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The effects of climate change on persistent organic pollutants (POPs) in the North Sea

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Abstract

The fate and cycling of two selected legacy persistent organic pollutants (POPs), PCB 153 and γ -HCH, in the North Sea in the 21st century have been modelled with combined hydrodynamic and fate and transport ocean models. To investigate the impact

- ⁵ of climate variability on POPs in the North Sea in the 21st century, future scenario model runs for three 10 yr periods to the year 2100 using plausible levels of both in situ concentrations and atmospheric, river and open boundary inputs are performed. Since estimates of future concentration levels of POPs in the atmosphere, oceans and rivers are not available, our approach was to reutilise 2005 values in the atmosphere,
- ¹⁰ rivers and at the open ocean boundaries for every year of the simulations. In this way, we attribute differences between the three 10 yr simulations to climate change only. For the HAMSOM and atmospheric forcing, results of the IPCC A1B (SRES) 21st century scenario are utilised, where surface forcing is provided by the REMO downscaling of the ECHAM5 global atmospheric model, and open boundary conditions are provided
- ¹⁵ by the MPIOM global ocean model.

Dry gas deposition and volatilisation of γ -HCH increase in the future relative to the present. In the water column, total mass of γ -HCH and PCB 153 remain fairly steady in all three runs. In sediment, γ -HCH increases in the future runs, relative to the present, while PCB 153 in sediment decreases exponentially in all three runs, but even faster in the future, both of which are the result of climate change. Annual net sinks exceed sources at the ends of all periods.

1 Introduction

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Persistent organic pollutants (POPs) are highly toxic chemicals. As their name suggests, they degrade slowly and, thus, have long half lives, generally on the order of years to tens of years. In productive ocean waters, which are often shallow and coastal, POPs enter the food web, bioaccumulate in different kinds of tissues and become haz-



ardous to living organisms including humans (AMAP, 1998). Hence, the study of POPs under a changing climate scenario is important and interesting.

POPs in the ocean are subject to a wide range of processes including mechanical, chemical, physical, and biological processes. For the North Sea, large amounts
of POPs enter the system from the surrounding countries. Major entrance pathways of POPs to the North Sea are through atmospheric deposition, river inputs and adjacent seas, i.e., the North Atlantic Ocean, the English Channel and the Baltic Sea (see Fig. 1). Ilyina et al. (2006), who developed the fate and transport ocean model (FAN-TOM), were the first to investigate the fate of POPs in the southern North Sea with a high resolution combined hydrodynamic and fate and transport model. O'Driscoll et al. (2013) extended the model domain to the entire North Sea system while improving several POPs processes in the model and the quality of input and forcing data.

In this study, we have selected two very different legacy POPs for the simulations. Lindane, γ -HCH, is a legacy POP that was widely used as an insecticide but was ¹⁵ banned under the Stockholm Convention. It is not hydrophobic and mostly dissolves in water, and has half lives of about 1.7 and 1.8 yr in water and sediment, respectively (Ngabe et al., 1993; Hornsby et al., 1996). PCB 153, on the other hand, is very hydrophobic, so it does not readily dissolve in water and mostly sorbs to organic material

- in aquatic environments. It is also subject to the terms of the Stockholm Convention. It causes a host of medical problems in humans, see, e.g., Ghosh et al. (2011) and references therein. It has half-lives of about 13.7 and 18.8 yr in water and sediment, respectively, (Sinkkonen and Paasivirta, 2000). For a further discussion of properties influencing the fate and transport of γ -HCH and PCB 153 in the marine environment, see O'Driscoll et al. (2013).
- Previous studies of the fate of POPs in shallow and marginal seas include those of Breivik and Wania (2002a), Breivik and Wania (2002b) and Pacyna et al. (1999) for the Baltic Sea; those of Castro-Jiménez et al. (2012) and Berrojalbiz et al. (2011) for the Mediterranean and Black Seas; and those of Iwata et al. (1993), Lakaschaus et al. (2005) and Schulz-Bull et al. (1998) for open seas; all of which were limited temporally



or spatially due to practical or analytical restraints; and those of Ilyina et al. (2006) and O'Driscoll et al. (2013) for the North Sea system mentioned above.

Recent POP global modelling compartmental studies include those of Scheringer (2008) and Wania and Su (2004), while Lammel and Stemmler (2012) investigated the

fractionation and current time trends of PCBs with a global atmosphere-ocean general circulation model. Wöhrnschimmel et al. (2012) have recently presented the fate of PCBs and HCHs up to 2050 with a global multi-media model.

In addition to these studies, Jonsson et al. (2003) have suggested that continental shelves are important sinks of PCBs, while Jurado et al. (2007) have identified sed-

iment resuspension as a key process capable of reintroducing POPs into the water column. O'Driscoll et al. (2013) have shown both of these to be true for the case of the North Sea.

However, there have to date been no studies investigating the fate of POPs in coastal or shelf seas with high resolution simulations under climate change scenarios. There-

¹⁵ fore, we feel the present study is an important contribution to the literature, by complementing previous studies and giving us insight into the effect of climate change on important POP processes in shelf seas, thus helping policy makers to make well informed decisions.

To investigate the impact of climate variability on POPs in the North Sea in the 21st century, future scenario model runs for three 10 year periods to the year 2100 (2006– 2015, 2046–2055 and 2090–2099) using plausible levels of both in situ concentrations and atmospheric, river and open boundary inputs are performed.

A 3-D hydrodynamic model is a necessary prerequisite tool for modelling their fate in the ocean. For this purpose, we have applied a very high resolution version of the

²⁵ Hamburg Shelf Ocean Model (HAMSOM) for the North Sea at the Institute of Oceanography, University of Hamburg, see O'Driscoll et al. (2013) for details.



2 Model description and approach

2.1 Model description

Here, we present a brief overview of both the HAMSOM and FANTOM models, for a more detailed description see O'Driscoll et al. (2013). Comprehensive descriptions of

⁵ both models are available in the literature for the FANTOM (Ilyina et al., 2006) and HAMSOM (Backhaus, 1985; Pohlmann, 2006).

Model bathymetry is obtained from Larsen and She (2001) and presented in Fig. 1. Time steps (5 min) are the same in both models.

The HAMSOM is a baroclinic shallow water equation ocean circulation model, which has been successfully applied to different regional seas, see, e.g., Mayer et al. (2010), Su and Pohlmann (2009), and O'Driscoll et al. (2013). Meteorological forcing is provided by the REMO downscaling of the ECHAM5 global atmospheric model IPCC A1B (SRES) 21st century scenario, see Jacob et al. (2001), Roeckner et al. (2006). Open boundary conditions (temperature, salinity and sea surface height) are provided by the

- global ocean model MPIOM, see Jungclaus et al. (2006). Temperature and salinity are prescribed under inflow conditions, while a radiation condition by Orlanski (1976) is utilised when the flow is outward. Locations of freshwater runoff into the model domain are shown in Fig. 1. Monthly climatological river runoff data are used for the entire run, see O'Driscoll et al. (2013).
- The FANTOM is a 3-D Eulerian model for simulating the fate of POPs and other pollutants in coastal regions and shelf seas. Model processes fall into 5 main categories: transport due to advection and diffusion; air-sea exchange; phase (re-)distribution; degradation; exchange between the water column and sediment (deposition and resuspension), see Fig. 2 for schematic of processes, O'Driscoll et al. (2013) for a short description and Ilyina et al. (2006) for full details. For reasonable simulation of POPs exchange between water column and sediment, the FANTOM has 20 sediment layers

representing the upper 2 cm of the sediment bed.



Both models (HAMSOM and FANTOM) have been evaluated for the period 1996-2005 (O'Driscoll et al., 2013) and the simulations were shown to be of a very satisfactory quality relative to observations.

2.1.1 Air-Sea gas exchange

For the FANTOM, gas exchange processes at the air-sea interface are based on the stagnant two-film theory formulated by Whitman (1923) and Liss and Slater (1974). A fugacity formulation is included as described by Mackay (2001). The chemical equilibrium of the POP between the air and water is controlled by the following parameters: temperature, wind speed, and the physical-chemical properties of the compound and its abundance in the environment. See O'Driscoll et al. (2013) for further details.

Fugacity capacities in air (Z_a) and water (Z_w) are calculated as:

$$Z_{\rm a} = \frac{1}{RT_{\rm a}}$$
 and $Z_{\rm w} = \frac{1}{H_{\rm C}(T_{\rm w})}$

respectively, where *R* is the ideal gas constant, T_a and T_w are air and water temperatures, respectively, and H_c is Henry's law constant at T_w . The volatilisational exchange rate is calculated according to Mackay (2001) and Wania et al. (2000):

$$D_{WA} = \frac{A_W}{\frac{1}{u_1 \cdot Z_a} + \frac{1}{u_2 \cdot Z_W}}$$

with A_w as water surface area and u_1 and u_2 as mass transfer coefficients, where u_1 and u_2 are functions of wind speed (Schwarzenbach et al., 1993). See O'Driscoll et al. (2013) for further details and discussion.

20 2.2 Model approach

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Since estimates of future concentration levels of POPs in the atmosphere, oceans and rivers are not available, our approach was to reutilise 2005 values in the atmosphere,



(1)

(2)

rivers and at the open ocean boundaries for every year of the simulations, while using the (final) result for POP concentrations in water and sediment in both phases of our 1996–2005 runs, see O'Driscoll et al. (2013), as the initial condition for all three future runs. In this way, we attribute differences between the three 10 yr simulations to climate

- ⁵ change only. Atmospheric input of POPs is provided by output from the atmospheric model of the MSC-E, EMEP (Gusev et al., 2009) for the year 2005, while concentrations for riverine input have been calculated from available datasets for the year 2005. We think this is a reasonable approach since concentrations in the atmosphere, rivers and oceans (primary sources) were greatly reduced in 2005 relative to 1996 (O'Driscoll et
- al., 2013) but capacitors (secondary sources) will continue to play an important role in the coming years due to their long-term storage ability, see discussions in Nizzetto et al. (2010) and Lohmann et al. (2007). Again, we stress that we run only one climate scenario, because we are interested in the impact of the climate on the fate of the POPs in the North Sea. For investigating the future development of the POPs, different
 projections and even ensemble runs would be necessary.

Locations of freshwater runoff into the model domain are shown in Fig. 1. Monthly climatological river runoff data for major Continental and British rivers are used for the entire period in both models (O'Driscoll et al., 2013).

3 Results and discussion

20 3.1 Hydrodynamics

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The basic hydrodynamic results for the model domain are as follows. Analysis of the atmospheric forcing data for the North Sea reveals a continuous increase of the spatially averaged 2 m air temperature of 2.38 °C within the scenario period 2001-2100, where warming in winter is 25% higher than the mean, but is 22% lower in summer. Similarly, the volume averaged water temperature of the North Sea increases by 2.0 °C (to 2100) with warming 4% weaker in summer and 4% stronger in winter in 2100 relative



to 2000, whereas sea-surface temperature (SST) trends show average increases of 1.66 and 2.31 °C in summer and winter, respectively (see Fig. 3a and b). A decrease in salinity of inflowing North Atlantic water combined with an increase of fresh Baltic Sea discharge cause a reduction in mean North Sea salinity of 0.59. The analysis of 10 m
wind speed does not show a significant change of the mean wind speeds throughout the year (in 2100). Local maximum wind speeds, however, indeed show an increase of 1.38 m s⁻¹ in winter and a decrease of 0.75 m s⁻¹ in summer. The duration of gale wind conditions per year, indicated by mean wind speeds greater than 17 m s⁻¹, increases by about 65 h or by 30 %. Since mean wind speeds hardly change, both more gale and more calm wind conditions tend to occur, particularly in winter.

The effect of the change in wind conditions during the 21st century on bottom erosion and deposition of suspended particulate matter (SPM), which are quite important for our POP dynamics, is shown in Fig. 3c and d, respectively. Plots show trends of relative frequency of erosion and deposition periods in percentage points per 100 yr, based on annual mean percentages of erosion and deposition for the 21st century. A slight increase/decrease in annual periods of erosion/deposition are found.

It is the effect of these changes on the studied POPs that are analysed. The full hydrodynamic analysis of the A1B scenario for the North Sea is to be discussed elsewhere.

$_{20}$ 3.2 Time series of surface fluxes of $\gamma\text{-HCH}$ and PCB 153 and total masses in water and sediment

Time series of surface fluxes are given in Fig. 4 (2006–2015), Fig. 5 (2046–2055) and Fig. 6 (2090–2099). Air-sea exchange of γ -HCH, top panels, is mostly due to dry gas deposition and volatilisation, which are much greater than the other processes (wet deposition, particle deposition and river input). In general, dry gas deposition exhibits an annual cycle with greatest values in the spring and summer with peak values around May, and least values in fall into winter, bottoming out in November-December when atmospheric concentrations are least (generally an order of magnitude or more less

than in the summer months (Gusev et al., 2009)). Volatilisation also exhibits a clear annual cycle, with greatest values in late summer and the early fall months (August–September) and least values in late winter and early spring (February–March). Dry gas deposition is generally 2–4 times greater than volatilisation, except between about
 September and December, when deposition is lowest. Volatilisation is still high at this

time but decreases with the total mass in water curve, 2nd panel, which in turn is due to the decrease in dry gas deposition.

Comparing the different time series, it is seen that in 2006–2015 there is very little inter-annual variability in dry gas deposition and volatilisation of γ -HCH (Fig. 4) with dry gas deposition fluxes peaking at around 50 kg day⁻¹ in May, volatilisation at about 20 kg day⁻¹ in August-September. Contrast this with the 2046–2055 and 2090–2099 runs, respectively. Maximum gas deposition fluxes increases in most years in both runs, generally approaching 60 kg day⁻¹ in May and clearly exceeding it in four and three years in the 2050 and 2090 runs, respectively. Volatilisation increases in the

¹⁵ 2046–2055 run, relative to the 2006 run, and is even greater in the 2090 run. So we conclude that climate change in the 21st century results in increased dry gas deposition and volatilisation of γ -HCH. This is further discussed and clarified in the next Sect. 3.3.

Clear annual cycles in total mass of γ -HCH in water (Figs. 4–6, second panels) is seen in the three ten year runs. Values are greatest around August and least around February, due to the accumulated net flux of dry gas deposition over volatilisation in the spring and summer and the net deficit (reverse) in winter, respectively. Clear annual cycles in total mass of γ -HCH in sediment, second panels, are also seen for all three runs with maximum values observed around September–October and minimum values

around March–April. The 1–2 month lag in these extrema, relative to the water column, is due to settling in summer and resuspension due to storm events and weather conditions in general in winter. Because of plankton blooms, more particulate organic carbon (POC) is contained in the water column in the spring and summer months. POPs sorb to this POC before ultimately sinking out of the water column and into sediment. In win-

ter months, winds and stormy weather lead to resuspension of POPs (see discussion in O'Driscoll et al. (2013)). Total mass is diminished somewhat in the first year of all three runs, which is consistent with the trend in 1996–2005 (O'Driscoll et al., 2013), where decreasing atmospheric concentrations and river input resulted in a downward trend of total mass in sediment. Note also that the total mass in water exceeds that in sediment by more than two orders of magnitude.

For PCB 153 (Figs. 4–6, third panels) volatilisation is greater than any of the surface sources, dry gas deposition and river input are generally 2–4 times less than volatilisation, while particle and wet deposition are much smaller. Volatilisation and river input are in phase with largest values in winter and lowest in summer, while dry gas deposition is highest in spring and summer and least in winter. Volatilisation generally exceeds the sum of the sources (deposition and river input), so that the North Sea is net volatilisational to the atmosphere for PCB 153, which was already shown to be the case for 1996–2005 (O'Driscoll et al., 2013), but can be net depositional in the summer months when the sum of dry gas, wet and aerosol deposition and river input can exceed volatilisation. The other main feature is the peaks, or rapid increases, in volatilisation due to storms.

A seasonal cycle in total mass of PCB 153 in water (Figs. 4–6, bottom panels) is seen with highest (lowest) values found in the summer (winter) months. Total mass is generally lowest in winter and starts to increase during the spring bloom (primary production) when depositional PCB 153 sorbs to POC in the water column. Values remain high through the spring and summer, when the North Sea can be net depositional for PCB 153, before decreasing in September–October, when the primary production decreases, reaching lowest values in January–February, thus completing the annual

²⁵ cycle. The spikes observed are the result of winter storms, which cause erosion of fine fraction of sediment and resuspension of the POP into the water column, resulting in rapid increases in total mass in water. The recovery time for these storms is about 1–2 months in the water column when concentrations return to pre-storm values. These events are also found in the sediment and γ -HCH records.

Total mass of PCB 153 in sediment (Figs. 4–6, bottom panels) decays exponentially with values reduced to less than half by the end of the three ten year runs. An annual cycle, though not obvious, takes place with maximum values in spring and summer, due to primary productivity and sinking on POC, and minimum values in winter due to erosion resulting from storms and strong winds. Since PCB 153 is hydrophobic (or lipophilic) most of it sorbs to POC before settling in the sediment, and we see that total mass in sediment is more than an order of magnitude greater than that in water. Therefore, continuous resuspension of PCB 153 is enough to keep a constant small amount of it dissolved in water but the total mass in sediment will decay exponentially unless it is supplemented through atmospheric or river input.

During storm events, erosion causes mobilisation and resuspension of PCB 153 into the water column, increasing its concentration there, thus resulting in a consequent increase in volatilisation. Because the total mass of PCB 153 in water is so much less than that in sediment, and because of increased volatilisation during and following

¹⁵ a storm, and net volatilisation in general, the total mass in sediment cannot recover following a storm event. This is in contrast to γ -HCH, which is generally net depositional from atmosphere to ocean, has total mass in water more than two orders of magnitude greater than that in sediment, and thus pre-storm mass in sediment can be recovered.

From this, we conclude that the change in number and strength of storms, and with this erosion events, has only a small impact on the concentration of γ -HCH in sediment and water.

3.3 Comparison of time series of total mass of γ -HCH and PCB 153 in water and sediment

Time series of total mass of γ -HCH and PCB 153 in water and sediment for the entire ²⁵ model domain for the three ten year runs are plotted against each other for comparison in Fig. 7. For γ -HCH in water (Fig. 7a) there is little inter-annual variability, the annual cycle generally faithfully repeating itself. The almost identical repetition of the annual cycle of dry gas deposition and volatilisation in 2006–2015 (Fig. 4, top panel) results in

the repeated corresponding annual cycle for total mass in water. Inter-annual variability in both dry gas deposition and volatilisation for both future runs (Fig. 7b and c, top panels) are responsible for the same variability in total mass in water. For example, the increase in dry gas deposition in the third and fourth years of the 2046 run, relative to

- the 2006 run, result in the increase in mass in water, while decreasing deposition and increasing volatilisation are responsible for the decrease in mass in water in the eighth and ninth years. In the 2090 run the increase in volatilisation, relative to that in dry gas deposition (Fig. 6) in the second to fifth and the last three years is responsible for the decrease in total mass in water.
- ¹⁰ Comparing total masses of γ -HCH in sediment for the three runs (Fig. 7b) shows that while the mass diminishes somewhat in the first year of all three runs, it continues to decrease between 2006–2011 (red) but remains steady thereafter; it continues to diminish in 2047–2050 (blue) but increases thereafter to 2055; and following a decrease resulting from a storm in 2091 it increases from 2092–2099. So there is an upward trend of mass in sodiment in the future runs relative to the present (2006–2015). This
- ¹⁵ trend of mass in sediment in the future runs relative to the present (2006–2015). This is due to increased dry gas deposition in the future runs, which causes an increase of the amount of γ -HCH sorbing to POC in the water column and, subsequently, resulting in sinking of an increased mass of the POP into the sediment. This small increase of total mass in sediment is not observed in the water column in Fig. 7a because it is small relative to total mass in the water column.

Comparing total masses of PCB 153 in water (Fig. 7c), it is seen the mass remains steady for all three cases. In sediment (Fig. 7d), total mass in the 2090–2099 run decreases faster than the 2046–2055 run, which decreases faster again than the 2006–2015 run. This is due to the increased number and intensity of storms observed in

the 2050 and 2090 runs. These storms cause resuspension of PCB 153 into the water column, part of which becomes available for volatilisation due to the equilibrium partitioning of the POP.

3.4 Annual fluxes of γ -HCH and PCB 153

Total annual mass fluxes of *γ*-HCH and PCB 153 for the last year of each of the three ten year runs (2015, 2055 and 2099) are presented in Fig. 8. The patterns are fairly similar for each of the two POPs but there are important differences. The sum of the sources is always less than the sum of the sinks, with some variability in the different years and chemicals.

For γ-HCH, dry gas deposition and volatilisation both increase somewhat in the future runs (2055, 2099), relative to the present (2015). Gas deposition is up by 7.5 % and 4.0 %, while volatilisation is up 15.9 % and 16.1 % in 2055 and 2099, respectively,
relative to 2015. These changes are due to increased air and water temperature and wind speed as described in the Sect. 2.1.1 above. Degradation in water decreases, down by 1 % and 3 % in 2055 and 2099, respectively, but remains higher than dry gas deposition. Exchange at the open boundaries is fairly negligible. Total sum of sources increase by 7.3 and 3.9 %, and sinks by 3.2 and 2.6 % in 2055 and 2099, respectively.

- For PCB 153, dry gas deposition decreases in the future runs, by 10.3% and 13.7% in 2055 and 2099, respectively, while volatilisation increases, by less than 1% in 2055 and 3% in 2099. Degradation in sediment decreases due to decreased mass there, to 90% and 84% of 2015 values in 2055 and 2099, respectively. Exchange at the open boundaries is fairly negligible. Sum of sources decreases by 5 and 7% in 2055 and 2099, respectively, while the sinks decrease by 2 and 1%, respectively.
 - 3.5 Spatial changes of concentrations in water and sediment

Distributions of vertically integrated seasonally averaged concentration differences for the summer season (JJA) and the winter season (DJF) of γ -HCH and PCB 153 between 2005 and the last year of the three model runs are plotted in Fig. 9 (2005–2015, 2005–2055 and 2005–2099). Clear seasonal trends and patterns are apparent in both

 $_{25}$ 2005–2055 and 2005–2099). Clear seasonal trends and patterns are apparent in both cases. PCB 153 values are mostly positive (decreased relative to 2005) while γ -HCH values are often negative (increased relative to 2005).

Starting with γ-HCH, the first feature that stands out is the region of decreased concentration (dark pink) in the very south of the model domain. The reasons for this are twofold. First, concentration in gas in the atmosphere is greatest along the British coast, particularly around southern England and the Thames estuary. Concentrations in 2005
 are substantially reduced relative to earlier years (e.g., about 2–4 fold less than in 2000

- and around 20–30 % less than in 2004, see Gusev et al. (2009)). Dry gas depositions are also greatest adjacent to the British coast and have also been shown to drop substantially between 1997 and 2004 (see Fig. 9 in O'Driscoll et al. (2013)). Secondly, the Thames and Rhine are two major river point sources. Although the total flux of river
- sources into the North Sea is more than an order of magnitude less than dry gas deposition, they are substantial sources locally. These concentrations have also dropped substantially annually since 1995 (see O'Driscoll et al. (2013) for details). Together, these changes combine and result in the reduced concentration band found in the very south of the model domain. Outside of this region, a number of regions of positive and
- ¹⁵ negative change are seen. The two regions of increased concentration in the future (blue) between East Anglia and the IJssel Meer and between Jutland and the Norwegian coast diminish in the future runs because of increased water temperature, leading to volatilization. The blue region close to the Atlantic open boundary is due to the inflow of Atlantic water. In summer, increases (blue) are greatest away from the British coast
- where gas concentrations have not been substantially reduced. This is modulated by the inflow of lower concentration Atlantic water which is particularly significant in 2099 when the region of increased concentration is substantially reduced.

For PCB 153, there are no notable differences in winter distributions between the three years. In summer, concentrations are somewhat reduced in 2055 and 2099 rel-

ative to 2015 (higher values, more pink), which is due to the decrease in dry gas deposition in the future runs (2055 and 2099) and reduced concentrations in sediment. Future decreases in concentration (larger positive values) in winter are found near British and Dutch rivers, between southern Britain and Holland, around German river sources, out into the German Bight and Wadden Sea, and into the Kattegat. This is

due to the decreased resuspendable content of PCB 153 in the sediment, compared to 2005, as a result of previously ongoing higher erosion activities, in combination to the anti-clockwise circulation that carries these polluted waters into the Kattegat. In summer, values are generally positive (decrease), with large values found near British and ⁵ continental rivers and offshore of the Norwegian coast.

Distributions of differences in summer and winter in sediment between 2005 and the last year of the 3 model runs are shown in Fig. 10 (2005–2015, 2005–2055 and 2005–2099). For γ -HCH, concentrations are generally reduced from 2005 values. The greatest losses (pink) are found in 2015 when dry gas deposition is less than in 2055 and 2099, with high values found particularly around the southern British and continen-

- ¹⁰ 2099, with high values found particularly around the southern British and continental coasts and southernmost regions of the North Sea. Patterns are similar in winter and summer but values are higher in summer (less pink) due to increased dry gas deposition. Concentrations in 2055 are higher than in 2099 due to increased dry gas deposition (Fig. 7). Increased concentrations (light blue) are seen off the western and
- ¹⁵ northern parts of Jutland in all three runs but are greater in 2055 and 2099, and, also, in the future runs, off parts of the British and continental coasts and small areas of the southern North Sea, which can be due to the increased dry gas deposition but also erosion and redeposition in coastal areas, particular close to river sources (see O'Driscoll et al. (2013) for distributions in 2004).
- For PCB 153, there is little notable change in distributions and concentrations between 2005 and the last year of each of the three runs. This is due to the large masses in sediment that have been either degraded or eroded (Figs. 4–8) and account for most of the difference. However, it is interesting to plot the differences at the end of the three 1 yr runs against themselves (Fig. 11). Beginning with the winter plots, decreases in
- 25 2055 relative to 2015 (dark pink) are found in the coastal regions of the southern North Sea, especially around the Wash, Thames, offshore of the Rhine and southern Dutch coast, and offshore of the Elbe and the Wadden Sea region, which is due to increased gale conditions in the 2055 run. Areas of increase are also found in the southern and northern North Sea but their magnitude is small, though there is a region of higher in-

crease around the Firth of Forth and Moray Firth which may be due to localised storms in the 2015 run. Decreases in 2099 relative to 2015 are again found in the aforementioned areas of the southern North Sea but this time extend along the entire British coast and an extended area seaward of the Wash. This is to be expected due to the increased stormy conditions. For the 2055–2099 case, large positive values are seen from East Anglia up to the northern Scottish coast, indicating stronger storm activity here in the 2090's, which is to be expected from examining the previous two plots. Large negative values are found around the Thames, central Dutch coast, Friesian Islands, German Bight, and Wadden Sea, and are also to be expected from the previous two plots. Summer patterns are similar to those in winter, since most of the erosion takes place in winter, but some differences are found which can be the result of both deposition and erosion.

4 Summary and conclusions

The impact of climate variability on the fate and cycling of two selected legacy POPs, γHCH and PCB 153, in the North Sea in the 21st century, is investigated with a combined hydrodynamic (HAMSOM) and Fate and Transport Ocean Model (FANTOM). Future scenario model runs for three 10 yr periods to the year 2100 (2006–2015, 2046–2055 and 2090–2099) using plausible levels of both in situ concentrations and atmospheric, river and open boundary inputs are performed. Our approach was to reutilise 2005
POP values in the atmosphere, rivers and at the open boundaries for every year of the simulations, while using the (final) result of our 1996–2005 runs, see O'Driscoll et al.

(2013), as the initial condition for all three future runs. In this way, differences between the three 10 yr simulations are attributed to climate change only.

Summarising the basic hydrodynamics results for the entire scenario period, 2001– 25 2100, it was found that the spatially averaged 2m air temperature increases continually over the entire period to an increase of 2.38 °C in 2100 over 2001, with above/below average warming in winter/summer. Volume averaged water temperature increases by

2.0 °C (to 2100) with weaker/stronger warming in summer/winter in 2100 relative to 2000, whereas SST increases by 1.66/2.31 °C in summer/winter. Salinity decreases by an average of 0.59. Mean wind speeds do not change significantly throughout the year. However, local maximum wind speeds increase/decrease in winter/summer. Pe-

riods of gale winds increase by 30 % over the 100 period, but longer periods of calm winds are also found, particularly in winter, and result in increased/decreased periods of erosion/deposition of sediment.

Dry gas deposition and volatilisation of γ -HCH increase in 2046–2055 and 2090–2099 relative to 2006–2015, and volatilisation in 2090–2099 is even greater than 2046–2055, and result directly from changing hydrodynamic, climate, conditions and forcing.

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Total mass of PCB 153 in sediment decreases exponentially in all three runs due to degradation in sediment, but also due to erosion and subsequent volatilisation, particularly during storms, and concentrations in rivers and the atmosphere are not high enough to sustain concentrations. However, it decreases even faster in the future runs

relative to the present because of the increased number of storms and erosion. This is in contrast to γ -HCH, which is also eroded during storms, but concentrations in sediment are recovered because so much of it is dissolved in water relative to that in sediment. In fact, increased dry gas deposition in the future runs causes more of the γ -HCH to sorb to POC in the water column with the result that there is more of it contained in sediment at the end of the future runs than at the end of the 2015 run.

Annual net sinks exceed annual net sources at the end of all periods, leading to a loss of POPs in the system. Annual fluxes into and out of the North Sea system for both POPs show a slight future decrease during the simulations and also the second and third periods relative to the first period. The North Sea is net volatilisational for PCB

²⁵ 153, while γ -HCH is net depositional at the North Sea surface. Exchange at the open boundaries is always fairly negligible for both POPs.

For the last year of each of the runs, concentrations of γ -HCH in the water column are decreased relative to 2005 between the Thames and Rhine estuary regions due to decreased river and atmospheric concentrations. Concentrations increase between

East Anglia and the IJssel Meer, and between Jutland and the Norwegian coast, where gas concentrations have not been substantially decreased, but increase less in the future runs relative to 2015 due to interannual variability in the inflow of North Atlantic water through the northern boundary of the model. For PCB 153 there are no notable

differences between the three runs in winter, but concentrations are somewhat reduced in summer in the future runs because of reduced dry gas deposition and reduced concentrations in sediment. In winter, future decreases are found near british and Dutch rivers, between southern Britain and Holland, around German river sources and in the German Bight and Wadden Sea, and into the Kattegat, which is due to less resuspend able sediment relative to 2005, while values are generally decrease in summer.

In sediment, concentrations of γ -HCH are generally reduced in the future runs relative to 2005, with greatest losses found in 2015 because of less dry gas deposition relative to 2055 and 2099. For PCB 153, there is little notable change in distributions and concentrations between 2005 and the last of each of the three ten year runs, which

- is due to the large amount of sediment that has been either degraded or eroded. Plotting the final year distributions against each other, decreases in 2055 and 2099 relative to 2015 are mostly found, especially around coastal regions of the southern North Sea, and extending to along and offshore of the British coast in 2099. The differences between 2055 and 2099 show generally more erosion in 2055 around coastal regions of the southern North Sea, and more erosion around the British coast in 2099, indicating
- stronger storm activity in the southern North Sea and along the British coast in 2046– 2055 and 2090–2099, respectively.

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Fig. 1. The model domain with topography (metres). River sources of freshwater are shown by magenta dots.

Fig. 2. Cartoon presenting the most important processes connected to the fate and transport of highly water-soluble and highly POC-attached persistent organic pollutants in the oceanic environment simulated by the FANTOM model. Uptake and transport through the food web is not included. From O'Driscoll et al. (2013).

Fig. 3. Distributions of 21st century trends. Top left **(a)**: SST in summer (June, July, August); top right **(b)**: SST in winter (December, January, February), both in °C per 100 yr; bottom left and right: relative occurrence of erosion and deposition, respectively, in percentage points per 100 yr.

Fig. 4. Time series of surface fluxes and total mass in water and sediment of γ -HCH, top two panels, respectively, and the same for PCB 153, bottom two panels, respectively, for the period 2006–2015. February and August (F and A) and the year number (1–10) are shown on the *x* axis. In the first and third panels, gas deposition is shown in black; volatilisation in red; river input in magenta; particle deposition in green; and wet deposition in blue.

Fig. 5. Same as Fig. 4. but for 2046–2055.

Fig. 6. Same as Fig. 4. but for 2090–2099.

Fig. 7. Time series of total mass of γ -HCH in water, (a), and sediment, (b), and PCB 153 in water, (c), and sediment, (d), for the three ten year periods 2006–2015, 2046–2055 and 2090–2099. February and August (F and A) and the year number (1–10) are shown on the *x* axis. The time-series presented in this paper are the sum values within the model domain.

Fig. 8. Histogram of total annual mass fluxes, [kg] log 10 scale, of North Sea sources and sinks of γ -HCH for 2015, 2055 and 2099, upper panels, and PCB 153 for 2015, 2055 and 2099, lower panels. Sources are deposition with particles, input through rivers, wet deposition, and gas deposition. Sinks are volatilization, degradation in water, degradation in sediment, and net outward flux through the open ocean boundaries (OBs). The sums of sources and sinks are given by the grey panels.

Fig. 9. Distributions of concentration differences averaged through the entire water column, 2005 minus 2015, 2005 minus 2055 and 2005 minus 2099, from left to right, respectively, for γ -HCH in winter and summer (top and second sets of panels), and for PCB 153 in winter and summer (third and bottom sets of panels). The zero contour line is shown in black. Units are ng L⁻¹.

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Fig. 10. Distributions of concentration differences in sediment, 2005 minus 2015, 2005 minus 2055 and 2005 minus 2099, from left to right, respectively, for γ -HCH in winter (top) and summer (2nd row) and PCB 153 in winter (3rd row) and summer (bottom). The zero contour line is shown in black. Units are ng g⁻¹ dry weight.

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Fig. 11. Distributions of concentration differences of PCB 153 in sediment at the end of the three runs, 2015 minus 2055, 2015 minus 2099 and 2055 minus 2099, from left to right, respectively, in winter (top) and summer (bottom). The zero contour line is shown in black. Units are ng/g dry weight.

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