

What Drives the Fate of Persistent Organic Pollutants in the North Sea? Insights from a Regional Model

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Abstract—Long-lived synthetic chemicals such as Persistent Organic Pollutants (POPs) are widespread in marine environments. Owing to its proximity to sources, the North Sea is a recipient of large number of these pollutants. Unlike the global ocean, shallow and coastal marine reservoirs like the North Sea do not always act as ultimate sinks for POPs. They may become efficient pathways for pollutants' transport to other compartments of the Earth system and to remote regions. Models have proved to be useful tools to study the complex range of processes that POPs undergo in the environment. Prerequisites for modeling of pollutants like POPs are realistic representation of the circulation, boundary and initial states, forcing, physicochemical properties, and processes formulation in the model. Here the significance of these prerequisites on the example of the regional hydrodynamic model FANTOM is discussed. Model simulations for a number of pollutants, such as HCHs, PCBs, and HBCD are presented and compared. Due to various environmental properties of these pollutants and different sources, the contribution of major controlling mechanisms to their fate in the North Sea is different.

Keywords: POPs, regional modeling, North Sea

INTRODUCTION

The North Sea is particularly vulnerable to persistent organic pollutants (POPs) as it receives large amounts of them as a result of direct introduction or deposition from the atmosphere. Monitoring campaigns show that nearly all known POPs have been detected in the North Sea. A number of models have been developed and successfully applied to study these pollutants in different environmental compartments. In the following I will discuss model results based on the regional model FANTOM (Ilyina *et al.*, 2006) in the light of importance of different processes controlling the fate of POPs in the North Sea for pollutants with different usage history and physicochemical properties.

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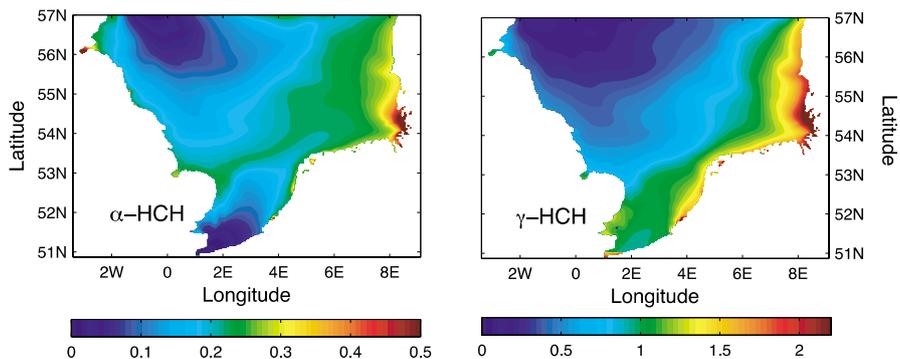


Fig. 1. Modeled annual mean (of the year 1998) vertically averaged concentrations (ng L^{-1}) of α -HCH (left) and γ -HCH (right).

We studied following pollutants: Isomers of hexachlorocyclohexane α - and γ -HCH—both having relatively high water solubility and being abundant in the North Sea in aqueous phase. A congener of polychlorinated biphenyls PCB 153 is lipophilic and is almost insoluble in water. PCBs and technical HCH (which contains α -HCH) have been banned in the countries around the North Sea in the 1980s; whereas γ -HCH has been used as an insecticide until mid 1990s. We also studied hexabromocyclododecane (HBCD) which is used as a flame retardant and has detectable levels in biota of the North Sea.

METHODS

Here the regional fate of POPs is discussed based on the results of the three-dimensional ocean model FANTOM. The model has been developed to study the fate of long-lived synthetic chemicals like POPs in the North Sea. It uses Eulerian description of transport and is complemented by processes that pollutants undergo in the marine environment such as diffusive air-sea exchange, wet and dry atmospheric depositions, partitioning between particle-bound and dissolved phases, degradation, sinking to the sea bottom with subsequent sedimentation and resuspension (see Ilyina *et al.*, 2006, 2008 for detailed description). The model has a horizontal resolution of $1.5' \times 2.5'$ and 21 vertical layers in the water column of varying thickness ranging between 5–10 m. There is also a sediment module of the upper 2 cm of the sediment bed, a layer in which most of the benthic biomass is found. POPs deposited into the sediment bed are not lost irrevocably from the model. They may be resuspended back into the water column due to the action of waves and currents (Dobrynin *et al.*, 2010).

The model has been now applied to other regions, i.e., the Malacca Strait (Pohlmann *et al.*, 2009) and the extended North Sea domain including adjacent basins—the Skagerrak, Kattegat, and the westernmost part of the Baltic Sea (O'Driscoll *et al.*, 2009).

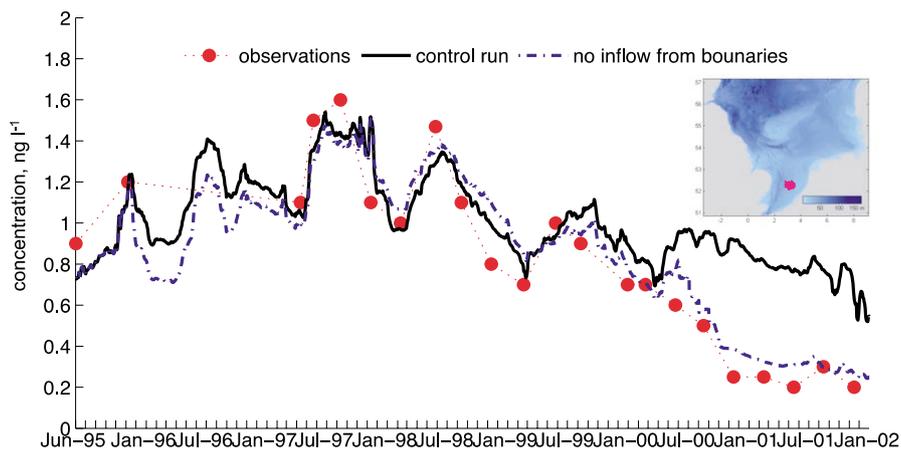


Fig. 2. Temporal evolution of modeled γ -HCH concentration (ng L^{-1}) in the surface layer calculated with constant fluxes prescribed at open water boundaries (black solid line) and from a run in which inflow from open boundaries was set to zero (blue dashed line). Red dots represent individual measurements at this location shown on the map.

RESULTS AND DISCUSSION

Flow field control on spatial distributions

The flow field in the North Sea is determined by tidal currents, meteorological conditions, and run-off from rivers (Otto *et al.*, 1990). Tidal currents enter the North Sea from the Atlantic Ocean through the northwest opening, and (a smaller part) in the southwest through the opening in the English Channel. Westerly winds prevail over the North Sea. The predominant circulation driven by winds and tides is counter-clockwise flowing along the coastline.

As a result, pollutants with local sources, for example from the rivers flowing into the North Sea, such as HCH isomers, PCB 153 and HBCD (Fig. 1) have pronounced positive offshore gradients. The highest concentrations are found along the coastline and close to rivers mouths. Low concentrations in the northwestern North Sea are due to the inflow of Atlantic water which typically has lower concentrations of POPs. The central North Sea, unless depositional fluxes from the air above exceed the outgassing fluxes, normally has lower concentrations of POPs.

Forcing control on concentrations

The outcome of a regional model strongly depends on the boundary and initial conditions. We tested the influence of the inflow of POPs from lateral open boundaries by prescribing zero concentrations at the boundaries in the model. Here an example with γ -HCH is discussed (Fig. 2). In one run (the control run) the flux of γ -HCH at the open boundaries was constant over the whole simulation

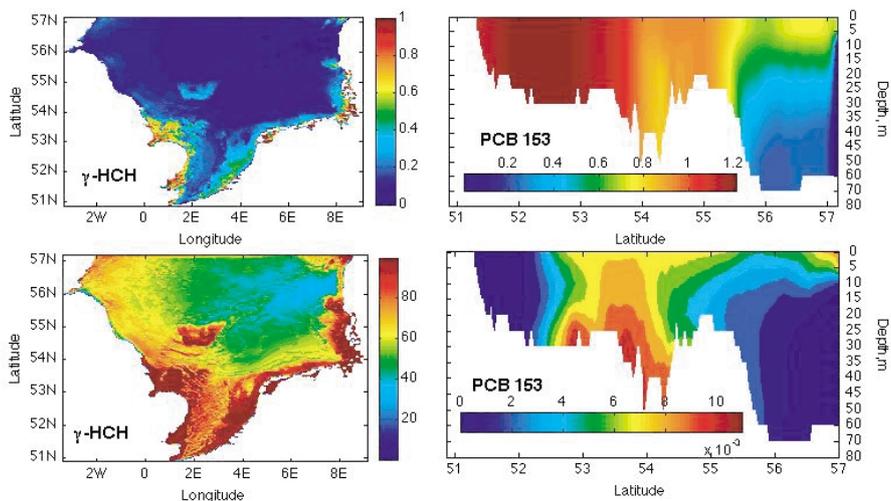


Fig. 3. Left panel: Surface particle-bound fraction (in % of total concentration) of γ -HCH (top) and PCB 153 (bottom). Right panel: Vertical distribution of total concentration (ng L^{-1}) of γ -HCH (top) and PCB 153 (bottom) along 3°E .

period from 1995 until 2001. In the other run, no inflow of γ -HCH from the open boundaries was assumed. Over the course of the simulation period, application of γ -HCH around the North Sea has been restricted, and its concentrations in seawater decreased substantially. However, in the control run, concentrations at the boundaries were constant and representative of the year 1995 so that the decrease was not captured. As a result, model results in the last two years of the simulation better agree with observations in the run in which inflow at the boundaries was set to zero. Overall, depending on the location, inflow through the open boundaries can introduce up to 50% variability in pollutant's seawater concentrations.

Control of physicochemical properties on partitioning behavior and persistency

Physicochemical properties of POPs, such as their partitioning coefficients between different Earth's compartments, and degradation half-lives are important controlling factors that determine environmental fate of these pollutants (Mackay *et al.*, 2000).

POPs released into the North Sea cycle in truly dissolved phase or as bound to organic particles, depending on their solubility and lipophilicity. Many POPs abundant in the North Sea have moderate or low water solubility (UNEP, 2003). The amount of POPs attached to particles is determined by their octanol-water partitioning coefficient (K_{ow}). Here, horizontal and vertical distributions of a relatively water-soluble γ -HCH and a lipophilic PCB 153 in the North Sea are

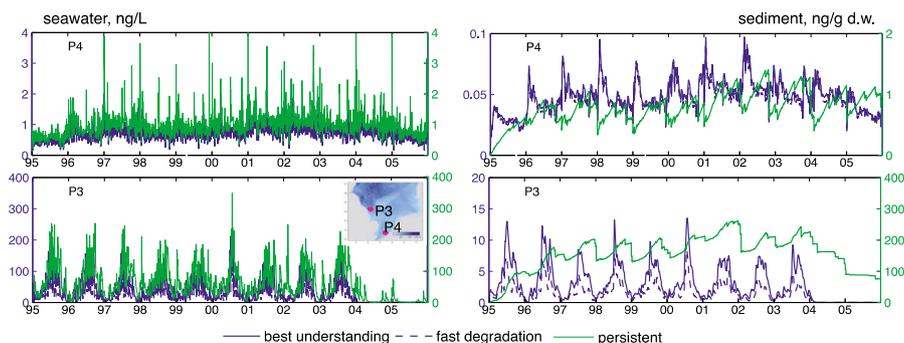


Fig. 4. Temporal evolution of HBCD concentration in seawater (left panel) and sediment (right panel) calculated under different degradation scenarios: best understanding (with degradation allowed only for particle-bound fraction and in sediment), fast degradation (with degradation in all compartments and fractions) and persistent (without degradation) at locations P4 (top) and P3 (bottom) shown on the map. Redrawn after Ilyina and Hunziker (2010).

compared (Fig. 3). Values of K_{ow} for PCB 153 are three orders of magnitude higher than for γ -HCH. Consequently, particle-bound fraction of PCB 153, expressed in % of total concentration, reaches 90% in areas with high content of particulate organic matter. In contrary, less than 1% of γ -HCH is attached to particles (Fig. 3). This implies that vertical and horizontal patterns of hydrophobic and lipophilic compounds, i.e., PCB 153 are shaped by the distribution of particles (given that there is sufficient amount of particulate matter available), whereas compounds with higher water solubility, i.e., the HCHs follow the water mass stratification. γ -HCH is usually well mixed in the water column in the entire model domain, except for periods when thermal stratification is formed during summer time. PCB 153 is removed from the surface with sinking particles so that highest concentrations are found at the bottom during calm periods (Fig. 3). Such vertical structure can be instantly redistributed during storms leading to resuspension of sedimented particles from the sea bottom.

Another controlling mechanism in the aquatic fate of POPs is their persistency in a specific compartment. We performed model scenarios with HBCD in which we differed its degradation half-lives in seawater and sediment (Fig. 4). Model scenarios ranged from a best understanding, in which degradation was only allowed for particle-bound fraction in seawater and sediment, to fast degradation with degradation in all compartments and fractions, and a persistent scenario without degradation (Ilyina and Hunziker, 2010). At a location P4, close to the River Scheldt estuary (Fig. 4), sources of HBCD remained at the same level throughout the simulation period. Concentrations in seawater and sediment did not show pronounced decrease or increase even in the persistent scenario. This indicates that persistency will not necessarily cause an increase in the concentration's temporal trend. At location P3, release of HBCD ceased by the

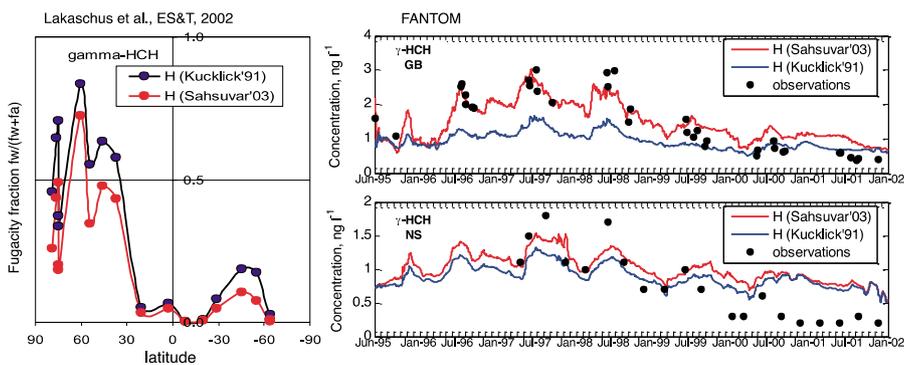


Fig. 5. Left panel: Fugacity fractions of γ -HCH versus latitude calculated using temperature dependencies of the Henry's law constant after Sahsuvar *et al.* (2003) and Kucklick *et al.* (1991). Redrawn based on data reported in Lakaschus *et al.* (2002). Right panel: Concentrations of γ -HCH (ng L^{-1}) in the surface layer in the south-eastern North Sea (top; location GB) and in the open North Sea (bottom; location NS) calculated using temperature dependencies of the Henry's law constant after Sahsuvar *et al.* (2003) and Kucklick *et al.* (1991).

year 2004 after the production site has been closed. As a result, concentrations of HBCD decreased in all scenarios almost immediately. Therefore, a temporal trend may rather reflect a change in emissions (i.e., absence of a steady state) than persistency.

Uncertainties in temperature dependency of the Henry's law constants

Some physicochemical properties of POPs, such as the temperature dependencies of the Henry's law constants (H_c) demonstrate large uncertainties. H_c is used to calculate the air-sea flux—one of the dominant entry or loss mechanisms for POPs in the North Sea (see Ilyina *et al.*, 2008). Our model experiments and observational data (Fig. 5) indicate that under ambient conditions and HCHs concentrations typical for 30–60°N, different temperature dependencies of H_c (i.e., reported by Kucklick *et al.*, 1991 and by Sahsuvar *et al.*, 2003) may alter and even reverse the direction of the air-sea flux of α - and γ -HCH. Our model experiments show that air-sea flux calculations using different H_c temperature dependencies are responsible for 20–50% variability in seawater concentration of γ -HCH.

In summary, regional modeling of POPs in marine environment requires realistic representation of hydrodynamic conditions in the area of interest, valid assumptions regarding boundary and initial conditions, knowledge of the compound's partitioning properties and degradation half-lives in the modeled compartments, and accurate formulation of processes that POPs undergo in the system. Of major importance is also compounds selection for modeling—correct representation of carrying matrices for POPs (i.e., in aqueous phase or on particles) have to be included in a model.

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