sediment enters the near-bottom water layer due to erosion and resuspension of the

previously deposited particles. It is diffused to the upper water layers and may be returned to the bottom sediment via deposition by settling. Dissolved fraction of the substance is involved in the gaseous air-sea exchange and can be volatilized back to the atmosphere. Degradation in the different compartments is represented by a first order rate decay coefficient. The model calculates three-dimensional concentrations of HBCD in the North Sea, concentrations in the upper sediment and fluxes between air – seawater, seawater – sediment and through the lateral boundaries. Emissions of HBCD are calculated either based on emission data as reported in the frame of the risk assessment for existing chemicals corrected for annual consumption data or based on annual consumption data and relevant emission fractions for the process.[13] Annual emission estimates were averaged over the year assuming no loss of HBCD in the river from source to river mouth and constant mass flows over time. Atmospheric concentrations were based on measurements from the Baltic island Gotland which are considered representative for the marine air. Degradation of HBCD is described by a half-life of 11 days for the particle bound fraction (i.e. suspended and settled in the sediment layer) based on the elimination rate determined for aerobic river sediments.[6] It is important to note that a significant uncertainty is associated with the estimates taken for the initial and boundary conditions. The potential impact of the assumptions on the conclusions is discussed for relevant conclusions.

Results and Discussion

Calculated concentration time series are presented for the water compartment and marine sediments at three selected locations (Fig.1). In line with the rapid elimination, steady state concentrations in the water phase and the sediment layer are established within months in the entire modeling domain. Yet, concentrations vary substantially across the model region and are determined by the HBCD discharge from adjacent rivers. Concentrations in seawater along the British coast shown for the location P5 (Fig. 1) decreased throughout the simulation period following the decrease in emissions. The same pattern is calculated for the sediment. Calculated spatial distribution of HBCD concentrations in the surface water layer and in the sediment are shown on Fig. 2 for the beginning, for the middle and for the end of the simulation period. Despite the considerable hydrophobicity of HBCD, about 80% of the total mass in the water compartment is freely dissolved while the particle bound fraction accounts for about 20% peaking in the bottom water layer (26%). There are steep gradients in concentrations with high values near the river mouths and low values in the central part of the North Sea remote from the sources. Calculated concentrations ranged from 10^{-4} to 10^2 ng/l in seawater and from 10^{-4} to 10^1 ng/g d.w. in the sediment.
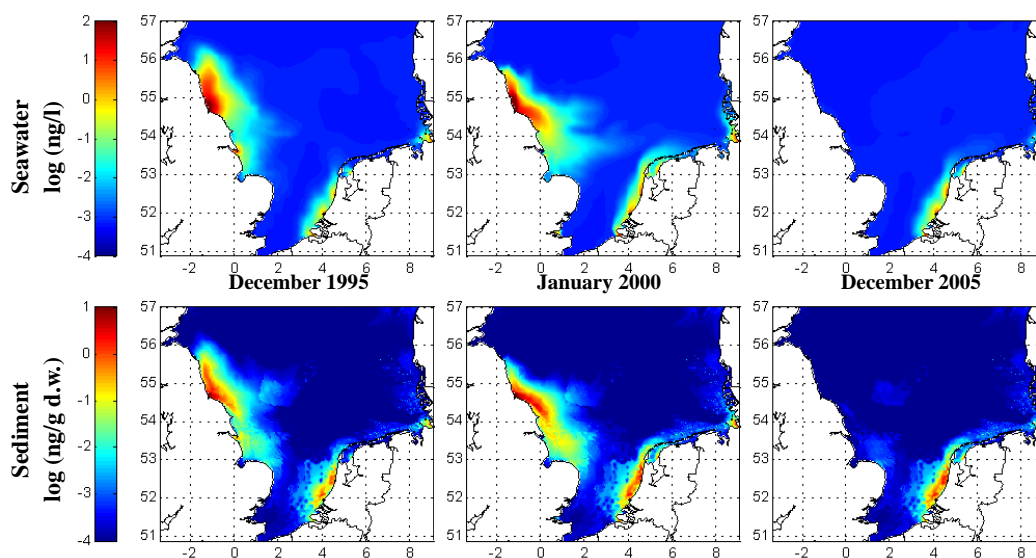

Figure 2. Spatial distribution of HBCD concentrations calculated by the model for the surface seawater (upper panel) and marine sediments (bottom panel). Note the logarithmic scale.

Large offshore gradients in the calculated concentrations make a comparison with available measurements difficult.

No data is reported for HBCD in marine waters and a direct comparison of calculated water concentrations is not possible. A significant amount of data is available for the blubber of harbour porpoise stranded at UK cost. Assuming a bioconcentration into lipids of approx. 10'000 and a biomagnification of 3 the concentration range calculated for the North Sea water (10^{-4} to 10^2 ng/l) converts to a calculated concentration in predatory fish (whole body) between $3 \cdot 10^{-3}$ to $3 \cdot 10^3$ ug/kg w.wt. Assuming a lipid content of 10% and that HBCD will prevail in the lipid, the concentration in the lipid is estimated to range from $3 \cdot 10^{-2}$ to $3 \cdot 10^4$ ug/kg lipid wt. Morris et al. (2004) report concentration of 440 to 6800 ug/kg lipid wt in the blubber of harbour porpoises (lipid content of the blubber ca. 90%) for the year 1998.[7] Law et al. (2006) report concentration from 64 to 19'208 ug/kg w.wt. for the period from 1994 to 2003 with a pronounced increase in the concentration after the year 2000.[10] Based on this calculation, modeled concentrations in seawater could be leading to levels reported for harbour porpoises in sections off the UK coast. However, calculated concentrations do not show any temporal trend for the UK cost. This applies also to the scenario without degradation, where steady state concentrations at and around location P5 are comparable to the calculated concentrations in the standard scenario (not shown).

Concentrations of HBCD in marine sediments measured in the period from 2002 to 2005 ranged from 0.03 to 6.5 ng/g d.w. in the southeastern part of the North Sea.[14] No temporal trend has been reported in this measured data. Modeled HBCD sediment concentrations show large offshore gradients in that region (Fig. 2) and are comparable to the range of measured values. The mean anti-clockwise pattern of sea currents commonly observed in the North Sea favors concentration accumulation in the southeastern North Sea and in the scenario without degradation the calculated concentrations showed a gradual increase over the 11 years period exceeding the measured concentrations already in the first year of the simulation (not shown). This comparison confirms that the overall persistency of HBCD in the environment is low. Further evaluation of the model results will reveal the amount of HBCD that is eliminated in the North Sea, the amount available for transport by ocean currents, and the net fluxes of the exchange with the atmosphere and the sediments. This will allow conclusions on the level of emission that is tolerable to the North Sea and that leads to acceptable quantities available for transport.

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