



Modeling the influence of climate change on the mass balance of polychlorinated biphenyls in the Adriatic Sea

Lara Lamon^{a,b}, Matthew MacLeod^{c,d}, Antonio Marcomini^{a,b,*}, Konrad Hungerbühler^c

^a Euro Mediterranean Centre for Climate Change, Via Augusto Imperatore 16, 73100 Lecce, Italy

^b Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari Venice, Calle Larga Santa Marta 2137, 30123 Venice, Italy

^c Safety and Environmental Technology Group, Swiss Federal Institute of Technology, Zürich CH-8093, Switzerland

^d Department of Applied Environmental Science, Stockholm University, SE-11418 Stockholm, Sweden

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ABSTRACT

Climate forcing is forecasted to influence the Adriatic Sea region in a variety of ways, including increasing temperature, and affecting wind speeds, marine currents, precipitation and water salinity. The Adriatic Sea is intensively developed with agriculture, industry, and port activities that introduce pollutants to the environment. Here, we developed and applied a Level III fugacity model for the Adriatic Sea to estimate the current mass balance of polychlorinated biphenyls in the Sea, and to examine the effects of a climate change scenario on the distribution of these pollutants. The model's performance was evaluated for three PCB congeners against measured concentrations in the region using environmental parameters estimated from the 20th century climate scenario described in the Special Report on Emission Scenarios (SRES) by the IPCC, and using Monte Carlo uncertainty analysis. We find that modeled fugacities of PCBs in air, water and sediment of the Adriatic are in good agreement with observations. The model indicates that PCBs in the Adriatic Sea are closely coupled with the atmosphere, which acts as a net source to the water column. We used model experiments to assess the influence of changes in temperature, wind speed, precipitation, marine currents, particulate organic carbon and air inflow concentrations forecast in the IPCC A1B climate change scenario on the mass balance of PCBs in the Sea. Assuming an identical PCBs' emission profile (e.g. use pattern, treatment/disposal of stockpiles, mode of entry), modeled fugacities of PCBs in the Adriatic Sea under the A1B climate scenario are higher because higher temperatures reduce the fugacity capacity of air, water and sediments, and because diffusive sources to the air are stronger.

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1. Introduction

The Adriatic Sea is an elongated portion of the Mediterranean Sea that separates the Italian Peninsula and the Balkans. The Adriatic Sea region is intensively developed with agriculture, manufacturing, shipping and tourism. Activities associated with these industries have introduced a range of synthetic pollutants into the Sea, including polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and organochlorine pesticides (OCPs). These persistent pollutants are also deposited to the region by long-range transport in air and water. Concern has increased, particularly in recent years, about the ecotoxicological and human health implications of the presence of PCBs in the Adriatic Sea environment (Picer, 2000).

Effective management strategies for PCBs in the Adriatic Sea can only be formulated based on knowledge of the sources, fate and transport pathways, and ultimate sinks in the system. It is convenient to assemble this information in the form of a mass balance based on a contaminant fate model that can then be used to evaluate alternative management scenarios, or to forecast the influence of possible changes in environmental conditions (Mackay, 2001). This approach has been demonstrated in the Great Lakes region of North America (Thompson et al., 1999), and in other marine environments, for instance in the Eastern Mediterranean by Mandalakis et al. (2005), and the San Francisco Bay by Davis (2004). Local areas of the Adriatic Sea system have also been studied using contaminant fate models, including the Lagoon of Venice (i.e. Dalla Valle et al., 2003) and the Sacca di Goro near the outlet of the Po River (Carafa et al., 2006). However, a mass balance that includes the sources and behavior of PCBs in the Adriatic Sea is missing. In fact there are no studies that combine monitoring data with modeling to gain insights into the key processes governing the fate of the chemicals in the Adriatic Sea.

* Corresponding author at: Department of Environmental Sciences, Informatics and Statistics, University Ca' Foscari Venice, Calle Larga Santa Marta 2137, I-30123 Venice, Italy. Tel.: +39 041 234 8548; fax: +39 041 234 8584.

E-mail address: marcom@unive.it (A. Marcomini).

Like POPs, climate change is also an issue of global concern. Evidence of climate change has been observed at both the global and local scales, including changes in surface temperatures, wind speeds, oceanic currents, precipitation, ocean salinity and occurrence of extreme weather events (Trenberth et al., 2007). In 1980, the World Climate Research Programme (WCRP) was established with the aim to determine how human activities influence climate change, and in 1989 the Intergovernmental Panel on Climate Change (IPCC) was launched by the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP). A few studies have already focused on how concentrations of persistent organic pollutants might change in response to climate variability or climate change, both at the global and at the local level (MacLeod et al., 2005; Dalla Valle et al., 2007; Lamon et al., 2009).

This study aims at (1) collecting information on PCB concentrations in the Adriatic Sea, (2) building a Level III fugacity model for the Adriatic Sea and evaluating the present mass balance of PCBs, (3) performing an uncertainty analysis in order to identify influential input parameters and evaluate uncertainty in the model, and (4) providing an estimate of the possible influence of climate change on the fate of selected persistent organic pollutants in the aquatic and atmospheric environment of the Adriatic Sea.

In this study we use climate projections for the Mediterranean area developed in a recent intensive study (SINTA, Gualdi et al., 2008) as inputs to parameterize a Level III fugacity model which was developed to study the fate and transport in the Adriatic Sea of three PCB-congeners that have been well-studied in the system: PCB 52, 138 and 153. We assess the influence of variation in eight environmental parameters between the present 20CE climate scenario and the forecast A1B climate scenario on the environmental fate and transport of these PCBs in the Adriatic Sea ecosystem. The eight environmental parameters are: (1) atmospheric temperature (*TA*), (2) atmospheric circulation (*U,V(AIR)*), (3) precipitation (*RAIN*), (4) sea water temperature (*TW*), (5) sea circulation (*U,V(SEA)*), (6) temperature effect on emissions (*EMISS*), (7) particulate organic carbon (*POC*) content in sea water, and (8) background concentrations of PCBs in air (*BC*).

1.1. The study area

The major axis of the Adriatic Sea is oriented in the northwest-southeast direction. The northern section is shallow and gently sloping, with an average depth of 35 m, whereas the central Adriatic Sea is 140 m deep on average, with the two Pomo Depressions reaching 260 m. The southern section is characterized by a wide depression more than 1200 m deep. Water exchange with the Mediterranean Sea takes place through the Otranto Channel, whose sill is 800 m deep (Artegiani et al., 1997). A large number of rivers discharge into the basin, with significant influence on the circulation and on nutrients inputs, particularly relevant being the Po River in the northern basin, and the ensemble of the Albanian rivers in the southern basin (Zavatarelli et al., 2000).

2. Methods

2.1. Model development

On the basis of its physical (Artegiani et al., 1997), biological and oceanographic characteristics (Zavatarelli et al., 2000), we have developed a fate and transport model for PCBs in the Adriatic Sea that divides it into three sub-regions: the North Adriatic Sea (NAS), the Central Adriatic Sea (CAS) and the South Adriatic Sea (SAS), as shown in the Supporting Material (SM) in Fig. SM1.

Each model region consists of 3 bulk model compartments; sediment, coastal water and atmosphere. The model takes into account

advective transport between the regions in air and water, advective transfer processes between compartments, and reversible diffusive exchange between compartments. Advection of air and water (including aerosols and suspended particles), deposition and resuspension of particles in water, dry and wet deposition from air, degradation by OH[•] reaction in air, and degradation in water and sediment are considered as intermedia and intramedium processes in the model, as it is shown in Fig. SM2.

We have applied the model to calculate steady state (Level III) mass balances, where total inputs of PCB are balanced by outputs. Air, coastal water and sediment were defined as bulk environmental compartments, and aerosols in air and suspended particulate matter (SPM) in water were also considered as two sub-compartments in equilibrium with the gas phase in the atmosphere and with the coastal water dissolved phase, respectively.

2.2. Model parameterization

Partitioning properties for the selected chemicals were taken from Schenker et al. (2005), internal energies of phase change are those recommended by MacLeod et al. (2007). Degradation half lives in air are derived by second-order hydroxyl radical reaction rate constants extrapolated from data presented by Anderson and Hites (1996) and OH[•] concentrations from the dynamic and spatially resolved global estimates by Spivakovsky et al. (2000). For the other compartments, estimates of degradation rate constants were taken from Wania and Daly (2002). The chemical parameters used in this study are shown in Table SM1.

Model input values for environmental parameters are defined for the Adriatic Sea according to Table SM2. The climate variables for the description of the environment come from the Simulations of climate change in the Mediterranean Area (SINTA) project, which was focused on a downscaling for the climate variables in the Mediterranean area (Gualdi et al., 2008). The climate projections were performed using the Regional Circulation Model (RCM) for atmospheric and marine temperatures and currents, and for precipitation for two climate scenarios. The present climate scenario is defined considering the year 1990 in the 20th century scenario (20CE) defined by the IPCC. The A1B scenario is defined considering the year 2100 as forecast under conditions described in the Special Report on Emission Scenarios by the IPCC (Nakicenovic et al., 2000). These data and the related estimates of uncertainty used in our Monte Carlo analysis are reported in Tables SM5–SM9. Mean values in these tables were used for model parameterization under the 20CE and the A1B climate scenarios.

2.3. Uncertainty analysis

Our model simulation is based on selected input parameters describing environmental properties, chemical properties, chemical release rates and background concentrations. We have estimated uncertainties in these inputs as confidence factors (*C_f*), where 95% of possible values lie between *C_f* times the median and the median divided by *C_f* (MacLeod et al., 2002). The *C_f*s for climate variables were calculated from the reference RCM output database, as it is shown in Tables SM5–SM9 (*C_f*s in parentheses); the variability in other properties were estimated based on values used in uncertainty analysis studies in the literature (MacLeod et al., 2002). The parameters defining compartmental dimensions were assigned *C_f* = 1, as it was assumed in previous studies (i.e. MacLeod et al., 2002). For background concentrations the uncertainty is defined by previous model experiments at the global scale (Lamon et al., 2009).

Monte Carlo analysis using the Crystal Ball™ software package was used to propagate variance in inputs to the model results and

identify input parameters that are most important in determining the variance of the outputs.

2.4. Emission scenario

Emissions of the three PCB congeners in the Adriatic Sea region were estimated from the maximum emission scenario by Breivik et al. (2007) by taking the average emission rate for the period 1990–2000. In order to focus attention on the effect of variability in climate parameters, we assume that the sources of PCBs are the same under both climate scenarios; the only change in emission under the A1B climate scenario is related to the influence of the change in temperature on the rate of volatilization of PCBs from primary sources. The information by Breivik et al. (2007) shows that the majority of primary PCB emissions to the atmosphere occur by passive volatilization from use and disposal of PCBs. The change in emission related to the difference in temperature (ΔT) between the 20CE and the A1B scenario was calculated using the following equation:

$$\frac{E_{20CE}}{E_{A1B}} = \exp \left[\frac{\Delta U_A}{R} \cdot \left(\frac{1}{T_{20CE}} - \frac{1}{T_{A1B}} \right) \right], \quad (1)$$

where (E_{20CE}/E_{A1B}) is the ratio of the emission rate by passive volatilization at temperatures T_{20CE} and T_{A1B} , ΔU_A is the internal energy of vaporization of the PCB congener (J mol^{-1}), and R is the gas constant.

3. Model experiments

As a prerequisite to compare the fate of PCBs under the two climate scenarios, we first build confidence that our selected emission scenario, physicochemical properties, and environmental fate model together provide a reasonable representation of PCBs in the Adriatic Sea environment. To this end, we compared the model calculations from the 20CE model scenario against measurements from the real environment to evaluate the performance of the model.

We then performed several model experiments to compare the fate of PCB 52, 138 and 153 under the 20CE and the A1B climate scenarios. In a first experiment we compare modeled concentrations and fugacities of all three PCBs under the 20CE and A1B scenarios. Then, we parameterized different sub-scenarios based on the 20CE scenario, where we replace one of the six factors that differ between the two climate scenarios with parameter values from the A1B scenario, changing one factor at a time, in detail: (1) atmospheric temperature (TA), (2) atmospheric circulation ($U,V(AIR)$), (3) precipitation ($RAIN$), (4) marine temperature (TW), (5) sea circulation ($U,V(SEA)$), and (6) temperature effect on emissions to the atmosphere ($EMISS$). We considered also a change in (7) POC (POC) which was assumed to behave as dissolved organic carbon (DOC) as it was estimated by Vichi et al. (2003), where an increase by 30% in a future climate change scenario was calculated. Our assumption that changes in POC are directly proportional to changes in DOC would be valid if both were proportional to changes in net primary productivity in the system. These are strong assumptions, and there are large uncertainties in the parameterization of POC in the future climate scenario, however the model results presented in the following paragraph demonstrate that the forecast changes of the magnitude of 30% do not have a strong influence on modeled fugacities/concentrations compared to other factors. Furthermore, we considered (8) the concentration of PCBs in background air flowing into the region (BC), as it was calculated by similar model experiments using BETR Global (Lamon et al., 2009) as reported in Table SM4. We use the factor of change, F , defined as the ratio of model results under the alter-

native scenario and 20CE scenario in order to compare the different scenarios.

4. Model results

4.1. Model evaluation

We evaluate the model performance by comparing the fugacity of each PCB congener in the different compartments calculated by the model against values calculated from measured concentrations. Fugacity (f , Pa) is a criterion of equilibrium partitioning of chemicals that is directly proportional to concentration (C , M m^{-3}). The proportionality constant between the two is the fugacity capacity (Z , $\text{Pa m}^3 \text{M}^{-1}$), thus,

$$C = f \cdot Z. \quad (2)$$

Fugacity can be thought of as the escaping tendency of the substance (Mackay, 2001): the higher the fugacity, the higher the tendency of the chemical to transfer to another phase. We use fugacity here rather than concentration because it allows the contamination level in air, water and sediment to be displayed on the same graph, using the same units, and because we can readily calculate the extent and direction of disequilibrium between PCBs in the air, water and sediments of the Adriatic Sea as fugacity ratios.

Fig. 1 shows fugacities calculated from measured concentrations of PCBs in air, water and sediment in the Adriatic compared to modeled fugacities (Pa). For the atmosphere, data from Manodori et al. (2006) and Klánová et al. (2007a,b) were used to estimate concentrations in the NAS and CAS. For the coastal water environment we used the measurements from Ferrara and Funari (2004). For the sediment, data from the Defence of the Sea System database (Si.Di.Mar, <http://www.sidimar.tutelamare.it/>) were compared to model outputs, assuming a sediment solid density of 2550 kg m^{-3} (Frignani et al., 2005). Error bars indicate the range of uncertainty in the model calculation determined in the Monte Carlo analysis, and the range of variability in measured data from our review of monitoring studies. The comparison between model results and observed values is possible for 8 of the 9 modeled compartments; no measured data was available for the air compartment in the South Adriatic Sea (SAS). The agreement between measured data and model results is always within one order of magnitude, and 71% of the results lay within a factor of 3.16 (Fig. 1A). For PCB 52, the model result is in good agreement especially for water and sediment in the NAS and CAS, and for air in the CAS. For PCB 138 the model agrees well with measurements in all regions, only in the case of the sediment compartment in the SAS and air in the CAS model results are outside of a factor of 3.16 of the measurements (see Fig. 1B).

For PCB 153 the modeled fugacity in sediment in the SAS is again furthest from the measured value, but for all the other results the modeled values are within a factor of 3.16 of values calculated from empirical measurement data (see Fig. 1C). The model thus shows some tendency to underestimate the fugacity in the sediment compartment. This may be attributable to overestimation of the degradation rate constant in the sediment or by an underestimation of the rate of deposition of SPM to the sediment. Another possible explanation is that the inventory of PCBs in sediments of the Adriatic is largely determined by higher loadings that occurred prior to 1990 that are not considered in our steady-state calculations.

The modeled ratios of fugacities between the compartments are also in good agreement with measured values for both PCB 138 and 153. For PCB 52, ratios between fugacities in water and sediment are also in good agreement, and the air to water fugacity ratio is within one order of magnitude for both regions. Mass balances

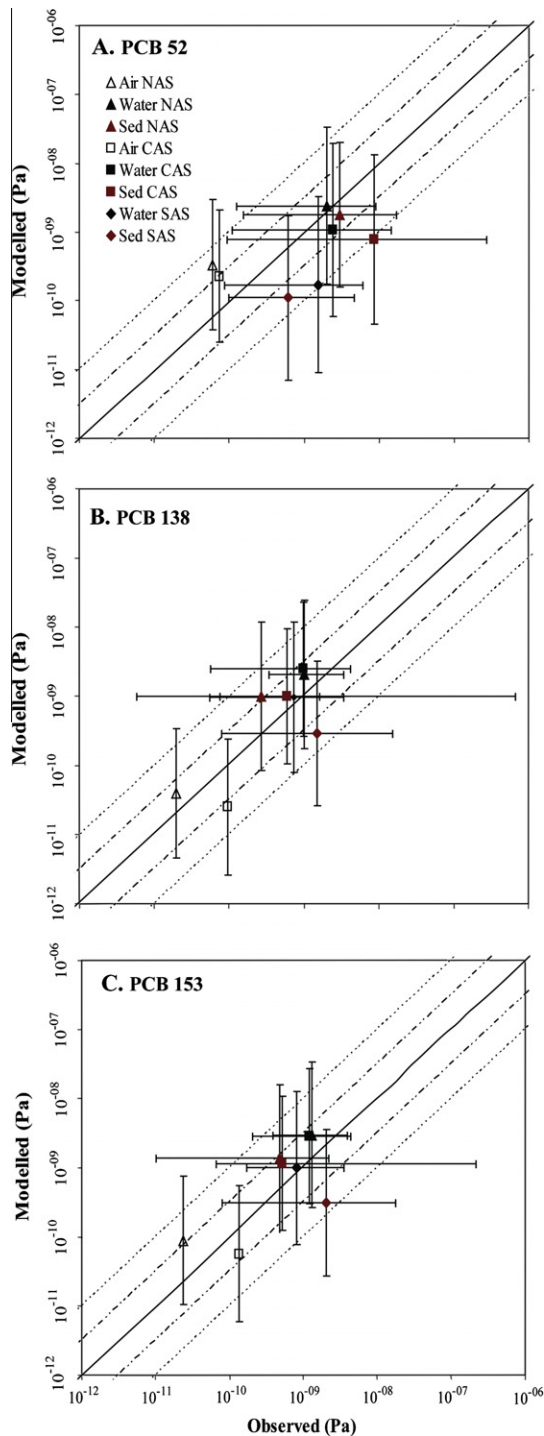


Fig. 1. Comparison of measured and modeled concentrations of (A) PCB 52, (B) PCB 138 and (C) PCB 153 in air, water and sediment. A range of variability is not shown for the air compartment because only a small set of measurement was available from passive sampling. Diagonal lines indicate perfect agreement, and agreement within factors of $10^{0.5}$ and 10. Horizontal error bars represent the range of variability in measurement data within the region, and vertical error bars represent the 95% confidence limits derived from our Monte Carlo uncertainty analysis.

for the three PCB congeners are shown in Fig. SM3 where fluxes are reported as $M h^{-1}$. The model indicates that PCBs in water of the Adriatic Sea are closely coupled to the atmosphere. The dominant source of all three PCB congeners to the model domain is inflow of contaminated air. A large fraction (46–70%) of PCBs that enter the air compartment are advected out to neighboring regions.

However up to 53% is deposited from air to water and may then be deposited from water to sediment. Degradation fluxes of PCBs are generally low, except in water in the SAS, which has a large residence time that allows degradation to become competitive with advective removal processes. The overall residence time for PCB 52, 138 and 153 in the model domain is, respectively 2, 20 and 12 years. The longer residence times of PCB 138 and PCB 153 are due to higher hydrophobicity and longer degradation half-lives in all compartments.

4.2. Sensitivity and Uncertainty analysis

Sample results of our sensitivity and uncertainty analysis for PCB 153 are shown in Fig. 2 as plots of confidence factors in input parameters versus confidence factors in outputs attributable to that input (MacLeod et al., 2002). The parameter contributing most to variance in model output is the solids concentration in air, and the water temperature in the water and sediment compartments, reflecting the importance of the environmental variables in determining the level of PCBs in the system. The background concentration of PCBs in air is contributing to variance in all compartments, reflecting the importance of inflow air as a source to the system. Furthermore, solids' density and aerosol dry deposition rate are influential in determining the modeled fugacity in air.

In water, the sediment–water mass transfer coefficient plays an important role, and half-life in sediment is prominent in determining the uncertainty associated to the modeled sediment fugacity.

Figs. SM4 and SM5 in the Supplementary Material shows the sensitivity results for PCBs 52 and 138. For the lower chlorinated PCB 52, the rate constant for reaction with OH radicals in air, background air concentration and atmospheric height, and water and sediment half lives contribute most to uncertainties in modeled fugacities. For the highly chlorinated PCBs 138 and 153 degradation is less important, whereas dry deposition velocity and solids density are important in determining the results. Environmental parameters playing an important role are solids concentration in air, solids' density, sediment burial rate for PCBs 138 and 153, which are more hydrophobic and hence have a higher affinity for the solids fraction in the different media. Climate variables that are most important in affecting the model results for PCB fugacities are water temperature and marine currents.

4.3. Model results for climate scenario experiments

Fig. 3 shows the factor F – the ratio of modeled fugacity (f), fugacity capacity (Z), or concentration (C) in the alternate climate scenario to f , Z and C in the 20CE scenario – for model experiments for PCB 153. $F(f,Z,C)_{A1B}$ represents the ratio of the values defined for each selected metric under the A1B and the 20CE climate scenarios. To understand which environmental variables are most important under our climate change scenario in determining differences in PCBs' environmental behavior, we calculated $F(f)$, $F(Z)$ and $F(C)$ also for the single-parameter climate scenarios, and compared the results with the F_{A1B} . Thus, F_{TA} , $F_{U,V(AIR)}$, F_{RAIN} , F_{TW} , $F_{U,V(SEA)}$, F_{E-MISS} , F_{POC} , F_{BC} , are factors of change for, respectively atmospheric temperature and circulation, precipitation, sea temperature and circulation, temperature effect on emissions, POC content in sea water, and background concentrations of PCBs in air.

Under the A1B scenario, modeled fugacities of PCB 153 are between a factor of 2.2 and 3.3 higher than under the 20CE scenario (white squares in Fig. 3A). Because of Eq. (2), higher fugacity under the A1B scenario may reflect either higher concentrations, or lower fugacity capacity (Z). Modeled concentrations under the A1B scenario are always within a factor of 1.6 of values for the 20CE scenario (white squares in Fig. 3C), and it is evident that higher fugacities under the A1B scenario are primarily a result of lower

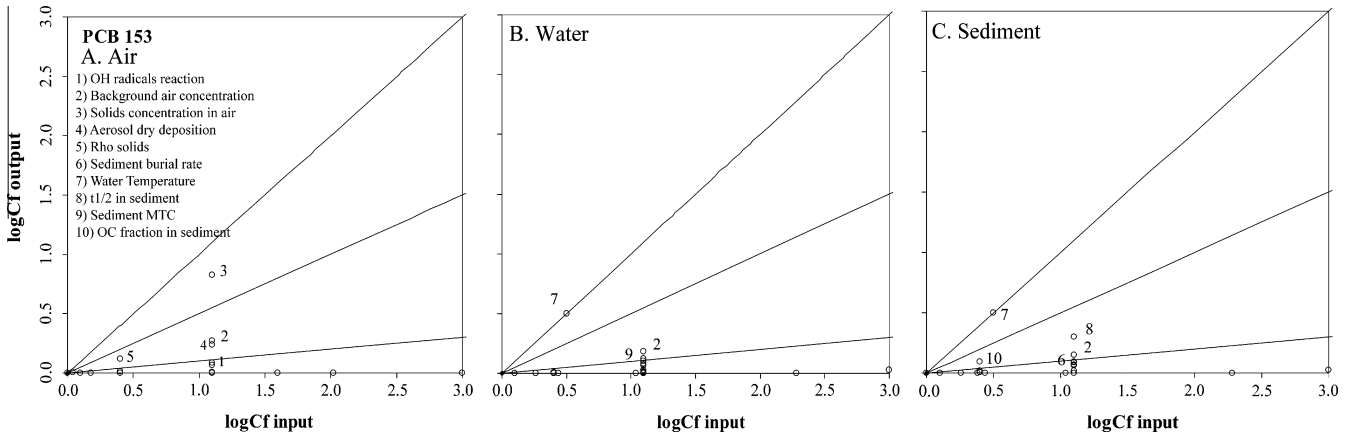


Fig. 2. Graphical analysis of contribution to uncertainty in steady state fugacity of PCB 153 in the CAS. Analysis for (A) atmosphere, (B) water and (C) sediment is shown in the graphs from left to right. The most important individual input parameters in terms of contribution to uncertainty in total steady state fugacity of PCB 153 are background air concentration for all compartments, and solids concentration in air and dry deposition are important in determining the output fugacity for air, whereas for water and sediment water temperature, and sediment half-life are more influential. Lines corresponding to sensitivity $S = 1, 0.5$ and 0.1 are shown for reference.

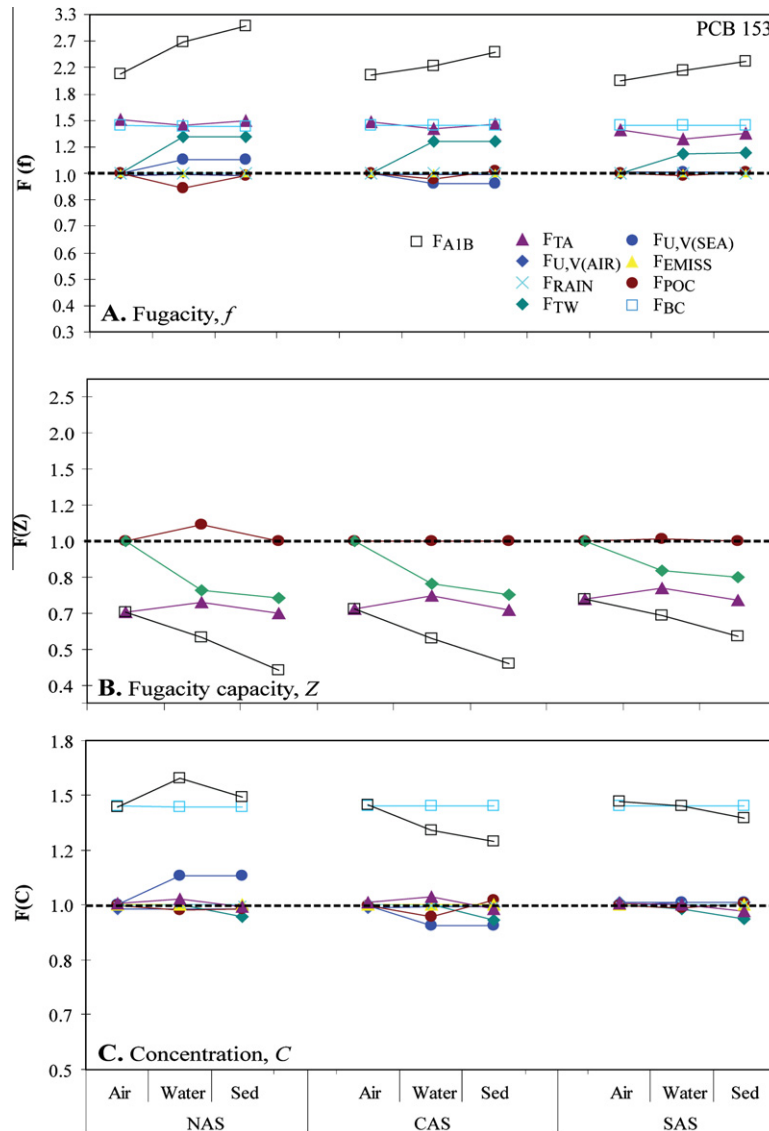


Fig. 3. Experiments results are shown here for PCB 153. (A) F – factor of change – for fugacities in the different compartments and regions is shown, (B) F values for Z are reported (only T_A , T_W and $U,V(SEA)$ and POC as these variables contribute to determine a change in Z) and (C) F for concentration in all compartments in all regions is shown. F_{A1B} represents the ratio between the fugacity under the 20CE and the A1B climate scenarios. F_{TA} , $F_{U,V(AIR)}$, F_{RAIN} , F_{TW} , $F_{U,V(SEA)}$, F_{EMISS} , F_{POC} , F_{BC} , stand respectively for atmospheric temperature and circulation, precipitation, marine temperature and circulation, temperature effect on emissions, POC content in marine water, and background concentrations of PCBs in air. The increase in F for fugacity can be explained either from a decrease in Z or by an increase in C .

fugacity capacities (white squares in Fig. 3B). Fig. SM7 shows the same information for PCB 138, which behaves very similarly to PCB 153.

$F(f)$ calculations for PCB 52 fall in the range 1.1–1.6, this means that modeled fugacities for this congener are between a factor of 1.1 and 1.6 higher under the A1B scenario compared to the 20CE climate scenario (white squares in Fig. SM6.A). Modeled concentrations under the A1B climate scenario are within a factor of 0.7 and 1.0 of values for the 20CE scenario (see white squares in Fig. SM6C), hence it is clear that the higher fugacities under the A1B scenario for PCB 52 are also primarily a result of lower Z (Fig. SM6B, white squares).

Furthermore, from comparison of Fig. 3, Figs. SM6 and SM7 a decrease in concentration under the A1B scenario is predicted only for PCB 52 in all environmental compartments, whereas an increase is expected for PCB 138 and 153 in all compartments, as the chemicals' mobility is enhanced under the A1B climate scenario.

Following the definition of fugacity by Eq. (2), Fig. 3A, B and C show cases where $F(f)_{A1B} > 1$ is attributable to both a $F(Z)_{A1B} < 1$ (as it is observed for F_{TW} , F_{TA} , F_{A1B}), or an increase in concentration C ($F_{U,V(SEA)}$ and F_{BC}). $F(f)_{BC}$ and $F(C)_{BC} > 1$ also influence the increase in $F(f)_{A1B}$. $F(f)_{TA} > 1$ and $F(f)_{TW} > 1$ are related to $F(Z)_{TA} < 1$ and $F(Z)_{TW} < 1$ as it is shown in Fig. 3B. POC does not strongly affect Z , in fact from Fig. 3 we see that the trends of $F(f)_{POC}$ and $F(f)_{U,V(SEA)}$ are determined almost entirely by $F(C)_{POC}$ and $F(C)_{U,V(SEA)}$.

Fig. 3 shows that the most influential environmental variables determining the fugacity of PCBs under the A1B scenario are BC , T_A , T_W , $U,V_{(SEA)}$, and POC . Otherwise, precipitation and the effect of temperature on primary emissions are not relevant parameters in determining the enhanced environmental fugacities under the A1B scenario. As far as precipitation is concerned, F_{RAIN} is very low and this is due to the fact that the highest expected variation in precipitation under the A1B scenario is only 0.13 mm y^{-1} in the CAS under the A1B scenario, as it is shown in Table SM7. From Figs. SM3, SM6 and SM7 we observe that BC is important in determining the mass balance of PCBs in the Adriatic Sea region. In fact BC is the most influential parameter in determining the increase in $F(f)_{A1B}$ and $F(C)_{A1B}$. This result is in agreement with previous studies showing that under a climate change scenario the temperature effect on primary volatilization of PCBs would increase concentrations globally (Lamon et al., 2009), thus background concentrations would be higher everywhere.

5. Discussion

We report a new mass balance model for PCBs 52, 138 and 153 in the Adriatic Sea. The agreement between measured and modeled fugacities shown in Fig. 1 demonstrates that under the 20CE scenario the model can account for much of the variability in monitoring data between sites and between air, water and sediment. Our mass balance indicates that the main source of PCBs to the region is inflow of background air, hence remote sources are more important than local ones in determining the pollutant concentrations in the Sea. This finding was not expected, in fact since in some areas there are some sources of pollution, we were expecting local sources to play a more prominent role in determining the PCBs concentration in environmental media. However, an analogous finding was reported by Mackay and Bentzen (1997) for the North American Great Lakes, where exchange between the atmosphere and water plays a primary role in determining water concentrations. Our mass balance indicates that in the Adriatic, the main input of PCBs comes from atmospheric deposition and sediment resuspension rather than from direct emissions to water. This finding strengthens the long range transport potential effect of

emissions and enhances the importance of remote sources in determining local pollution.

Furthermore, from the mass balance presented in this study we see that OH^\cdot reaction is important for PCB 52 (in Fig. SM4), but the influence of this parameter is much lower for PCB 138 and 153 (Fig. SM5 and Fig. 2 respectively). Similar findings are reported in a mass balance of the Eastern Mediterranean by Mandalakis et al. (2005), where the main depletion pathway of PCBs from atmosphere was OH^\cdot reaction for PCBs with up to 6 chlorines, whereas for higher chlorinated PCBs the main depletion pathway was deposition from atmosphere; our model output is in fact sensitive to aerosol deposition for both PCBs 138 and 153 ($S > 0.1$ in Fig. 2 and Fig. SM5). OH^\cdot reaction is less important in our study because we consider a smaller area where advection is more efficient.

Results from the model experiments for the climate change scenarios show that PCB concentrations in the environment change by up to 58% in the A1B scenario in response to changes in environmental conditions. However, fugacities are expected to increase by a larger factor of 1.2–3.3 in air, water and sediment under the A1B climate scenario. This is driven primarily by lower fugacity capacities of the bulk air, water and soil compartment under higher temperatures in the A1B scenario. Although our study was focused on the abiotic environment, we note that lower fugacity capacities of air, water and soil could have implications for the partitioning of pollutants into homeothermic organisms. Assuming that lipid levels remain constant for homeotherms, their fugacity capacity would not change in a warming environment. Thus, chemicals that have an enhanced tendency to escape from warmer air, water and sediment compartments under a climate change scenario would achieve higher equilibrium concentrations in the bodies of homeotherms.

Our model experiments for the A1B climate change scenario identified background concentration, temperature, sea currents and POC as the climate and environmental parameters affecting the distribution and fugacity of PCBs in the study area, whereas precipitation, wind speeds and effect of temperature on local primary emissions were less influential in changing modeled fugacities in the future climate scenario (Fig. 3, Figs. SM6 and SM7). These results are consistent with the sensitivity analyses. Background inflow concentration (BC) is the most important single factor in determining the increase in $F(f)_{A1B}$, and this is consistent with a previous modeling study conducted at the global scale (Lamon et al., 2009).

We stress that this work is not a comprehensive assessment of possible interactions between climate change and POPs. We considered only a subset of environmental variables that may be affected by climate forcing, and have not so far explicitly considered the watershed in our assessment. However, the model results presented here provide some initial estimates of the possible effects of climate change on the fate and transport of PCBs in the Adriatic Sea. Our model assessment forecasts that under the influence of a climate change scenario pollutants with properties similar to PCBs will have increased mobility, and that the most influential parameter in determining this behavior is increasing temperature. The overall residence time tends to increase under the assumed A1B climate change scenario for highly chlorinated PCBs congeners, whereas it tends to decrease for the lighter PCB 52. This reflects the higher mobility expected for light PCBs congeners under the A1B climate scenario. Our results demonstrate that future exposure to legacy chemicals in the Adriatic Sea region will depend foremost on the temporal trend of primary and secondary emissions in Europe and globally.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2012.02.010](https://doi.org/10.1016/j.chemosphere.2012.02.010).

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