



Modelling the influence of climate change on the chemical concentrations in the Baltic Sea region with the POPCYCLING-Baltic model



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HIGHLIGHTS

- IPCC A2 and B2 climate scenarios are compared to a baseline scenario.
- The entire plausible range of neutral persistent organic chemicals is modelled.
- Temperature, precipitation, wind speed and particulate organic carbon are assessed.
- Concentration changes are within a factor of 3.0 due mostly to changes in temperature.
- Changing emission mode re-enforces or counteracts effects of climate parameters.

ARTICLE INFO

Article history:

Received 2 November 2013
Received in revised form 5 February 2014
Accepted 7 February 2014
Available online 22 April 2014

Handling Editor: H. Fiedler

Keywords:

Climate change
Baltic Sea
Persistent organic chemicals
Multimedia model

ABSTRACT

The effect of projected future changes in temperature, wind speed, precipitation and particulate organic carbon on concentrations of persistent organic chemicals in the Baltic Sea regional environment is evaluated using the POPCYCLING-Baltic multimedia chemical fate model. Steady-state concentrations of hypothetical perfectly persistent chemicals with property combinations that encompass the entire plausible range for non-ionizing organic substances are modelled under two alternative climate change scenarios (IPCC A2 and B2) and compared to a baseline climate scenario. The contributions of individual climate parameters are deduced in model experiments in which only one of the four parameters is changed from the baseline scenario. Of the four selected climate parameters, temperature is the most influential, and wind speed is least. Chemical concentrations in the Baltic region are projected to change by factors of up to 3.0 compared to the baseline climate scenario. For chemicals with property combinations similar to legacy persistent organic pollutants listed by the Stockholm Convention, modelled concentration ratios between two climate change scenarios and the baseline scenario range from factors of 0.5 to 2.0. This study is a first step toward quantitatively assessing climate change-induced changes in the environmental concentrations of persistent organic chemicals in the Baltic Sea region.

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1. Introduction

Climate change (CC) presents a serious threat to human society and the environment. Empirical evidence for, and model projections of climate-induced changes at local, regional and global scales have been compiled by the Intergovernmental Panel on Climate Change (IPCC, 2001, 2007). Since climate conditions play a role in the fate and transport of chemical pollutants, it is interesting to study how CC may influence exposure and risks associated with chemicals, and several recent reviews and computer

modelling studies have provided estimates of CC-induced impacts (Macdonald et al., 2005; Dalla Valle et al., 2007; Schiedek et al., 2007; Lamon et al., 2009; Borgå et al., 2010; UNEP/AMAP, 2011). In most instances, the reviews and modelling studies have focused on the Arctic, where the effects of CC have been, and are predicted to continue to be, particularly rapid and severe. Relatively little attention has so far been focused on how CC could affect the fate of chemicals in other regions, with the exception of the Mediterranean Sea region (Dalla Valle et al., 2007; Lamon et al., 2012).

The Baltic Sea is one of the largest brackish seas in the world and is situated between continental temperate and subarctic climate zones. Human activities in the Baltic Sea region have already put pressure on its marine ecosystem. The most serious

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environmental problem is widely recognized to be the continuing eutrophication of the Baltic Sea (HELCOM, 2009a,b), but inputs of chemicals also threaten the Baltic Sea ecosystem and its future sustainable use. Pollution of the Baltic Sea has, for example, resulted in problems with algal blooms, dead sea-beds, depletion of fish stocks and dioxin levels in fatty fish above EU guideline levels (Karl et al., 2002; HELCOM, 2007a). Climate warming in the Baltic Sea region has been strong, averaging $0.08\text{ }^{\circ}\text{C decade}^{-1}$, compared to an average of $0.04\text{--}0.05\text{ }^{\circ}\text{C decade}^{-1}$ for the entire globe (1861–2000) (HELCOM, 2007b; Heino et al., 2008; Lehmann et al., 2011). As far as we are aware, the potential of CC to increase the Baltic Sea's vulnerability to chemicals has previously not been investigated.

In this study, we use an established regional multimedia chemical fate model to make preliminary estimates of the CC-induced effects on the environmental concentrations of persistent organic chemicals in the Baltic Sea region. We set our focus in this work on “perfectly persistent” chemicals that are not degraded in the environment because they are of regulatory interest and also because they provide a bounding case. Considering perfectly persistent chemicals also removes the difficulty of assigning environmental half-lives to chemicals and of estimating how temperature could potentially affect these half-lives within the entire chemical space. It is expected that the degradation of persistent organic chemicals will probably increase as a result of higher temperature, but to what extent is unclear (Gouin et al., 2013). It has been shown, however, that even for persistent chemicals such as PCBs (Kong et al., 2013) that degradation is a key input parameter in controlling future predictions of contaminant levels. Therefore, it is recommended that if information is available on how temperature affects degradation for specific chemicals this should be accounted for in models that estimate how climate change affects chemical fate. The overall goal of this study is to investigate the effects of single or multiple climate projections for temperature (T), wind speed (W), precipitation (P) and particulate organic carbon (POC) in the Baltic Sea water column on the concentrations of persistent chemicals in the Baltic Sea region. We have pursued this goal by modelling the environmental concentrations of all plausible combinations of partitioning properties for non-ionizing organic chemicals emitted to air, water and soil under three climate scenarios in the Baltic Sea region using the POPCYCLING-Baltic model.

2. Material and methods

2.1. Model description

The POPCYCLING-Baltic model describes the environment of the Baltic Sea region as 85 environmental compartments, and uses different spatial resolution in the atmosphere and surface compartments (see Table A.1). The 85 compartments are connected by inter-compartmental transfer processes. In terms of environmental characteristics and chemical contamination, each of the 85 compartments is considered as well-mixed. Emissions of chemicals can be directed into specific model compartments or defined as advective flows with air or water from neighbouring regions outside the model domain (Wania et al., 2000).

A large dataset of environmental parameters characterizes the model environment, including monthly temperature and wind speed, yearly precipitation, and POC concentration. Other important factors influencing the movement of persistent chemicals are also included in the model using simplified relationships, e.g., ice cover and forest canopy development (for details see Wania et al., 2000).

To facilitate running many model simulations, we adapted the default version of the POPCYCLING-Baltic model to be capable of running in batch mode. A Gauss elimination algorithm was incorporated into the model to efficiently solve the mass balance equations for steady-state, non-equilibrium concentrations (MacLeod et al., 2001). Steady-state concentrations calculated by the model provide a bounding case to study the influence of climate change on chemical concentrations, and also reduce the computational effort so that many scenarios and chemicals can be modelled. Fig. A.1 in the Supplementary Information demonstrates that model results based on the original and newly-incorporated algorithms are different by less than 1% for a selected illustrative case.

The hypothetical persistent chemicals modelled in this work are characterized by equilibrium partition coefficients between air, water and octanol, and their corresponding internal energies of phase transfer for temperature correction (MacLeod et al., 2007). Information on the temperature dependence of partition coefficients can be found in Appendix A. Fig. A.3 and the short discussion that accompanies it demonstrate that our assumptions about temperature dependence of partition coefficients imply that low-volatility chemicals are more sensitive to the temperature change than the volatile chemicals. In this study, we consider all combinations of partition properties within a chemical space with $\log K_{AW}$ ranging from -11 to 4 , $\log K_{OA}$ from 0 to 15 , and $\log K_{OW}$ from -2 to 10 . This property range represents all plausible combinations of partitioning properties of non-ionic organic substances (Mackay et al., 2006).

2.2. Model scenarios

2.2.1. Climate scenarios

The IPCC published a set of greenhouse gas emission scenarios that consider alternative paths for technological advances, socioeconomic improvements, alternative structures of energy systems and land-use changes and different future demographic status (IPCC, 2000). Climate data specifically for the Baltic Sea region are available from the Rossby Centre Coupled Regional Climate Model (RCCRCM) which was driven with data from two general circulation models, HadAM3H and ECHAM4/OPYC3 (Räisänen et al., 2004). We used the output climate datasets for three climate scenarios to parameterize POPCYCLING-Baltic. The three scenarios correspond to the IPCC A2 and B2 family climate scenarios, which represent a differentiated world with high and low greenhouse gas emissions, respectively, and the baseline scenario (BL), which represents the prevailing climate conditions between 1961 and 1990 (Räisänen et al., 2004).

Three climate parameters that are shared by the RCCRCM and POPCYCLING-Baltic are selected to investigate the CC-induced effects on chemical concentrations, namely, temperature, wind speed, and precipitation. We extracted climate data for each parameter and reprocessed them in accordance with the compartmentalization scheme of POPCYCLING-Baltic. Specifically, the extracted datasets contain projected daily data for temperature (atmospheric, terrestrial, coastal water and open water), wind speed (over open water, coastal and terrestrial units) and precipitation for the period 2071–2100 (for the A2 and B2 scenarios) and 1961–1990 (for the BL scenario). The daily values are averaged over the entire period and used as model inputs to POPCYCLING-Baltic. The three scenarios provide three datasets of levels and spatial variations in temperature, wind speed and precipitation to drive the POPCYCLING-Baltic model. The long-term average surface air temperature is forecast to be higher by $2.1\text{--}3.4\text{ }^{\circ}\text{C}$ in the B2 and A2 scenarios during the period of 2071–2100 compared to the BL scenario (Tables A.3–A.5). Meteorological data suggest that the wind speed in spring has increased in recent years for most parts of the Baltic Sea, but decreases have also been observed

during autumn (HELCOM, 2007b; Lehmann et al., 2011). The monthly means of projected wind speed for the Baltic Sea coastal areas also show higher wind speed in early spring, and lower wind speed in the autumn (Tables A.6–A.8). Precipitation is projected to increase on average, but large spatial variations are observed (Table A.9).

There are two separate groups of model inputs related to wind speed. One group is the monthly wind speeds used for deriving the mass transfer coefficient for diffusive air–water exchange, and the second group are the yearly-averaged advective fluxes of air between the atmospheric compartments and to and from the outside of the model domain (Wania et al., 2000). The extracted data for daily wind speeds under the three studied climate scenarios are used to derive both the monthly and yearly wind speeds that are required as inputs to the model. The monthly data for wind speeds suggests very small forecast changes under the two climate change scenarios vs. the BL scenario, which also indicates small changes in the flow rates of air, i.e., the advective air fluxes.

We also investigate the influence of potential changes in the POC concentration in water under climate change conditions because of POC's importance in determining the fate of hydrophobic persistent organic chemicals (UNEP/AMAP, 2011). However, there are no data available from the RCCRCM, so two POC scenarios are postulated based on the following limited empirical evidence. On the basis of the production of organic matter at the expense of CO₂, Schneider and Kuss (2004) used measured partial pressure of CO₂, and estimated a factor of 2.5 (maximum uncertainty: 1.8–3.8) increase in the net production of POC in the Baltic Sea since the beginning of the last century. Assuming increasing water temperature of 0.008 °C per year, increasing input of nutrients of 1% per year, and increasing light intensity of 0.02% per year, Dzierzbicka-Glowacka et al. (2011) forecast a two- to three-fold increase in POC concentration in late spring and a shift towards postponed maximum POC concentration in 2050 in the southern Baltic Sea. There is no comparable forecast for the concentration of POC in the northern Baltic Sea. The catchment of southern Baltic Sea is the most densely populated area and receives the highest inputs of nutrients from agricultural activities and industrial development, leading to increased production of POC. In contrast, the northern Baltic Sea is surrounded by less populated areas and its catchment is covered by large pristine forests and other vegetation. The increase in POC concentration in the northern Baltic Sea is therefore expected to be smaller than in the southern Baltic Sea. For the whole Baltic Sea we have made two estimates of the average factors of increase in the POC concentration, i.e., 1.5 and 2.0 under the B2 and A2 climate scenarios, respectively. The default POC balance implemented in the original version of the POPCYCLING-Baltic model is used as the baseline POC scenario.

2.2.2. Chemical emission scenarios

The default version of the POPCYCLING model requires the specification of annual national emission rates by the thirteen countries surrounding the Baltic drainage basin. However, it is not possible to develop realistic country-specific emission scenarios for the investigated hypothetical chemical property combinations and the climate scenarios. Instead, we seek to compare and contrast the CC-induced effects on chemicals that are emitted in the Baltic Sea region to each of air, water and soil. Therefore, three hypothetical and illustrative emission scenarios are developed. In all simulations a fixed emission of chemical (1000 kg year^{−1}) is assumed to be continuously emitted into the Baltic Sea region, evenly divided between the thirteen countries. In the emission to air scenario, emissions are 100% to the atmospheric compartments. In the emission to water scenario, 50% of emissions are directed to fresh water and 50% to coastal water compartments, and in the

emission to soil scenario, 50% of emissions are directed to agricultural soil and 50% to forest soil compartments.

2.3. Data interpretation

The POPCYCLING-Baltic model calculates concentrations of chemicals in each of the model's 85 compartments. We calculate the average chemical concentration in each environmental medium, i.e., air (A), agricultural soil (AS), forest soil (FS), forest canopy (FC), fresh water (FW), fresh water sediment (FWS), coastal and open ocean water (COW), and coastal and open ocean sediment (COWS) in the entire model domain. Then, media-specific concentration ratios (MCRs) are calculated to quantify the changes in concentrations at the regional-scale under the two climate scenarios as:

$$\text{MCR}_{A2} = \frac{C_{A2,i}}{C_{BL,i}} \text{ and } \text{MCR}_{B2} = \frac{C_{B2,i}}{C_{BL,i}}$$

where the numerators represent the modelled environmental concentrations under the two future climate scenarios, the denominator represents the modelled concentration under the BL climate scenario, and *i* specifies one of the eight environmental media.

Adopting the two-dimensional “chemical partitioning space” approach (Meyer et al., 2005; Gouin and Wania, 2007) “chemical MCR space” plots are constructed to present the calculated MCRs as a function of log *K*_{AW} (y-axis) and log *K*_{OA} (x-axis). As shown in Figs. 2–4, each point corresponds to a MCR for a hypothetical chemical with a specific combination of partitioning properties. The diagonal lines from the upper left to the lower right represent chemicals with equal log *K*_{OW}. MCRs higher than 1 are represented by warm colours, and MCRs lower than 1 are represented by cold colours. For a better representation of results, the chemical concentration ratio space plots are divided into four sub-zones in lines with the major modes of transport for organic chemicals (Wania,

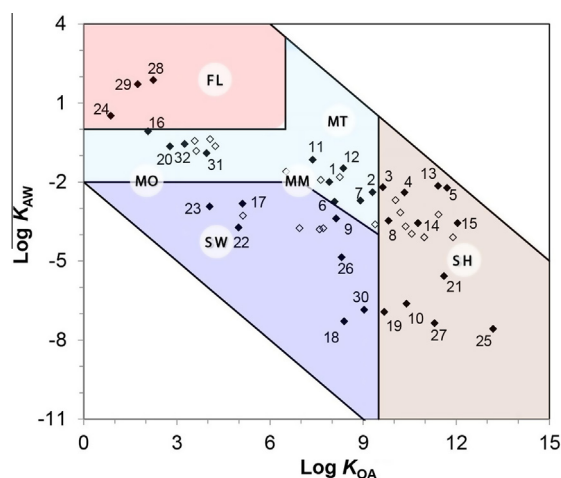


Fig. 1. Hypothetical chemical space characterizing different transport modes of organic chemicals. Gouin and Wania (2007) studied POPs with log *K*_{AW} ranging from −4 to 3, log *K*_{OA} from 3 to 12, and log *K*_{OW} from −1 to 10 (FL: volatile fliers; SW: water-soluble swimmers; SH: particle-bound single hoppers; MT: very hydrophobic, semi-volatile multiple hoppers); *real organic chemicals*: 1. PCB-28; 2. PCB-118; 3. PCB-153; 4. PCB-180; 5. PCB-209; 6. aldrin; 7. chlordane; 8. DDT; 9. endrin; 10. *a*-HCH; 11. HCB; 12. mirex; 13. HpCDD; 14. HCDF; 15. OCDF; 16. 1,3-butadiene; 17. 2-nitrotoluene; 18. aldicarb; 19. atrazine; 20. benzene; 21. BaP; 22. BCEM; 23. BCEE; 24. chloroethene; 25. chrysene; 26. diphenylamine; 27. mecoprop; 28. *n*-hexane; 29. *n*-pentane; 30. simazine; 31. styrene; 32. toluene (points 1 to 15 are representative persistent organic pollutants listed by the Stockholm Convention; The full names and data for partitioning properties can be found in Table A.2).

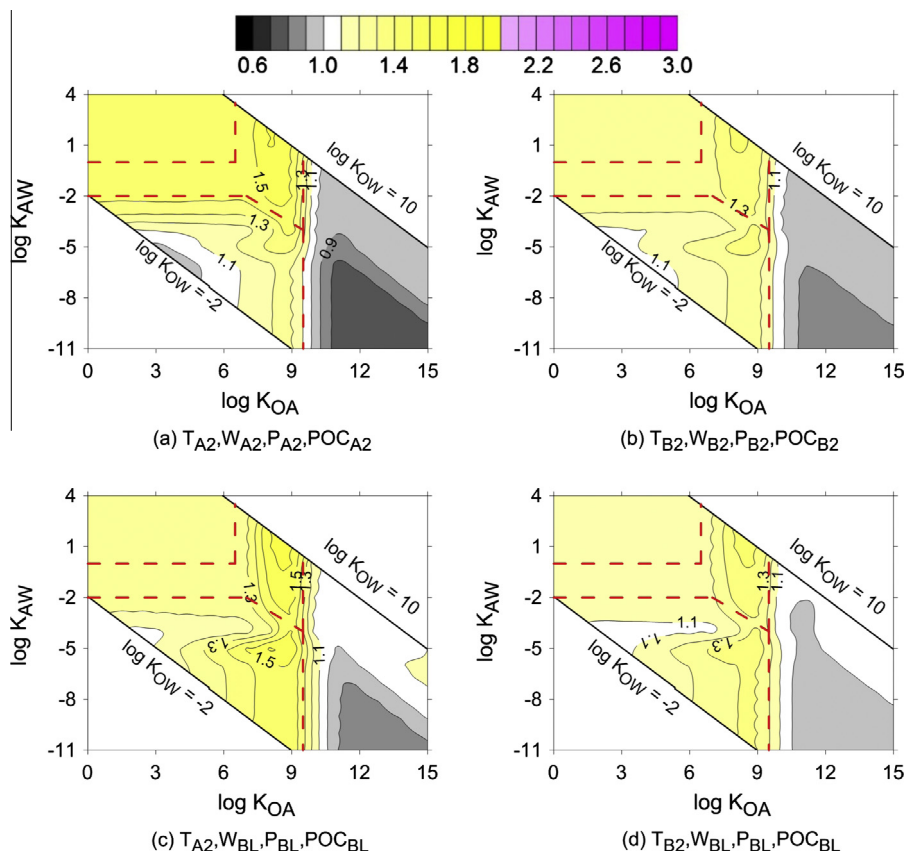


Fig. 2. Ratios of modelled chemical concentrations in air when emissions occur to air (chemicals in the bottom left and top right corner of the chemical space were excluded from this study due to unrealistic property combinations). The dashed lines divide the chemical space into four sub-zones in lines with the major modes of transport for organic chemicals; also see Fig. 1).

2006; Gouin and Wania, 2007). As shown in Fig. 1, six hypothetical property combinations can be identified to represent chemicals characterized by different modes of transport, i.e., volatile fliers, water-soluble swimmers, particle-bound single hoppers, water soluble and relatively volatile multiple hoppers, multimedia multiple hoppers, very hydrophobic and semi-volatile multiple hoppers. Fig. 1 allows findings based on hypothetical chemicals to be mapped to real chemicals with similar partitioning properties.

3. Results and discussion

In total, we created 240 MCR plots that illustrate model results for two climate change scenarios, three emission scenarios, five investigated climate parameter combinations, and eight environmental media. For simplicity and brevity twelve MCR plots have been selected to illustrate the CC-induced effects on the atmospheric concentration of chemicals under three emission scenarios, i.e., Figs. 2–4, and Fig. 5 summarizes the minimum and maximum MCRs from all scenarios in scatter plots. Our selection of atmospheric concentration ratio plots does not indicate any discrimination against the results of modelled MCRs for the other environmental media. In Figs. 2–4 the top panels (a and b) show MCRs when all four climate parameters are considered, and the bottom panels (c and d) when only temperature is considered. To better understand the MCRs shown in Figs. 2–4 more information can be found in Appendix B–D. Fig. 6 presents MCRs for a POP with $\log K_{AW}$ of -2 and $\log K_{OA}$ of 10 to demonstrate the re-enforcing or counteracting effects when multiple parameters are taken into account simultaneously.

3.1. Varied emission mode

3.1.1. Emission to air

Fig. 2(a) shows that when emissions occur only to the air compartment, climate change (A2 scenario, considering all four climate parameters) leads to an increase in concentrations in air of up to a factor of 1.3 and 1.6 for multimedia multiple hopper and very hydrophobic, semi-volatile multiple hopper chemicals, respectively. Conversely, climate change can cause about 10–30% decrease in the concentration of particle-bound single hopper chemicals in air. The increase in the concentration of multimedia multiple hopper and very hydrophobic, semi-volatile multiple hopper chemicals in air can be attributed to increased volatilization from the surface compartments, consistent with results shown in Figs. B.2–B.5 which show decreased chemical concentrations in surface compartments. Referring to Fig. 1 it can be seen that the atmospheric concentration of about 2/3 of the presented persistent organic chemicals would increase, e.g., PCB-118, HCB and mirex. The decrease in the concentration of particle-bound single hopper chemicals with $\log K_{OA} > 10$ in air can be attributed to increased outgoing advective flux with air and increased wet deposition (including deposition in rain water and sorption to particles in air) to surface compartments as a result of increased precipitation. The deposited chemicals accumulate mainly in water and sediment in the coastal and ocean compartments (see Figs. B.7(a) and B.8(a)). Emission to air is also the only emission mode in which the concentrations of single hopper persistent organic chemicals in air are forecast to decrease. Referring to Fig. 1 the chemicals falling into this area represent chemicals such as 1,2,3,4,7,8-HCDF, 1,2,3,4,6,7,8,9-OCDF and benzo[a]pyrene.

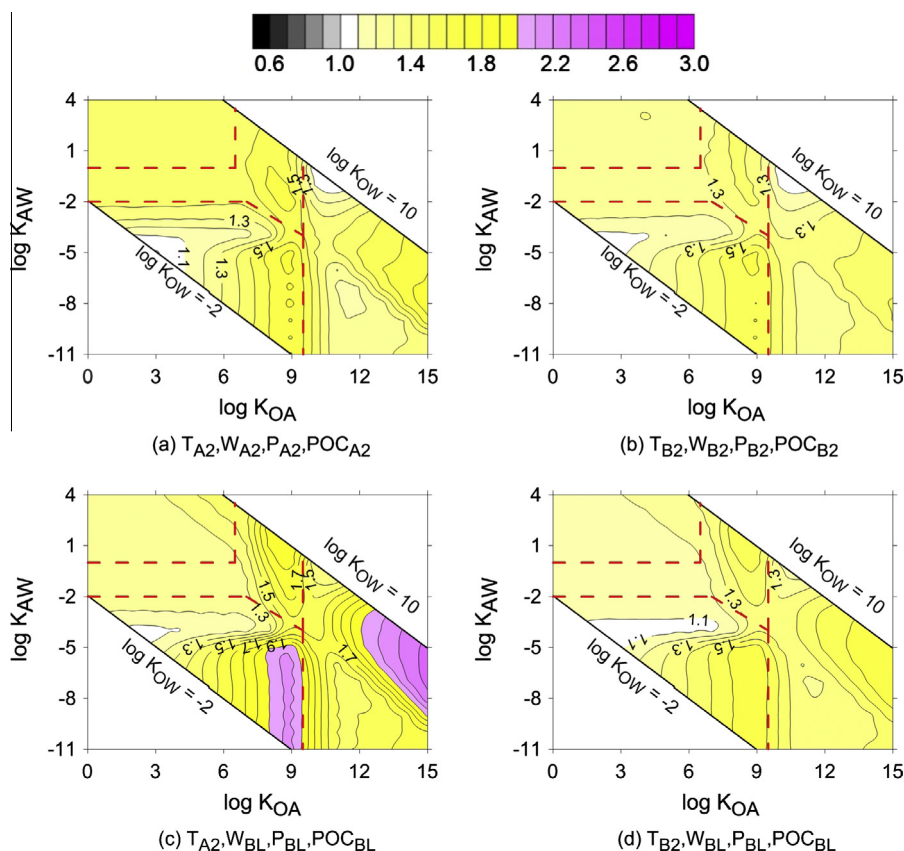


Fig. 3. Ratios of modelled chemical concentrations in air when emissions occur to water.

When emissions are to air, a strong re-enforcing effect can be seen, i.e., stronger increases in modelled concentrations in coastal and open ocean water when all four climate parameters are considered in future scenarios (Fig. 5(a)). When all four climate parameters are considered the increase in the coastal and open ocean water concentration of very hydrophobic, semi-volatile multiple hopper chemicals can be up to 2.2 (Fig. 5(a)). The higher precipitation leads to a factor of 1.7 increase in wet deposition while more POC causes a factor of 1.5 more adsorption (also see Fig. B.7(a, g and i)). The combination of these two processes leads to a re-enforcing effect on the chemical concentrations in coastal and open ocean.

3.1.2. Emission to water

When emissions are directed to water, more pronounced increases in modelled concentrations are observed relative to when emissions are to air (considering all four climate parameters under the A2 climate change scenario). MCRs are generally all higher than 1 (Fig. 3(a)), and the highest MCRs are up to 2.7 observed for the forest soil compartment (Fig. 5(b)). The higher ratios are driven mostly by the effect of temperature (also see Fig. C.3(c)). For some chemicals with extreme property combinations MCRs higher than 2 are observed for air, agricultural soil and forest soil when only temperature is considered. For example, MCRs presented in Fig. 3(c) show that the A2 temperature projection can lead to a factor of up to 2.1 increase in the concentration of water soluble persistent organic chemicals with $\log K_{AW}$ of -11 to -5 and $\log K_{OA}$ of 8 – 9.5 , e.g., atrazine (Fig. 1). The same modelling scenario can lead to a factor of up to 2.4 increase in the concentration of particle-bound single hopper chemicals with $\log K_{AW}$ of -8 to -3 and $\log K_{OA}$ of 12 – 15 . But this factor of up to 2.4 is of relatively less relevance for the majority of real organic chemicals (Fig. 1). These

increases consist of increased volatilization from water and stronger partitioning of those chemicals to particles in the atmosphere (Fig. 3(a)).

In this emission mode, the counteracting effect due to inclusion of more climate parameters is more obvious. As shown in Figs. 3(a) and 5(b) the MCRs for the air compartment are up to 1.6 after inclusion of precipitation, wind speed and POC. The possible increases by a factor of up to 2.4 as a result of temperature-driven volatilization are counteracted by the decreasing effects which may refer to more dissolution and wet deposition by precipitation, more transportation out of the model domain by wind, and stronger retain by POC in water. Moreover, the MCRs for the forest soil compartment decreases from 2.7 to about 1.9 as a result of the same counteracting effect after inclusion of all four climate parameters (Fig. C.3(a)).

3.1.3. Emission to soil

The largest CC-induced increases in concentrations in air are observed for emissions to soil which can be attributed to the strong volatilization from the soil compartments (Figs. 2(a), 3(a) and 4(a)). In comparison to the previous two emission scenarios, considering all four climate parameters under the A2 climate change scenario can lead to a factor of up to 2.2 for the particle-bound single hoppers with $\log K_{AW}$ from -8 to -3.5 and $\log K_{OA}$ from 10 to 15 (Fig. 4(a)). As shown in Fig. 1, this property combination covers some legacy persistent organic pollutants such as PCB-180, PCB-209, and most polychlorinated dibenzo-p-dioxins. Moreover, the modelled increase in concentration can even be up to 2.3 for chemicals with $\log K_{AW}$ from -3 to 3 and $\log K_{OA}$ from 13 to 15 (Fig. 4(a)), for which there are few real examples.

Fig. 4(c) suggests that the atmospheric concentrations of some particle-bound single hopper chemicals can be increased by factors

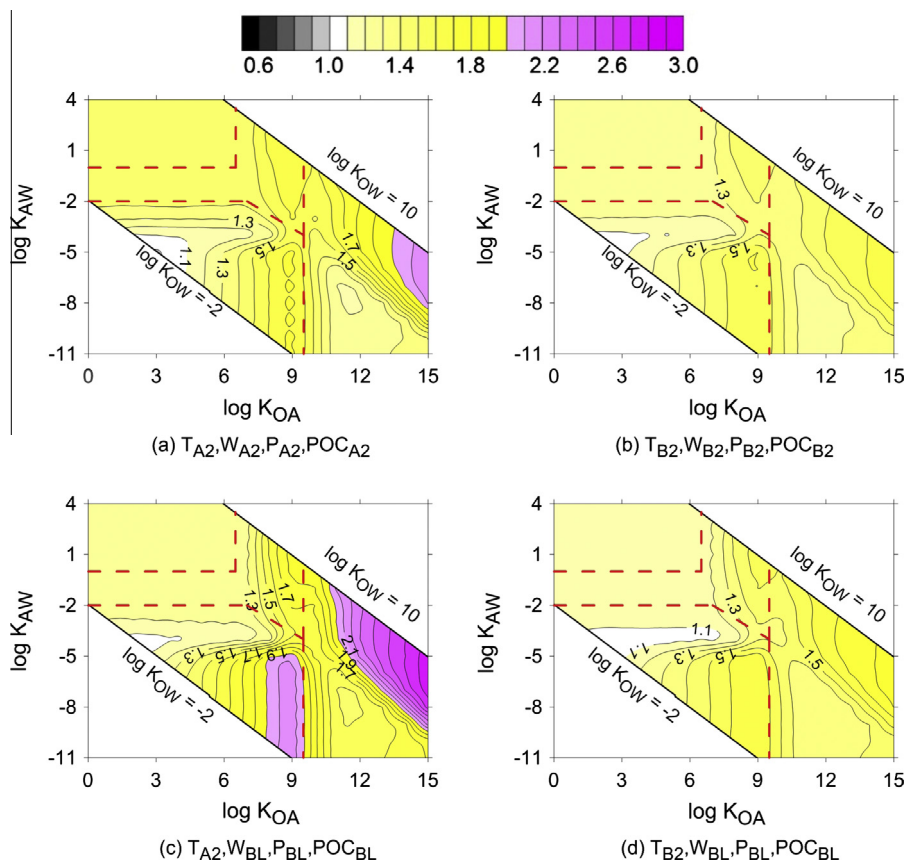


Fig. 4. Ratios of modelled chemical concentrations in air when emissions occur to soil.

up to 2.8 for the A2 climate scenario when temperature alone is considered. Large predicted increases (factors up to 2.4) are also observed in the forest canopy compartment for particle-bound single hopper chemicals with $\log K_{AW}$ from -4 to 0 and $\log K_{OA}$ from 10 to 12 (see Fig. D.2(c)). These increases are caused by high temperature-driven volatilization of chemicals to the air and high deposition and sorption to the forest canopy. In some cases these increases are caused by artefacts due to the assumptions made in the design of the POPCYCLING-Baltic model. For example, the terrestrial temperature for the Danish Strait area is predicted to be above 5°C throughout the year in the A2 climate change scenario (Fig. A.2), and in such cases the POPCYCLING-Baltic model simulates the forest canopy to be fully developed even in the winter since litterfall does not occur if the temperature remains above 5°C . From February to October the forest canopy keeps accumulating particle-bound single hopper chemicals as the canopy unrealistically remains intact during the winter in the A2 climate change scenario.

In this emission mode the counteracting effects are also noticeable. For example, when only temperature is considered the chemical concentrations in air are predicted to increase by a factor of up to 2.8 (Fig. 4(c)), but this factor decreases to about 2.2 due to further consideration of POC, wind speed and precipitation (Fig. 4(a)). This can be attributed to the counteracting effect between temperature-driven volatilization, wind and precipitation-driven deposition and POC caused sorption.

3.2. Comparison of climate variables

3.2.1. Temperature

Among the four investigated variables, temperature is the most influential on the predicted concentrations regardless of emission mode and climate change scenario (Fig. 5). When only temperature

is considered, the MCRs are up to 2.8 under the A2 climate change scenario for emissions to soil (Fig. 5(c)). This can be attributed to two effects considered in the POPCYCLING-Baltic model, namely (i) the temperature correction of bulk partition coefficients between the environmental compartments, and (ii) the effect on diffusive mass transfers where the temperature-corrected partition coefficients are components in the two-film model.

3.2.2. Particulate organic carbon

POC is important in determining the environmental fate of hydrophobic persistent organic chemicals (Wania et al., 2000; Smith and McLachlan, 2006; Steinacher et al., 2010). Changes in POC are generally the second most influential parameter affecting the fate of persistent organic chemicals in our climate scenarios. The assumed increase in POC can lead to changes by factors of 0.7 – 1.6 in modelled chemical concentrations in ocean water or sediment compartments when emissions are to water (Fig. 5(b)). These changes in concentration are attributable to the altered partitioning of chemicals between the dissolved and particulate phase in water (Smith and McLachlan, 2006). For example, the increased concentration of POC leads to a factor of 1.3 decrease in the dissolved phase of multimedia multiple hopper chemicals with $\log K_{AW}$ from -2 to -4 and $\log K_{OA}$ from 5 to 8 (MCRs are not shown). This decrease may also lead to reduced bioavailability of these chemicals, resulting in an overall reduction in net bioaccumulation in aquatic organisms (Borgå et al., 2010).

3.2.3. Precipitation

Changes in precipitation have less influence on modelled chemical concentrations than temperature and POC. When only precipitation is considered, the MCRs are up to approximately 1.5 under the A2 climate change scenario for emissions to air (Fig. 5(a)). Concentrations in air decrease as a result of increased

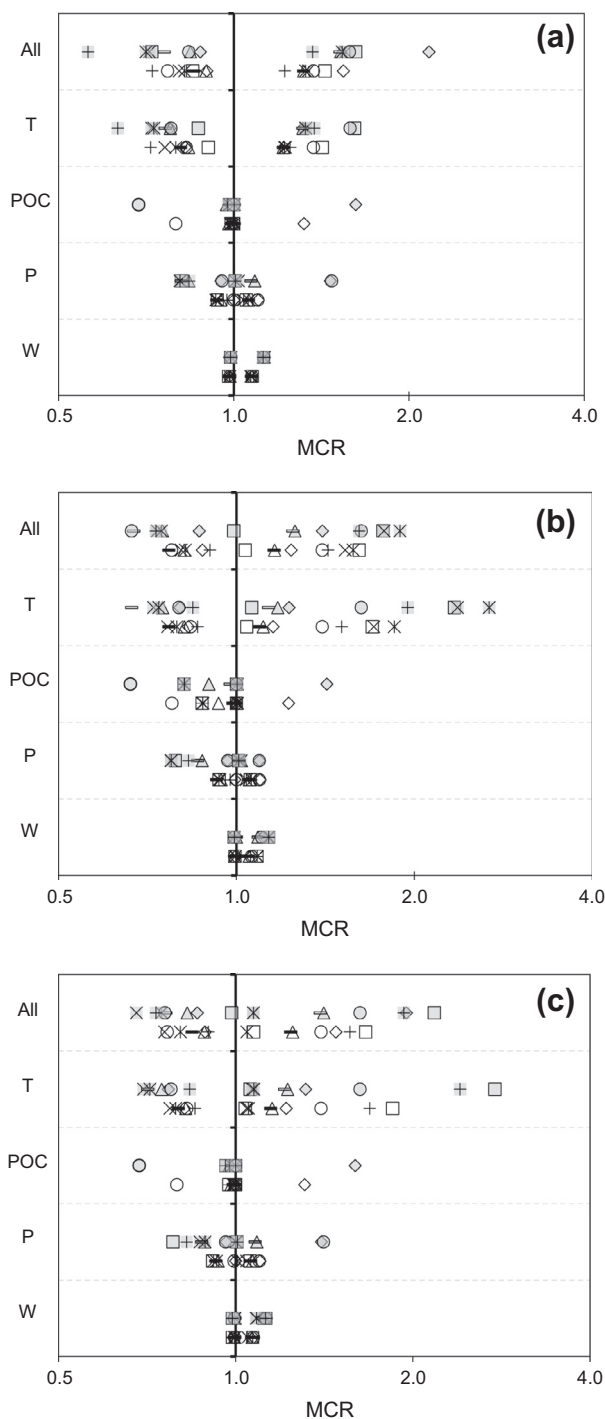


Fig. 5. Summary of calculated minimum (<1) and maximum (>1) MCRs when emissions occur (a) 100% to air, (b) 50% to fresh water and 50% to coastal water, and (c) 50% to agricultural soil and 50% to forest soil (the markers filled with grey indicate the A2 scenario; the empty markers indicate the B2 scenario). MCRs corresponding to each of the eight environmental media are indicated by the following symbols: air: □, agricultural soil: ×, forest soil: •, forest canopy: +, fresh water: △, fresh water sediment: –, coastal and open ocean water: ◇, and coastal and open ocean sediment: ○. T is temperature, POC is particulate organic carbon, P is precipitation, W is wind speed, and All indicates all of the four parameters were considered. Note the x-axis is \log_2 -transformed to correctly reflect a same factor of 2 change, i.e., the length is the same from 1 to 0.5 or 2 and from 2 to 4).

precipitation scavenging of chemicals from air, whereas concentrations in surface water compartments increase because of increased run-off from terrestrial compartments. This predicted change is highest for hydrophobic chemicals with $\log K_{ow} > 7$ (Figs. B.7(g)

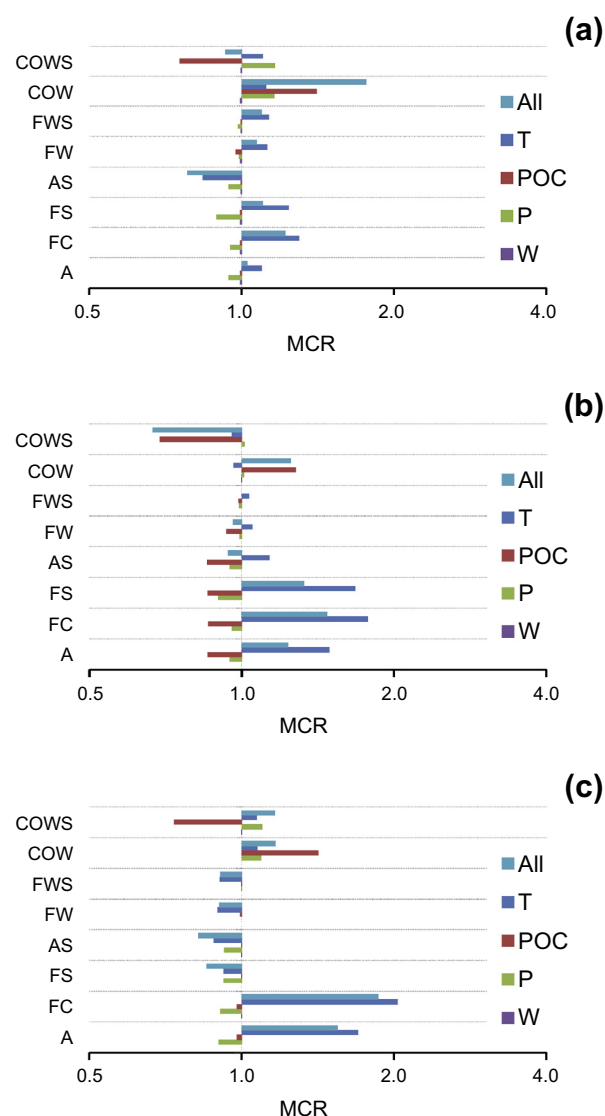


Fig. 6. MCRs for a POP with $\log K_{AW}$ of -2 and $\log K_{OA}$ of 10 under the A2 climate change scenario: emission to (a) air, (b) water, and (c) soil (air (A), agricultural soil (AS), forest soil (FS), forest canopy (FC), fresh water (FW), fresh water sediment (FWS), coastal and open ocean water (COW), and coastal and open ocean sediment (COWS); Note the x-axis is \log_2 -transformed to correctly reflect a same factor of 2 change, i.e., the length is the same from 1 to 0.5 or 2 and from 2 to 4).

and B.8(g)). For volatile chemicals, the modelled influence of increased precipitation is negligible. If emissions are to water or soil, MCRs > 1.0 are few regardless of the physical–chemical property combination (see the panel (g and h) in MCR plots in Appendix C and D).

3.2.4. Wind speed

Previous studies that focused on the global-scale fate and transport of persistent chemicals indicated that changes in large-scale wind fields and wind speed can significantly influence the environmental fate and levels of chemicals (Lamon et al., 2009). In this study wind speed is considered to affect both the mass transfer at the diffusive boundary between air and water and the flow of air between the atmospheric compartments and outside of the model domain. However, when only wind speed is considered, MCRs have a very narrow range from 0.99 to 1.02 (Fig. 5), which is consistent with the small differences in wind speed between the three climate scenarios for the Baltic Sea regional environment.

3.2.5. All four climate parameters

For many chemicals with different property ranges either counteracting or re-enforcing effects can be observed when multiple parameters are taken into account simultaneously (Fig. 6). As discussed earlier, the changing emission mode is also important. For example, under the A2 climate change scenario when emissions are to air, the MCR for a POP with $\log K_{AW}$ of -2 and $\log K_{OA}$ of 10 is approximately 1.80 based on all of the four studied parameters for the Baltic Sea water (Fig. 6(a)). The concentration ratios based on each single parameter for the same chemical and media are 1.41 (POC), 1.16 (P), 1.12 (T) and 1.00 (W). This indicates a re-enforcing effect of the single climate parameter-induced effects. This can be attributed to several intensified processes which include air-to-surface deposition, terrestrial-to-water runoff, sorption to POC, and dissolution to ocean water. When the emission mode changes to soil, a counteracting effect is clear (Fig. 6(c)). For example, when emissions are to soil, for the Baltic Sea water the greatest calculated MCR is 1.42 obtained based solely on POC. When all of the four studied parameters are taken into account, the MCR becomes 1.17 suggesting a counteracting effect. The reasons for this are the intensified volatilization from water and partitioning to the other surface compartments when all of the four parameters are considered. These processes trap the chemical in the terrestrial environment and prevent transport to the Baltic Sea water and binding to POC.

3.2.6. Climate scenario A2 vs. B2

The A2 scenario is a more extreme greenhouse gas emission scenario than the B2 scenario and thus the projected changes in climate parameters are also consistently larger. The range of MCRs is also consistently broader under the A2 climate scenario than under the B2 scenario (A2: MCRs range from approximately 0.6 to 2.8 ; B2: MCRs range from 0.7 to 1.9 , see Fig. 5). This confirms a stronger net influence on the chemical concentrations in the Baltic Sea region under the A2 climate scenario.

3.3. Comparison of CC impacts on media-specific chemical concentrations

Table 1 summarizes the modelled CC-induced impacts on the media-specific concentrations of six studied groups of persistent organic chemicals. It demonstrates that regardless of emission mode CC will increase the atmospheric concentration of studied chemicals with the exception of most particle-bound single hoppers and some water soluble swimmers in the Baltic Sea region. Indeed the water soluble swimmers that are predicted to

decrease in air have extreme partitioning properties, i.e., $\log K_{AW}$ from -7 to -5 and $\log K_{OW}$ from -2 to -1 (Fig. 2(a)). Only particle-bound single hoppers are forecast to decrease in a case of emissions to air. In the other environmental media the modelled CC-induced effects are not monotonic and vary with the studied groups of chemicals and emission mode. For example, the multimedia multiple hoppers are forecast to decrease in forest and agricultural soil, fresh water sediment and fresh water in all three emission modes. But their concentrations are forecast to both increase and decrease in the other environmental media as a result of varied property combinations and emission mode.

3.4. Applications of MCRs and MCR plots

To date, this is the first modelling study attempting to assess the influence of CC-induced effects on the environmental concentrations of all plausible non-ionizing persistent organic chemicals in the Baltic Sea region. The MCR plots demonstrate that for legacy persistent organic pollutants CC-induced changes are up to a factor of 2.0 , and for organic chemicals with extreme property combinations, CC-induced changes are not over a factor of 3.0 . Furthermore, the MCR plots can be used to provide a preliminary idea of how CC-induced effects may affect the concentrations of any specific persistent organic chemicals in the Baltic Sea region.

There have been a few multimedia fate modelling studies which have previously assessed the influence of CC-induced effects on the environmental concentration of persistent organic pollutants. In spite of the fact that different methodologies have been followed, a similar magnitude of potential CC-induced changes in environmental concentrations has been derived as in this study. For example, Lamon et al. (2012) studied the CC-induced impacts on the mass balance of PCB-52, -138 and -153 in the Adriatic Sea based on the IPCC A1B climate change scenario, which is considered to be intermediate between the A2 and B2 scenarios. The atmospheric and marine temperature was assumed to increase by 2.3 – 2.9 °C and 1.4 – 2.2 °C, respectively. On average the precipitation was assumed to decrease by approximately 7% , and the wind speeds were assumed to vary by 8% under the A1B scenario compared to the baseline scenario. Lamon et al. (2012) suggested a factor of up to 1.6 change in the concentrations of studied PCB congeners in air, water and sediment under the A1B climate change scenario. Our calculated MCRs for chemical property combinations that correspond to PCB-52, -138 and -153 are less than a factor of 2.0 in similar environmental media regardless of emission mode. These comparisons indicate that the findings of this study may be extrapolated from the Baltic Sea region to other global regions, i.e., the

Table 1
Summary of the modelled climate change-induced impacts on the concentrations of hypothetical perfectly-persistent organic chemicals (considering all four studied climate variables).

	Air	Forest canopy	Forest soil	Agricultural soil	Fresh water	Fresh water sediment	Coastal and open ocean water	Coastal and open ocean sediment
Volatile fliers	+/+	+/+	±/±	±/±	+/-	+/-	+/±	+/-
Water soluble and relatively volatile multiple hoppers	+/+	+/+	±/±	+/-	+/±	+/±	+/±	+/±
Water soluble swimmers	±/±	-/-	-/±	-/±	-/±	-/-	-/±	+/+
Multimedia multiple hoppers	+/+	±/±	-/-	-/-	-/-	-/-	+/±	+/±
Very hydrophobic and semi-volatile multiple hoppers	+/+	±/±	-/-	-/-	±/-	±/-	+/+	-/-
Particle-bound single hoppers	-/+	±/±	±/±	-/±	±/-	±/-	±/±	±/±

“+” indicates increase; “-” indicates decrease; “±” indicates both increasing and decreasing impacts were observed for that specific group of chemicals. Symbols from left to right correspond to emission to air, water and soil. Note that here the predicted impacts are not discriminated according to the studied climate scenarios, because in general the impacts from the two climate scenarios are the same.

MCRs can be used as a first estimate of CC-induced changes in regions other than the Baltic Sea. In another study, Lamon et al. (2009) modelled the global levels of PCB-28 and -153 in air under the IPCC A2 climate change scenario and found a factor of up to 2.0 increase in the concentrations of PCB-28 and -153 under the A2 climate change scenario for the Baltic Sea region. This is also in good agreement with the results of this study.

4. Conclusions and outlook

The POPCYCLING-Baltic model is currently the state-of-the-art for conducting chemical fate assessments in the Baltic Sea region. In previous studies, POPCYCLING-Baltic was shown to simulate the environmental fate and levels of organic chemicals in the Baltic Sea region in a useful way (Breivik and Wania, 2002a,b; Mattila and Verta, 2008; Armitage et al., 2009). For example, the model was used to successfully reproduce many aspects of the long-term fate of hexachlorocyclohexanes (HCHs) in the Baltic Sea. However, by using POPCYCLING-Baltic in this study we are constrained by the description of fate processes that are included in the model and thus, given the limitations of the model, we are not able to account for some potentially important additional direct effects of CC, e.g., changes in ocean currents, melting of permafrost and glaciers, and intermittent extreme meteorological events (Macdonald et al., 2005; UNEP/AMAP, 2011). Another limitation is that this study and nearly all previous modelling studies focusing on CC-induced impacts on chemical fate (Gouin et al., 2013) have so far focused mainly on direct (rather than indirect) effects of CC (changes in temperature, precipitation, wind speed). Indirect effects of CC (e.g. land use changes, percentage vegetation cover and type, carbon cycling, species range and abundance and chemical emissions) may also have a substantial impact on chemical transport and fate (Gouin et al., 2013; Wöhrnschimmel et al., 2013), but limitations in process understanding and associated uncertainties make indirect CC-induced effects more challenging to model.

Regional-scale CC-induced effects on the chemical concentrations in the environment have previously been assessed for a few persistent organic contaminants in the Mediterranean region (Dalla Valle et al., 2007; Lamon et al., 2012). This study investigated CC-induced effects on the environmental concentrations of hypothetical perfectly-persistent chemicals with property combinations encompassing the entire plausible range for non-ionizing organic substances in the Baltic Sea region. Changes in the environmental concentrations could be within a factor of 3.0, however, our work also highlighted important limitations for the use of POPCYCLING-Baltic (and similar multimedia models) for assessing the CC-induced impacts on the transport, fate and distribution of chemicals in the environment under CC scenarios. It is clear that the research should continue to include other CC-induced direct and indirect effects. There is a clear need to take into account of the interaction between multiple stressors when managing regional environments. For example, in addition to considering hazardous chemicals and climate change in the Baltic other environmental problems should be considered simultaneously, e.g. decline of species abundance and diversity, eutrophication and salinity changes. For the Baltic ecosystem the Nest decision support system has been developed to model the biogeochemical cycles of organic matter and nutrients, as well as the Baltic Sea food web (Wulff et al., 2007). Coupling a chemical fate model to the biogeochemical and food web models developed for the Nest decision support system is an on-going activity at the Baltic Sea Centre at Stockholm University. This improved system will allow a more detailed and integrated assessment of potential changes in pollutant dynamics in response to multiple stressors and chemical management scenarios.

Acknowledgments

The Ph.D. studies of Deguo Kong are funded by ArcRisk, which is a Collaborative Project supported under the Seventh Framework Program of the European Community for research, technological development and demonstration activities (FP7-ENV-2008-1, Grant Agreement Number: 226534). We acknowledge the Rossby Centre of the Swedish Meteorological and Hydrological Institute for providing climate data used in this study.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.02.044>.

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