



Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Mass budgets and contribution of individual sources and sinks to the abundance of γ -HCH, α -HCH and PCB 153 in the North Sea

Tatjana Ilyina^{a,*}, Gerhard Lammel^{b,c}, Thomas Pohlmann^a

^aCentre for Marine and Atmospheric Sciences (ZMAW), Institute of Oceanography, University of Hamburg, Bundesstr. 53, 20146 Hamburg, Germany

^bZMAW, Max Planck Institute for Meteorology, Bundesstr. 53, 20146 Hamburg, Germany

^cMasaryk University, Research Centre for Environmental Chemistry and Ecotoxicology, Kamenice 3, 62500 Brno, Czech Republic

ARTICLE INFO

Article history:

Received 4 December 2007

Received in revised form 11 March 2008

Accepted 4 April 2008

Available online 4 June 2008

Keywords:

Modeling

Fate

Transport

Marine environment

FANTOM

ABSTRACT

Mass budgets of hexachlorocyclohexanes (α -HCH and γ -HCH) and a polychlorinated biphenyl (PCB 153) for 1995–2001 were calculated based on model simulations and observations for the North Sea as a whole and the German Bight, a coastal shallow subregion. For the North Sea the air–sea fluxes of the three pollutants were net depositional and dominated by local sources (γ -HCH and PCB 153) or atmospheric deposition (α -HCH). The air–sea fluxes were net volatilizational in the German Bight. Unlike HCH, PCB 153 does not show a downward trend in the North Sea marine environment during the study period. Due to its physicochemical properties it is expected to readily enter the food chains. Model results suggest that during studied period, the North Sea was a sink for PCB 153 and a source of HCHs for the outer world.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

The fate and behavior of persistent organic pollutants (POPs), e.g. hexachlorocyclohexanes (HCHs) and polychlorinated biphenyls (PCBs) in the environment has attracted considerable scientific and political interest arising from concern of human and wildlife exposure to these chemicals and their discovery in pristine environments far from the sources. POPs are ubiquitously distributed in the global oceans as a consequence of atmospheric deposition and river inputs (e.g. Tanabe et al., 1983; Iwata et al., 1993; Bidleman et al., 1995; Lakaschus et al., 2002). The study of processes and pathways that POPs undergo in the aquatic environment is particularly important as the hydrosphere is where many POPs resist degradation (hence, accumulate) and are more prone to bioaccumulation (hence, enter the food chains). Oceans can be considered as a global reservoir and ultimate sink compartment of many POPs (e.g. Iwata et al., 1993). However, in response to long-term uptake of POPs coastal and even open ocean water bodies may turn into net volatilizational, i.e. act as sources to the atmosphere, seasonally or permanently (Bidleman et al., 1995; Bruhn et al., 2003). In shallow seas like the North Sea the sinking particles carrying POPs down to the bottom sediments may enter

the water column via resuspension. Therefore, even when primary pollutant sources are reduced, remobilization from water bodies could act as a secondary source for the atmosphere.

Mass budgets of POPs and POPs-like chemicals in the marine environment are required to evaluate both scientific knowledge and chemicals management options. For a south-eastern part of the North Sea (the German Bight), such budget calculations were already performed for several POPs based on measurements (Hühnerfuss et al., 1997). However, measurements of most POPs in seawater are too sparse to allow a comprehensive assessment of their pathways and fluxes in and out of the North Sea or its subregions. Furthermore, mass budgets of sea areas based on field data are uncertain as the variability of the concentrations in both time and space can be high in particular in shelf seas and coastal areas (e.g., Bruhn et al., 2003). A multimedia mass balance model was used to budget the fate of the sum of 6 PCBs (Wania et al., 2001) and HCH (Breivik and Wania, 2002) in the Baltic Sea based on constant water fluxes. Mass budgets of POPs-like contaminants in seas have not been assessed so far with a three-dimensional hydrodynamic model capable to resolve environmental conditions and processes. Many pollutants sources in the North Sea are land-based. Thus, finer spatial resolution of the model can improve the representation of distribution of POPs in the near-coastal areas and their transport with sea currents. For instance, by comparing the results of a meso-scale and a large-scale circulation model Pohlmann (2006), showed that especially in the coastal North Sea along the Dutch and German coast, a meso-scale model better captures the

* Corresponding author. Present address: School of Ocean and Earth Science and Technology, Department of Oceanography, University of Hawaii at Manoa, 1000 Pope Road, Honolulu, HI 96822, USA. Tel.: +1 808 956 3679; fax: +1 808 956 7112.
E-mail address: ilyina@soest.hawaii.edu (T. Ilyina).

observed patterns of temperature and salinity and more accurately quantifies the kinetic energy of residual flow. This study is the first attempt to estimate mass budgets and the contribution of individual key processes to the burdens of organic pollutants using a model with high spatial and temporal resolution. We address α -HCH, γ -HCH and PCB 153 in the North Sea. This choice of substances includes different physicochemical properties, i.e. lipophilicity (PCB) vs. water solubility (HCHs; Table 1), as well as different historical usage and emission trends, i.e. banned in Europe three decades ago (α -HCH, PCB 153) vs. usage restrictions introduced in the 1990s (γ -HCH).

2. Model description

FANTOM (Fate and Transport Ocean Model) is a three-dimensional numerical model designed for simulating the long-term fate of pollutants in the shelf and coastal aquatic environment. A full description of the model, its forcing and model validation is given by Ilyina et al. (2006) and Ilyina (2007). The pollutants can enter the model domain via rivers, adjacent seas or atmospheric deposition. In seawater they are transported with vertical and horizontal ocean currents and large-scale turbulent diffusion calculated by a circulation model (Pohlmann, 1996). A pollutant is either dissolved or bound to particulate organic carbon (POC) present in seawater. POC concentrations in the North Sea were calculated by an ecosystem model (Pätsch et al., 2002). The particle-bound fraction is a function of substance lipophilicity and is subject to gravitational sinking and deposition to the bottom sediments. Particles can also re-suspend back to the water column when sediments are disturbed by ocean currents and waves. Sediment compartment is represented by the upper 2 cm of the sediment bed, a layer where nearly all the benthic biomass is found. Degradation in seawater is described by a first order rate decay coefficient (Table 1). It is assumed to double per 10 K temperature increase. The reversible air–sea gaseous flux of pollutants is determined based on the two-film model in accordance with the fugacity concept formulation (Schwarzenbach et al., 1993). Henry's law constant H_c ($\text{Pa m}^3 \text{mol}^{-1}$) is used to describe the equilibrium partitioning of POPs between air and water. Experimentally derived relationships for H_c are calculated from a temperature dependant equation (Table 1; Paasivirta et al., 1999; Sahsuvar et al., 2003) using intercept b and slope m (K) at sea surface temperature T_w (K):

$$\log H_c = b + \frac{m}{T_w} \quad (1)$$

The dry atmospheric particle deposition flux is calculated as a product of the pollutants particle-bound concentration in air and dry deposition velocity. The wet deposition flux is calculated as a product of the pollutant concentration in precipitation based on measurements, which includes both the dissolved and particulate phases, and the precipitation rate.

Model calculations were initialized by measurements-based POPs seawater concentrations (DOD, 2005). Oceanic boundary conditions were extrapolated from the measured values used for the model initialization. Boundary conditions were based on monitoring data of POPs in air (Fig. 1; EMEP, 2005) and in the rivers (OSPAR, 2002; DOD, 2005; DONAR, 2005). Monthly mean concentrations of POPs in air and rain available from the few coastal stations (i.e. for PCB 153 only from Lista, for γ -HCH and α -HCH also from Westerland and Kollumerwaard) were interpolated on the entire model grid. River loads were calculated as a product of the daily fresh water discharge and the concentration of POPs at the last tidal gauge station of each river (Fig. 1). Measurements in the rivers were available as annual (for the British rivers), monthly (for the rivers Ems and Weser) or weekly and bi-weekly (for the other continental rivers) mean concentrations. Note that the seasonal and spatial variability of the atmospheric deposition fluxes are uncertain as only precipitation rates were available in gridded form. Pollutant concentrations in air and precipitation (Fig. 1) were only available at a few coastal monitoring stations and were extrapolated to the entire model domain (Ilyina et al., 2006). As air pollutants' concentrations show no or negative spatial trend from coastal areas to the open sea, the pollutant deposition fluxes might be somewhat overestimated.

The model was applied to the southern North Sea, a shallow region with the mean depth of 50 m and a maximum depth of 160 m (Fig. 2). The horizontal resolution of the model is 1.5' to 2.5' corresponding to 2.5–3 km. The model has 21 vertical layers of varying depth. The simulation period was from July 1995 to December 2001.

Mass budgets of γ -HCH, α -HCH and PCB 153 calculated by FANTOM include exchange fluxes between the air and seawater as well as between seawater and the upper sediment and the sinks and sources to the seawater burden. These calculations were performed for two regions further on named as the North Sea (entire model domain, i.e. south of 57 °N) and the German Bight (northern border at 55 °N and the western border at 6°25'E; Fig. 2). The total mass change (ΔM_{POP}) was integrated over a period of time (Δt) for these two sea regions. It is given as:

$$\frac{\Delta M_{\text{POP}}}{\Delta t} = \text{NetGas} + \text{Dep} - \text{Deg} + \text{NetFlow} + \text{Riv} - \text{NetSink} \quad (2)$$

with gaseous dry deposition flux minus the volatilization flux (NetGas), wet and dry particle depositions (Dep), degradation rate in seawater (Deg), net flows through the lateral boundaries into and out of the model domain (NetFlow), river input flow (Riv), the loss rate due to sinking minus rate of resuspension from the bottom sediments (NetSink). The annual mass change is obtained by integrating these fluxes over time, i.e. one year in this study. Inventories calculated that way demonstrate the contribution of an individual key process for the abundance of studied POPs in the North Sea.

Table 1

Physicochemical properties of γ -HCH, α -HCH and PCB 153 at 298 K and temperature dependencies of Henry's law constant used in FANTOM (cf. Eq. (1))

	γ -HCH	α -HCH	PCB 153
Saturation vapor pressure, p (Pa)	6.6×10^{-3a}	8.4×10^{-3a}	4.1×10^{-5c}
Water solubility, s (mg l^{-1})	7.4^a	2.0^a	8.8×10^{-4c}
Octanol-water partitioning coefficient, K_{ow} (-)	3.98×10^{3b}	5.89×10^{3b}	5.62×10^{6c}
Degradation rate in seawater, k_{deg} (s^{-1})	2.7×10^{-8b}	2.3×10^{-8b}	1.6×10^{-9c}
Intercept of the temperature dependent Henry's law constant, b (-)	10.14 ± 0.55^d	10.13 ± 0.29^d	14.05^e
Slope of the temperature dependent Henry's law constant, m (K)	-3208 ± 161^d	-3098 ± 84^d	-3662^e

^a Rippen (2000).

^b Klöpffer and Schmidt (2001).

^c Beyer et al. (2002).

^d Sahsuvar et al. (2003).

^e Paasivirta et al. (1999).

Download English Version:

<https://daneshyari.com/en/article/4413974>

Download Persian Version:

<https://daneshyari.com/article/4413974>

[Daneshyari.com](https://daneshyari.com)