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INFLUENCE OF CLIMATE CHANGE ON THE ENVIRONMENTAL BEHAVIOUR AND DISTRIBUTION OF PERSISTENT ORGANIC POLLUTANTS (POPs)

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Summary

The climate temporal reconstruction shows how the Earth's climate is in continuous change. Evidence of climate change has been observed at both the global and regional scales. Since climate change is a global problem, the UNFCCC (United Nations Framework Convention on Climate Change) (1994) and the Kyoto Protocol (1997) were signed with the aim at collecting and exchanging information on greenhouse gases, to launch national and international strategies in order to limit the emissions.

Like climate change, also the environmental contamination caused by Persistent Organic Pollutants (POPs) is a global concerning issue. POPs are in fact defined in the UNECE (United Nations Economic Commission for Europe) Convention on Long-Range Transboundary Air Pollution (CLRTAP) (by the UNECE, 1979), and in the UNEP Stockholm Convention (2001), where the concept of long range transport is also introduced and strongly related to persistency.

This Ph.D. thesis aims at investigating which effects climate change would exert on the environmental distribution of POPs, priority pollutants which behavior is affected by climate variables.

In the theoretical section the concepts about climate change and POPs are introduced, and also the methods which will be used in the applicative part are described. In the second theoretical part a review on the consequences of climate change on POPs behavior and on POPs-related monitoring, modeling and regulation issues, is presented.

In the application section, multimedia fate and transport models are applied in order to develop the considerations made previously through the development of two case studies. The first model exercise aims at understanding which factors are more effective in determining POPs environmental behavior under a climate change scenario through the application of a global fate and transport model (BETR Global) to two climate scenarios, a present climate scenario and the A2 climate change scenario, a reference climate change scenario defined by the Intergovernmental Panel on Climate Change (IPCC). The second case study consists on the creation of a level III fugacity model for the Adriatic Sea, and is evaluated and then is parameterized following the A1B climate change scenario as it is defined by the IPCC in order to investigate which is the effect of climate change on POPs environmental distribution and concentration.

Sommario

Ricostruzioni temporali dell'andamento climatico dimostrano come esso sia in continuo cambiamento. Sono numerose le osservazioni sperimentali a scala regionale e globale a favore della teoria del cambiamento climatico, che ha portato alla stipula a livello sovranazionale del protocollo di Kyoto (1997) e dell'UNFCCC (United Nations Framework Convention on Climate Change) (1994), convenzioni che mirano a raccogliere e scambiare dati ed informazioni sui gas serra, e a lanciare strategie nazionali ed internazionali finalizzate a diminuire l'emissione di tali gas.

Anche i microinquinanti organici (POP, Persistent Organic Pollutants) costituiscono una questione di interesse sovranazionale; compaiono infatti le definizioni di POP e di inquinamento atmosferico di lungo raggio (LRT) nella convenzione CLRTAP (Convention on Long-Range Transboundary Air Pollution) (UNECE, 1979). Anche la Convenzione di Stoccolma stabilita dall'UNEP (2001) introduce il concetto di LRT e lo correla a quello di persistenza.

Questa tesi di dottorato ha l'obiettivo di studiare in quale modo il cambiamento climatico possa influenzare il comportamento ambientale dei POP, sostanze prioritarie il cui comportamento ambientale dipende anche dalle variabili climatiche.

Nella sezione teorica della tesi saranno introdotte le tematiche di cambiamento climatico, POP e la metodologia che sarà poi sviluppata nella sezione applicativa seguente, e sarà presentata anche una analisi delle conseguenze che il cambiamento climatico può avere sui vari aspetti connessi ai POP, in particolare sul monitoraggio, sulle attività modellistiche e sulle applicazioni legislative.

Nella seconda sezione saranno applicati modelli di fugacità per sviluppare le considerazioni di cui sopra attraverso due casi di studio. Il primo esercizio modellistico consiste nell'applicazione di un modello esistente a scala globale adattato a due scenari climatici, di cui uno presente a rappresentare lo stato attuale, ed uno scenario di cambiamento climatico A2 come definito dal Pannello Intergovernativo sul cambiamento climatico (IPCC). Il secondo consiste nella costruzione di un modello di fugacità di III livello a scala regionale i cui risultati sono confrontati con valori provenienti da osservazioni sperimentali, e poi è parametrizzato in modo da rappresentare lo senario A1B come definito dall'IPCC in modo da valutare quali fattori influenzino significativamente la distribuzione ambientale dei composti organici considerati.

List of contributions

PUBLISHED PAPERS

L. Lamon, H. von Waldow, M. MacLeod, M. Scheringer, A. Marcomini, K. Hungerbühler, Modeling the global levels and distribution of polychlorinated biphenyls in air under a climate change scenario. Environmental Science & Technology Aug 2009, vol. 43, pp. 5818-5824.

L. Lamon, M. Dalla Valle, A. Critto, A. Marcomini, Introducing an integrated climate change perspective in POPs modelling, monitoring and regulation. Environmental Pollution, July 2009, vol. 157, pp. 1971-1980.

PAPERS IN PREPARATION

L. Lamon, MacLeod M., A. Marcomini, K. Hungerbuehler. Climate change influence on POPs environmental distribution: A regional-scale case study. The Adriatic Sea project.

EXTENDED ABSTRACTS

Lamon L., von Waldow H., MacLeod M., Scheringer M., Marcomini A., Hungerbühler K.,, 2009, Modeling the effects of a climate change scenario on organic pollutants atmospheric distribution. A global case study. Dioxin 2009, Beijing.

Lamon L., von Waldow H., MacLeod M., Scheringer M., Marcomini A., Hungerbühler K., 2008, Assessing the effect of climate change on the global distribution of PCBs, Short paper, Dioxin 2008, Birmingham.

ABSTRACTS

Lamon L., Dalla Valle M., Critto A., Marcomini A., Climate change implications on POPs monitoring, modelling and regulation, SETAC 2008, Warsaw.

PARTICIPATION TO EVENTS

10th-12th June 2009: participation to the CMCC annual meeting in Ugento, Lecce, Italy.

17th -22nd August 2008: attendance and poster presentation at the DIOXIN 2008: Looking to the future, developing the next generation. Birmingham.
25th -29th May 2008: attendance and poster presentation at the SETAC 2008, Warsaw.
25-27 November 2008: Attendance to the European Conference on ‘Global change and marine ecosystems’, organised by EUR-OCEANS. Rome, Italy.
3rd and 4th December 2007: Workshop CMCC “IL CMCC: ATTIVITÀ, RISULTATI, PROSPETTIVE”, University of Sassari, Italy.
19th May 2007: Participation to the 3rd workshop on climate change in the 21st century. Future prospects of the health of our planet and mankind. Venice S Elena.

CHAPTER 1: INTRODUCTION

1.1 Motivation and objectives

The complexity of climate change issues encouraged the establishment of an Intergovernmental Panel on Climate Change (IPCC) in 1988, supported by the World Meteorological Organization (WMO) and the United Nations Environment Program (UNEP) in order to provide the policymakers an objective source of information about the causes of climate change, its potential environmental and socio-economic consequences and the adaptation and mitigation options to respond to it. Other research centers started to put some efforts in understanding climate change impacts, for instance in Italy the Euro-Mediterranean Centre for Climate Change was funded with the aim to study climate impacts on the Mediterranean Sea and on its coastal areas.

Persistent Organic Pollutants (POPs) are also a problem of global concern, since they are persistent and undergo Long Range Transport (LRT). As international agreements were needed to implement a global action aimed at managing and reducing the release of POPs and to prevent the spreading of other similar compounds in the environment, the UNEP Stockholm convention was signed worldwide (2001).

POPs behavior is a complex phenomenon, driven by several space- and time-dependent factors, as the distribution and characteristics of emission sources, transport and deposition processes, and on physical-chemical properties of the substances. Since these factors are affected by climate change, UNEP emphasized the importance of addressing activities in environmental (especially atmospheric) modeling towards the focus on existing linkages between regional air quality and climate change, at both the regional and the global scales and to forecast the main influence of climate change on POPs behavior (UNEP, Report on the executive body on its twenty-fifth session held in Geneva from 10 to 13 December 2007).

Temperature plays an important role in affecting POPs mobility, but several other factors influence significantly POPs behavior and should therefore be taken into account. Some examples are given by wind and oceanic current patterns, precipitations distribution, land cover characteristics and so on.

The alteration of any of these factors will in turn influence the parameters controlling the environmental distribution and fate of POPs, such as reaction rate constants (i.e. partitioning and degradation rates), the release rates from secondary sources (e.g. contaminated soil), uptake rates, bioaccumulation dynamics.

To date, only few studies focus on the existing interactions between climate change and POPs behavior and distribution (Mckone et al., 1996; Eisenreich, 2005; Dalla Valle et al., 2007; Becker et al., 2008). Some information is available for specific case studies, in particular about the Arctic environment, undoubtedly the most vulnerable and affected area with respect both to POPs contamination and climatic changes (e.g. Macdonald et al., 2005).

However, still many uncertainties and challenges have to be addressed and there is still paucity of experimental data and scientific background information from which to evaluate the real significance of climate change influence on POPs behavior and fate.

Therefore, the main objective of this Ph.D. thesis is to investigate which is the effect of climate change on POPs environmental distribution. In particular, this thesis aims at:

1. identifying which is the existing knowledge in the field of multimedia modeling about climate change effects and implications on POPs behavior
2. analyzing a global scale case study on climate parameters on POPs environmental behavior and distribution using a global fate and transport model
3. considering the Adriatic sea as a regional scale project oriented to do another step into the analysis of climate change impacts on POPs behavior at the regional scale, and this is done through:
    a. identifying the available data in order to define a mass balance for the Adriatic sea

b. using the fugacity concept in order to study the POPs mass balance in the Adriatic sea
c. identifying which are the consequences of a climate change scenario on the distribution of POPs.

The structure of this Ph.D. thesis is presented in the next paragraph.

1.2 Thesis structure

The present thesis is made of different contributions consisting of the main findings of this Ph.D.

It consists of a theoretical part and of a methodological part, where the methods introduced in the first chapters are applied for different case studies.

The theoretical part is structured as follows:

CHAPTER 2 contains an introduction to all the topics which will be treated afterwards. This chapter will consider first the topic of climate change, second the POPs issues, and third an introduction to the method used through the whole thesis is introduced with a special emphasis on partition coefficients used in the multimedia models applied in the following chapters.

CHAPTER 3 consists in a review of the implications climate change would have on POPs behavior, and takes into account the different aspects and fields dealing with POPs, respectively monitoring modeling and regulation. The contents come from the first paper published during the Ph.D. (see Lamon et al., ‘Introducing an integrated climate change perspective in POPs modelling, monitoring and regulation’, reference given in *List of publications*, in the previous section).

The methodological part consists on the application of the methods introduced earlier in chapter 2, and it is organized in the two chapters, as it follows:

CHAPTER 4 consists on the global scale application and case study. It is focused on the identification of the climate parameters which are important in determining the PCBs atmospheric distribution. Two climate scenarios are defined, one representing the present climate and the other representing a future climate (A2 scenario as defined in the Special Report on Emission Scenarios, Nakicenovic et al. 2000). The two climate scenarios differ for four climate parameters (namely temperature, precipitation patterns, oceanic currents and wind fields in upper and lower air). As it will be shown in the chapter 4, temperature effect on partitioning and on primary emissions and the effect of wind speeds in PCBs transport are more influential than precipitation and oceanic currents in determining the PCBs distribution in the atmosphere.

CHAPTER 5 consists in the regional scale case study, and is focused on the use of the same method applied previously. In this case a first activity of available data collection was carried out, in order to build a level III fugacity model. Second, a level III fugacity model was built and was adapted to a climate change scenario. Also in this case concentration values calculated under a present climate scenario were compared to environmental concentrations obtained under a future scenario (A1B as described in the Special Report on Emission Scenarios -SRES, Nakicenovic et al., 2000). In this case the two climate scenarios differ on atmospheric temperature, oceanic temperature, wind patterns, oceanic currents and precipitation.

CHAPTER 6 summarizes all the results and the findings of the presented studies, and identifies possible future research activities inherent to the topics treated within the thesis.

1.3 The CMCC as a project

This Ph.D. thesis is funded by the Euro Mediterranean Centre for Climate Change (CMCC, www.cmcc.it), which is a scientific research structure aiming at enlarging the knowledge on the field of climate variability, its causes and its consequences, through the development of mathematical model simulations with global and regional modeling tools. Such simulations are used directly to study climate change impacts on the economy, on agriculture, on sea and earth ecosystems, on coastal zones and on human health. Several research centers spread in Italy are part of this consortium and are devoted to investigating the different aspects of climate change impacts.

This project was initially considered within the development of a climate change-driven Decision Support System (DSS), which takes into account the climate change impacts on the Northern Adriatic Sea. This DSS integrates the information derived by different model applications, like hydrodynamic impacts (e.g. storm surge, sea level rise, given by SHYFEM), biogeochemical models (i.e. the impacts of climate change on the biogeochemical cycles of nutrients), and multimedia fate models, in particular persistent organic pollutants (POPs) fate and transport fugacity models.

The goal of "Impacts on soil and coasts" Division is to study the impact of climate changes on ecosystems (of earth and sea) and on the coastal zones, as well as to study the hydrogeological risk related to meteorological events. Nonetheless, the division is aimed to understanding the impacts of climate changes on electrical power systems and to study effective control strategies, based on satellite/ICT technologies, for mitigating their effects.

The ISC division activities are structured as follows:

a. Working Group 1: "Comparative Risk Analysis, Integrated Evaluation and Decision Support Systems. Application for the mitigation of the impacts on coastal zones", has as main goal the development of a Decision Support System (DSS) that integrates all the model outputs developed by the Working Group 3.
b. Working Group 2: "Impacts on the Monitoring Activity of Territory and the Prevention of Hydrogeological Disasters", aims at studying and developing models, algorithms and software for the analysis of hydrogeological phenomena (floods and landslides) related to extreme meteorological events. Such phenomena are, generally, circumscribed (basin and/or slope scale), hence it is necessary to optimize numerical codes and to couple the meteorological model with models evaluating impact of such phenomena on the soil at high resolution.
c. Working Group 3: "Modeling Activity and Historical Data Analysis for the Upper Adriatic", has as main goal to supply tools to WG 1 to identify and to quantify the main risks and impacts which can hit coastal zones of such area. Obtained results and developed tools will make up the DSS applied to the case study of WG 1 in order to supply necessary tools for mitigation or adaptation.
d. Working Group 4: "Satellite data products, algorithms and models for management-control and planning of power systems and impacts studies". Working Group 4 will be involved in the reception and processing of satellite

data as well as in the development new algorithms devoted to support impact studies. In particular, the working group is involved in the assessment of the impact of the environmental and climatic variables on the electrical productivity levels of dispersed generators stemming, out from renewable sources, and on the real exploitation limits of electrical power lines.

Working Groups 1 and 3 will deal with the development of tools and methodologies for the analysis of regional risk, for the evaluation and the comparison of risks related to climatic changes in coastal zones at regional scale.

This thesis is focused on the section about POPs fate and transport affected by climate change, which is expected in the WP3 of the CMCC project. Data were provided by the CMCC for the climate scenarios applied in the case study in chapter 5.

PART 1: Theoretical part

CHAPTER 2 AN OVERVIEW

2.1 Climate change issues

The many research studies that have reconstructed past climate conditions of our planet demonstrate how climate has been continuously changing. However, never in the past changes have been as rapid as those which are being experienced in modern times, and there is now strong evidence that this is due to human influence (Solomon et al., 2007). Dated ice cores show that the atmospheric concentration of carbon dioxide (CO_2) had been fluctuating between 180 to 300 ppm over the last 650 000 years, but then a sharp increase from 280 ppm of the pre-industrial period to 379 ppm in 2005 has been observed. The annual growth rate over the last 10 years has been the highest ever observed since the beginning of continuous direct atmospheric measurements (Solomon et al., 2007). Greenhouse gases are thought to be responsible for the current and unequivocal warming trend: global average surface temperature increased from 1850-1899 to 2001-2005 by 0.76 °C ± 0.19 °C. The rate of warming averaged over the last 50 years (0.13 °C ± 0.03 °C per decade) is nearly twice that for the last 100 years (Solomon et al., 2007). Numerous long-term changes in climate have been observed at both the global and local scales; these include changes in surface temperatures and ice cover in the Arctic, widespread changes in precipitation amounts, ocean salinity, wind patterns and aspects of extreme weather including droughts, heavy precipitation, heat waves and intensity of tropical cyclones (Trenberth et al., 2007). Climate changes may influence also human health as the increase in temperature may lead to population thermal stress, and the predicted extreme events may cause famines (Confalonieri et al., 2007).

Climate change will have a wide range of consequences both on the natural environment and on human activities (Bloomfield et al., 2006, Macdonald et al., 2003, 2005; Willby et al., 2006; Zepp et al., 2003). Being climate change possibly the greatest challenge that humankind currently faces, most countries joined international agreements on future perspectives and policy, e.g. the Kyoto protocol (1997, http://unfccc.int/kyoto_protocol/items/2830.php), and the United Nations Framework Convention on Climate Change (UNFCCC, 1994, http://unfccc.int/2860.php).

2.1.1 Climate change scenarios considered in this thesis

In this thesis the A2 and the A1B scenarios were assumed as climate scenarios, and were compared with the present climate scenario (referred to as 20CE in the present work) that came from the same circulation models (i.e. the A2 and the 20CE climate scenarios both come from the output of the of the ECHAM5/MPI-OM model, and both the A1B and 20CE climate scenarios applied at the regional case study come from the SINTEX-G model, as it will be elucidated in the next chapters).

As it is explained in more detail in the SRES report (Nakicenovic et al., 2000), the A1 storyline and scenario family describes a future world of very rapid economic growth, global population that peaks in mid-century and declines thereafter, and the rapid introduction of new and more efficient technologies. Major underlying themes are convergence among regions, capacity building and increased cultural and social interactions, with a substantial reduction in regional differences in per capita income. The A1 scenario family develops into three groups that describe alternative directions of technological change in the energy system. The three A1 groups are distinguished by their technological emphasis: fossil-intensive (A1FI), non-fossil energy sources (A1T) or a balance across all sources (A1B) (where balance means that the society is not relying too heavily on one particular energy source, on the assumption that similar improvement rates apply to all energy supply and end use technologies).

On the other hand, the A2 storyline and scenario family describes a very heterogeneous world. The underlying theme is self reliance and preservation of local identities. Fertility patterns across regions converge very slowly, which results in continuously increasing population. Economic development is primarily regionally oriented and per capita economic growth and technological change more fragmented and slower than other storylines. Table 2.1 shows a summary of the temperature change and of the sea level rise forecasted by the different SRES (Solomon et al., 2007).

2.2 POPs: regulations and definitions

Persistent Organic Pollutants (POPs) are defined as chemicals which resist to the environmental chemical, physical and biological degradation, this is why they are defined persistent.

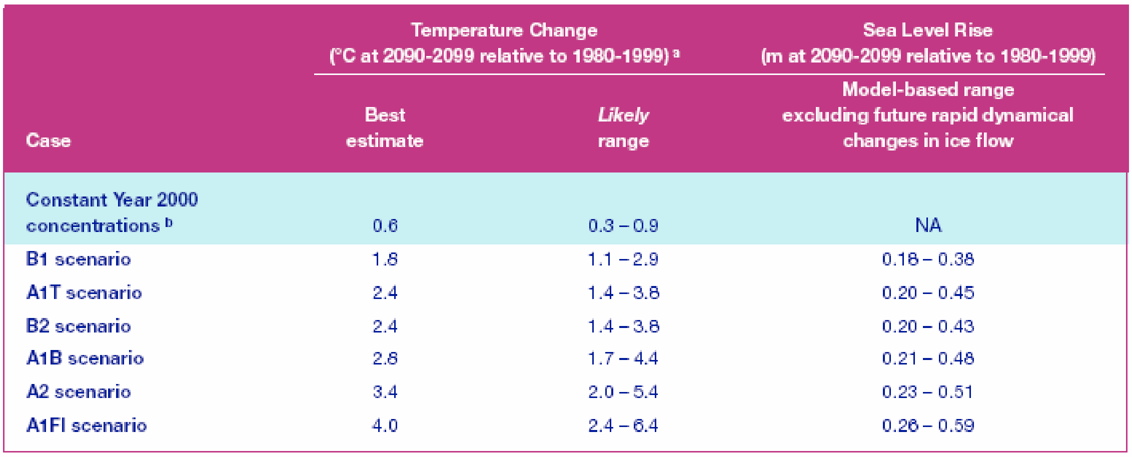
Because of their persistence, POPs have been detected in all the environmental compartments, even in areas remote from the occurring emissions, like open ocean and polar regions, where POPs have been never manufactured nor used (e.g. Wagrowski and Hites, 2000). Indeed, atmospheric transport has been suggested as the main route dispersing these semivolatile compounds thousands of km away from industrialized and densely populated areas (Halsall et al., 2001).

In general, they are characterized under the chemical point of view as highly lipophilic, have a low water solubility, and are substances with big molecular masses and low volatility. Due to their wide distribution, ability to bioaccumulate in the biotic tissues, and potential harmful effects such as immunotoxicity, neurotoxicity, developmental toxicity, carcinogenicity, mutagenicity, and endocrine disruption potentials, POPs have remained in the center of scientific attention for the last decades (WHO 2003).

In 1995 the United Nations Environmental Program (UNEP) defined and classified POPs with the aim at reducing or eliminating their producing and use.

Also the United Nations Economic Commission for Europe (UNECE) established with the Convention on Long Range Transport and Atmospheric Pollution (CLRTAP, entered into force in 1983 but signed in 1979) the stop to the production of substances (aldrin, chlordane, chlordecone, dieldrin, endrin, hexabromobiphenyl, mirex and toxaphene), and others have been highlighted in order to be eliminated in a second step (DDT, heptachlor, hexaclorobenzene, PCBs).

The CLRTAP together with the Stockholm Convention (2001) banned the production of persistent pollutants listed in table 2.2, recognized as ‘the dirty dozen’.



	Temperature Change (°C at 2090-2099 relative to 1980-1999) [a]		Sea Level Rise (m at 2090-2099 relative to 1980-1999)
Case	Best estimate	*Likely* range	Model-based range excluding future rapid dynamical changes in ice flow
Constant Year 2000 concentrations [b]	0.6	0.3 – 0.9	NA
B1 scenario	1.8	1.1 – 2.9	0.18 – 0.38
A1T scenario	2.4	1.4 – 3.8	0.20 – 0.45
B2 scenario	2.4	1.4 – 3.8	0.20 – 0.43
A1B scenario	2.8	1.7 – 4.4	0.21 – 0.48
A2 scenario	3.4	2.0 – 5.4	0.23 – 0.51
A1FI scenario	4.0	2.4 – 6.4	0.26 – 0.59

Table 2.1 Projected global average surface warming and sea level rise at the end of the 21st century in each climate change scenario. [a] These estimates are assessed from a hierarchy of models that encompass a simple climate model, several Earth Models of Intermediate Complexity (EMICs), and a large number of Atmosphere-Ocean Global Circulation Models (AOGCMs). [b] Year 2000 constant composition is derived from AOGCMs only. (From Solomon et al., 2007, Technical Summary).

Afterwards the Aarhus Protol entered into force in 2003, and expressed a new objective focused on POPs biomagnification along the trophic chain. It considers the dirty dozen plus polycyclic aromatic hydrocarbons (PAHs) (Scheringer, 2009) and other chemicals recognized this year also by the Stockholm Convention.

An amendment to the Stockholm Convention was published in May 2009 (UNEP, 2009) where new POPs are ratified. These new POPs are α- and β-hexachlorocyclohexane, chlordecone, hexabromobiphenil, hexa- and hepta-chlorobiphenyl ether, lindane, pentachlorobenzene, perfluorooctane sulfonic acid and its salts, and perfluorooctane sulfonyl fluoride and tetrabromodiphenyl ether and pentabromodiphenyl ether. According to the Convention (UNEP, 2004) these chemicals were chosen depending on their risk profile and risk management.

The Stockholm Convention was envisioned by the international community to be a dynamic treaty, this is why it provides a rigorous scientific process through which new chemicals with POPs characteristics can be added to the treaty. Several additional POP candidates await international attention. They are reviewed initially by the POP Review

Committee (POPRC), and the Conference of Parties (COP) will finally address other dangerous chemicals.

Furthermore, currently, approximately 80,000 chemicals (although the exact figure is unknown) are produced, marketed, used, and disposed of worldwide. Each year, hundreds of new chemicals are added to this ever-growing list. So far, very little is known about toxicity of these chemicals. For regulating all these unknown chemicals and their production and use in Europe, the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), was established (Regulation EC N. 1907/2006 of the European Parliament and of the Council).

Table 2.3 summarizes the screening criteria to be considered to classify new POPs as it is given in the Stockholm Convention.

Table 2.2. List of the 12 chemicals reported under the Stockholm convention for elimination or restriction.

Chemical	Description	Stockholm convention action
Aldrin ($C_{12}H_8Cl_6$)	It is used as an insecticide and as an ectoparaciticide. Aldrin was first prepared in the late 1940s and is manufactured by the reaction of hexachlorocyclopentadiene with bicycloheptadiene (both derived from hydrocarbons obtained from petroleum).	Elimination
Chlordane ($C_{10}H_6Cl_8$)	It is formed by hesachlorocyclopentadiene. It Being hydrophobic, chlordane adheres to soil particles and enters groundwater only slowly owing to its low solubility. It was used as a pesticide.	Elimination
Dieldrin ($C_{12}H_8Cl_{6O}$)	Dieldrin is closely related to its metabolic precursor aldrin and much of the toxicological information on aldrin is referable to dieldrin. It is used in agriculture.	Elimination
Endrin ($C_{12}H_8Cl_{6O}$)	Endrin is produced via a multistep route from hexachlorocyclopentadiene. It is a stereoisomer of dieldrin. It was used as a spray to control pests in agriculture.	Elimination
Heptachlor ($C_{10}H_5Cl_7$)	It is roduced by reaction of hexachlorocyclopentadiene and cyclopentadiene. It is more active than chlordane as an insecticide.	Elimination
Hexachlorobenzene (C_6Cl_6)	It is formed by reaction of benzene and Cl2 or by hexachlorocyclohexane and sulfurylchloride. It is a fungicide. It is toxic to aquatic organisms and carcinogenic to humans.	Elimination with some exceptions.
Mirex ($C_{10}Cl_{12}$)	Mirex was produced by the dimerization of hexachlorocyclopentadiene in the presence of aluminium chloride. Its oxidation produces chlordecone, another insecticide which is also banned.	Elimination
Toxaphene ($C_{10}H_{11}Cl_5$ to $C_{10}H_6Cl_{12}$)	It is a mixture of approximately 200 organic compounds. It was used as an insecticide and is considered carcinogenic.	Elimination
Polychlorinated PCBs ($C_{12}H_{10-x}Cl_x$, where x = 1-10)	PCBs were used as coolants and insulating fluids (dielectric fluids) for transformers and capacitors,as plasticizers in paints and cements, stabilizing additives in flexible PVC coatings of electrical wiring and electronic components, as pesticide extenders, as reactive flame retardants, as lubricating oils, as hydraulic fluids, etc. hey were produced as mixtures of isomers at different degree of chlorination. Some congeners are carcinogenic	Prevention for unwanted emissions; elimination of production.
DDT ($C_{14}H_9Cl_5$)	It is a poison against arthopods, and was widely used in agriculture as an insecticide and against malaria.	Restriction
Polychlorinated dibenzo-p-dioxins ($C_{12}H_{8-x}O_2Cl_x$, with x=1-8)	Members of the PCDD family have been shown to bioaccumulate in humans and wildlife due to their lipophilic properties, and are known teratogens, mutagens, and suspected human carcinogens. Dioxins occur as by-products in the manufacture of organochlorides, in the incineration of chlorine-containing substances such as PVC (polyvinyl chloride), in the bleaching of paper, and from natural sources such as volcanoes and forest fires.	Prevention for unwanted emissions
Polychlorinated dibenzo-p-dibenzofurans ($C_{12}H_{8-x}OCl_x$ (with x=1-8)	PCDFs can be formed by pyrolysis or incineration at temperatures below 1200 °C of chlorine containing products, such as PVC, PCBs, and other organochlorides, or of non-chlorine containing products in the presence of chlorine donors. They can occur with PCDD.	Prevention for unwanted emissions

Table 2.3. screening creteria presented in the Stockholm Convention, annex D for he evaluation of potential POPs. Once the screening criteia are met, also a risk profile must be drawn for the chemical under analysis (UNEP, 2001).

Information requirements and screening creteria	***Chemical Identity*** (i) Names, including trade name or names, commercial name or names and synonyms, Chemical Abstracts Service (CAS) Registry number, International Union of Pure and Applied Chemistry (IUPAC) name; and (ii) Structure, including specification of isomers, where applicable, and the structure of the chemical class;
	Persistence (i) Evidence that the half-life of the chemical in water is greater than two months, or that its half-life in soil is greater than six months, or that its half-life in sediment is greater than six months; or (ii) Evidence that the chemical is otherwise sufficiently persistent to justify its consideration within the scope of this Convention;
	Bioaccumulation (i) Evidence that the bio-concentration factor or bio-accumulation factor in aquatic species for the chemical is greater than 5,000 or, in the absence of such data, that the log Kow is greater than 5; (ii) Evidence that a chemical presents other reasons for concern, such as high bioaccumulation in other species, high toxicity or ecotoxicity; or (iii) Monitoring data in biota indicating that the bio-accumulation potential of the chemical is sufficient to justify its consideration within the scope of this Convention;
	Potential for Long Range Transport (i) Measured levels of the chemical in locations distant from the sources of its release that are of potential concern; (ii) Monitoring data showing that long-range environmental transport of the chemical, with the potential for transfer to a receiving environment, may have occurred via air, water or migratory species; or (iii) Environmental fate properties and/or model results that demonstrate that the chemical has a potential for long-range environmental transport through air, water or migratory species, with the potential for transfer to a receiving environment in locations distant from the sources of its release. For a chemical that migrates significantly through the air, its half-life in air should be greater than two days; and
	Adverse effect (i) Evidence of adverse effects to human health or to the environment that justifies consideration of the chemical within the scope of this Convention; or (ii) Toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.

2.2.1 POPs in the environment

POPs are emitted either in the atmosphere or in water. The main source for open oceans is the *atmosphere*, whereas relevant sources for seas of minor surface are both air and rivers discharges. Atmospheric emissions and LRAT allow the distribution of POPs widely through the global environment, hence atmospheric POPs deposition may be the process by which they impact water and air qualities also in remote areas. In the atmosphere POPs partition between the aerosol and the gas phases, and are removed by degradation, dry and wet deposition and diffusive gas exchange between the atmosphere and the surfaces.

In the *water column* POPs may be found as dissolved, sorbed to colloids or to suspended particles. Their distribution in the environment is also affected by advection of atmospheric and water masses. The oceans can act as a source to atmosphere when POPs partition from the surface mixed layer, or as a sink when atmospheric deposition and partitioning occur (Wania and Daly 2002).

Soil plays also a crucial role in POPs cycling. It has in fact a high POPs-storing capacity, defined as a ‘reservoir capacity’, which is dependent on the organic carbon content in soils and on the long half life of POPs in soils (Mackay, 2001). Sometimes soils can act also as a source of POPs to the atmosphere, for instance soil can hence act as a deposition sink for POPs, as a source to the atmosphere, or as a storage compartment (Bidleman and Leone, 2004). The balance between these different processes is complex, and depends among other, on the compound properties and on the soil characteristics (Dalla Valle et al., 2005).

Considering their persistence, POPs can hence dynamically migrate from surfaces to air repeatedly. They may repeatedly recycle or ‘hop’ between environmental surfaces and the atmosphere, and reach areas remote from the emission region. The process of global fractionation and grass hopping driven by atmospheric transport have been studied e.g. by Gouin et al. (2004) and by Meyer et al. (2002). The global fractionation process implies a migration of selected congeners to colder areas becoming fractionated on latitudinal or altitudinal gradients. This phenomenon is explained by the fact that highly volatile chemicals tend to migrate to higher latitudes, where they ‘condense’ or deposit because of the colder temperature, whereas less volatile ones stay at the latitude where they are emitted (Scheringer et al., 2004).

The ‘grass hopping’ process consists instead on the way chemicals reach higher latitudes or altitudes. When a chemical is emitted to air, it may undergo different volatilization cycles (Gouin et al., 2004), or no volatilization may occur. These aspects are then related to the persistence of the chemical in the area closed to the emissions (Gouin et al., 2004; Lohmann et al., 2007) and hence to its exposure as an absolute concentration and as duration in time.

Sediments may also act as a sink for POPs depositing from the water column. Burial also occurs in sediments as a removal process. Sediments may also act as sources of POPs to the water column through molecular diffusion and mainly through sediment resuspension. The influence of the sediments is noted on a major degree in coastal regions, where the dynamics of contaminants are affected by the differential characteristics of coasts respect to the open sea, i.e. enhanced stratification due to freshwater input from rivers, influence of tides, greater human influence, enhanced interaction between the surface layer and the sea floor.

2.3 Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a class of organic compounds, in particular they are part of the dirty dozen POPs. Chemically, they have 1 to 10 chlorine atoms attached to a biphenyl, which is a molecule composed by two benzene rings. Each chlorine occupies a position as it is shown in figure 2.1. A PCB congener is a single, unique molecule, whilst a homologue is a category of PCBs, indicating all the PCBs with the same number of chlorine atoms. In theory 209 congeners are possible, but only about 130 of these have been identified in commercial products (WHO 2003). Table 2.4 shows the homologues and the related numbers of PCB congeners in each class.

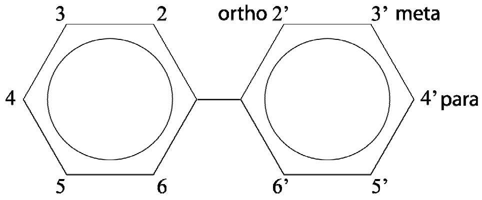


Figure 2.1. Biphenyl where chlorine atoms react to form PCBs mixtures.

Their density ranges from 1.182 to 1.566 kg/L. They have in general low water solubility, but they are soluble in organic solvents. Aqueous solubility was determined for 26 different congeners, and ranges from $1.08 \cdot 10^{-5}$ to $9.69 \cdot 10^{-10}$ mol/L and generally decreases with relative molecular mass (WHO 2003). They have a low electric conductivity, a very high thermal conductivity and a very high thermal and chemical resistance, i.e. they are very stable.

In general, PCBs melting point and lipophilicity increase with increasing degree of chlorination; vapor pressure and water solubility instead decrease.

PCBs have been identified in almost every environmental compartment or matrix. When compared to other chemicals, PCBs have very high K_{OW} values: log K_{OW} are in the range from 4.5 for monochlorobiphenyls to >8 for higher chlorinated PCBs.

Consequently, PCBs tend to adsorb to non-polar surfaces and accumulate in lipophilic matrices along the aquatic and terrestrial food-chain.

Table 2.4. Here PCB Homologs are listed, and the number of PCBs congeners per each homolog is indicated.

Homolog	*Cl Substituents*	*PCB Congeners*
Monochlorobiphenyl	1	3
Dichlorobiphenyl	2	12
Trichlorobiphenyl	3	24
Tetrachlorobiphenyl	4	42
Pentachlorobiphenyl	5	46
Hexachlorobiphenyl	6	42
Heptachlorobiphenyl	7	24
Octachlorobiphenyl	8	12
Nonachlorobiphenyl	9	3
Decachlorobiphenyl	10	1

2.3.1 Manufacture and use of PCBs

PCBs are among the POPs that have been of most interest and concern (Macdonald et al., 2003). They belong to a broad family of man-made organic chemicals known as chlorinated hydrocarbons. PCBs were manufactured from 1929 until their manufacture was banned in 1979. They have a range of toxicity and vary in consistency from thin, light-colored liquids to yellow or black waxy solids. Due to their non-flammability, chemical stability, high boiling point, and electrical insulating properties, PCBs were used in hundreds of industrial and commercial applications including electrical, heat transfer; as plasticizers in paints, plastics, and rubber products; in pigments, dyes, and carbonless copy paper; and many other industrial applications. A summary of the applications of PCBs is presented in Table 2.5.

Table 2.5. Uses of PCBs.

Uses		Examples of products, and the places they are used
Insulating oil	*For transformers*	Transformers for buildings, hospitals, railroad vehicles, vessels, etc.
	For capacitors	Capacitor for fluorescent lights and mercury lamps. Household electrical appliances, such as air-conditioners, washing machines, monochrome television sets, and microwave ovens.
		Fixed paper capacitors for motors, capacitors for direct currents, capacitors for accumulation of electricity .
Heat medium (heating and cooling)		Heating and cooling agent in various chemical, food, synthetic resin industry. Preheating agent of the fuel oil of vessels, central heating systems, and panel heaters.
Lubricating oil		Lubricating oil for high temperature, fluid for oil-hydraulic circuits, vacuum pump oil, etc.
Plasticizer	*For insulation*	Covering and insulating tape of an electric wire.
	For resistances to flame	Mixed to polyester resin, polyethylene resin, rubber, etc.
	Others	Mixed to adhesives, varnish, wax, and asphalt.
Dot impact printer		Non carbonic papers (solvents), electronic type copying papers
Paints and printer inks		Paints for fire-resistance, corrosion-resistance, chemical-resistance, and waterproof. Printer inks.
Others		Coating of papers, sealants of cars, coloring of china glassware, color television parts, the effect extension agents of agricultural chemicals, oil additive agents.

The production of PCBs involves the electrophilic chlorination[1] of biphenyl with chlorine gas, in the presence of a catalyst; hence they were manufactured as a mixture of various PCB congeners, through progressive chlorination of biphenyl in order to reach a certain percentage of chlorine by weight. Commercial mixtures with higher percentages of chlorine contained higher proportions of the more heavily chlorinated congeners, but all congeners could be expected to be present at some level in all mixtures. While PCBs were manufactured and sold under many names, the most common was the Aroclor series. For information on the percent weight of PCB congeners present in some common Aroclors. *Aroclor* is a PCB mixture produced from approximately 1930 to 1979. It is one of the most commonly known trade names for PCB mixtures. There are many types of Aroclors and each has a distinguishing suffix number that indicates the degree of chlorination. The numbering standard for the different Aroclors is made of four digits: the first two refer to the number of carbon atoms in the phenyl rings (for PCBs this is 12), the second two numbers indicate the percentage of chlorine by mass in the mixture (for example, the name Aroclor 1254 means that the mixture contains approximately 54% chlorine by weight).

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[1] electrophilic aromatic halogenation is a type of electrophilic aromatic substitution. This organic reaction is typical of aromatic compounds and a very useful method for adding substituents to an aromatic system. It acts in presence of a catalyst (e.g. a Lewis acid is needed for benzene derivatives).

2.3.2 PCB Congeners analyzed in this thesis

The PCB congeners without chlorine atoms at the ortho positions (see figure 2.1) can assume a coplanar conformation. The congeners 3,4,4’,5-, 3,3’,4,4’-, 3,3’,4,4’,5- and 3,3’,4,4’,5,5’-PCB (non-ortho PCB congeners, respectively PCBs 81, 77, 126, and 169), which are also substituted in both *para* and at least two *meta* positions, and a maximum of an *ortho* position, are in their coplanar conformation approximate stereoisomers of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the most toxic dioxin congener (WHO 2003). These congeners exhibit similar biological effects to those caused by dioxins, and they are also referred to as dioxin-like. These chemicals are usually considered together with dioxins in reports assessing organic chemicals toxicities.

On the other hand, non-dioxin-like PCB congeners are poorly characterized from a toxicological point of view. The available toxicological information suggests that typical effects of PCB exposure, including the critical effects of carcinogenicity, immunotoxicity and neurobehavioural alterations, are caused by all PCB congener classes (i.e. by both the dioxin-like and the non-dioxin-like congeners). However, underlying mechanisms involved are probably different.

Notwithstanding the fact that dioxin like PCBs are more studied under the toxicological point of view, environmental measurements are broadly available for other congeners, like the PCB 28, 52, 138 and 153. In fact these are the priority congeners which are monitored by the International Council for the Exploration of the Sea (ICES, 2007), which does not take into account the dioxin like PCBs, but considers the list of PCBs listed by the WHO as analytically simple POP (WHO, 2007). Evidence for this different analytical rendering is also discussed in Duinker et al. (1988). This is the reason why more data were available on these congeners, which are non dioxin like PCBs. In detail, PCB 28 and 153 will be considered in chapter 4, and PCB 52, 138 and 153 in chapter 5. This ensemble of PCBs was chosen in order to consider a degree of chlorination as broad as available data permitted.

2.4 POPs and climate variability

As the environmental behaviour of POPs depends on the complex interaction of many factors, any significant environmental alteration is likely to affect their distribution and fate. Temperature plays an important role in affecting POPs mobility but also several other parameters are key factors in influencing POPs behaviour and should therefore be taken into account. Some examples are given by wind and oceanic current patterns, precipitations distribution, land cover characteristics and so on. The alteration of any of these factors will in turn influence the parameters controlling the environmental distribution and fate of POPs, such as reaction rate constants (i.e. partitioning and degradation rates), the release rates from secondary sources (e.g. contaminated soil), uptake rates, bioaccumulation dynamics.

These aspects will be treated in more detail in Chapter 3.

2.5 Methods developed within this thesis

In order to study mathematically the environment, it is necessary to consider it consists of a number of connected phases or compartments. Examples are the atmosphere, terrestrial soil, a lake, the bottom sediment under the lake, suspended sediment in the lake, and biota in soil or water. The phase may be continuous (e.g., water) or consist of a number of particles that are not in contact, but all of which reside in one phase (e.g., atmospheric particles –aerosols-, or biota in water).

Some compartments are in contact, thus a chemical may migrate between them (e.g., air and water, as it was considered in paragraph 2.2.1), while others are not in contact, thus direct transfer is impossible (e.g., air and bottom sediment). Some phases are accessible in a short time to migrating chemicals (e.g., surface waters), but others are only accessible slowly (e.g., deep lake or ocean waters), or effectively not at all (e.g., deep soil or rock).

Some confusion is possible when expressing concentrations for mixed phases such as water containing suspended particulate matter (SPM). An analysis may give a total or bulk concentration, or alternatively, the water may be filtered to give the concentration or amount of chemical that is dissolved in water or absorbed into the particles. Concentrations in soils, sediments, and biota can be expressed on a dry or wet weight basis. Occasionally, concentrations in biota are expressed on a lipid or fat content basis.

Once the volume of each compartment has been determined, equations describing the processes by which a mass of chemical enters and leaves each compartment may be applied, defining the mass balance, following the Lavoisier’s law of conservation of mass.

2.5.1 Eulerian and Lagrangian coordinates

Chemicals' environmental behavior may be deduced from a Lagrangian (moving parcel) or Eulerian (box) model or using a flow equilibrium approach.

Box or Eulerian models consist in considering the environment as divided or segmented into a number of volumes or boxes, which are fixed in space and are usually treated as being well-mixed in chemical composition. This has the advantage that only one concentration need be defined per box.

The Lagrangian approach is also widely used in atmospheric and river modeling, and consists in defining a parcel of air or water and follow it, and the chemical in it, in time as the parcel moves from place to place.

There are also situations where there is marked heterogeneity in concentration, and it is preferable to set up diffusion/advection/reaction differential equations and solve them either numerically or analytically. This may be done when describing chemical migration in sediments and soils, or when analyzing atmospheric dispersion, or aquatic and oceanic systems (Mackay 2001).

In principle, all approaches should give comparable results.

2.5.2 The chemical potential

The whole energy content of a molecule (associated with the bonds of the molecule, with the bonds vibration, flexations and rotations, interactions of the molecule with the surroundings) is the internal energy and is dependent on the temperature, pressure, and chemical composition of the system. When talking about the "energy content" of a given substance, people are usually not concerned with the energy status of a single molecule, but rather with an average energy status of the entire population of one type of organic molecule in the system. To describe the average "energy status" of a compound *i* mixed in a milieu of substances, Josiah Willard Gibbs introduced in 1873 an entity referred to as *total free energy* (or Gibbs free energy), *G*, of this system, which could be expressed as the sum of the contributions from all of the different components present, as shown in equation 2.1:

$$G(T, p, n_1, \ldots n_i, \ldots n_n) = \Sigma \sum_{i=1}^{N} n_i \cdot \mu_i \qquad (2.1)$$

Where n_i is the amount of compound i (mol) in the system containing N compounds, and the entity μ_i is referred to as the chemical potential of the compound i and is defined by the following expression (2.2):

$$\mu_i(J \cdot mol^{-1}) \equiv \left[\frac{\partial G(J)}{\partial n_i(mol)} \right]_{T,p,n \neq ni} \tag{2.2}$$

μ_i expresses the free energy added to the system at constant T, p and composition with each added increment of compound i.

When adding an incremental number of molecules of i, some free energy is introduced in the form of internal energies of substance i as well as by the interaction of i with other molecules in the system. As more chemical is added, the composition of the mixture changes and, consequently, μ_i changes as a function of the amount of i (mol).

Finally, Gibbs recognized in 1876 that the *chemical potential* could be used to assess the tendency of the component i to be transferred from one system to another or to be transformed within a system. This is analogous to the use of *hydrostatic head potential* for identifying the direction of flow between water reservoirs[2] (Schwarzenbach et al., 2003).

2.5.3 The fugacity concept

The conventional approach in environmental modeling is to use concentrations and a variety of rate constants. Another approach, that is ultimately algebraically identical, is to use fugacity as a surrogate for concentration. The models presented in this thesis are based on the fugacity concept, which is reviewed briefly here. The interested reader is referred to the text by Mackay (2001) for a complete description of the approach. *Fugacity* was first introduced by G.N. Lewis (1901) as an equilibrium criterion that was a convenient surrogate of chemical potential. Fugacity comes from the verb *fugere,* which describes an escaping tendency. It is essentially a partial pressure (measured in Pa) and is assumed to be proportional to concentration (and logarithmically related to the chemical potential).

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[2] Equilibrium (no net flow in either direction) is reached, when the hydrostatic head potentials of the two reservoirs are equal. Similarly, chemical equilibrium is characterized by equal chemical potentials for each of the constituents. As with hydrostatic head potential, chemical potential is an intensive entity, meaning it is independent of the size of the system (in contrast to the total free energy G, which is an extensive function).

If a given number of moles (n_i) of a pure gaseous compound are confined to a volume V, at a temperature T, the molecules will exert a given pressure p_i on the walls of the box as they press upon it seeking to pass. For an ideal gas the pressure is proportional to the amount n_i. At constant T, a change in the chemical potential of the compound may be caused by a change in pressure p_i (2.3):

$$(d\mu_i)_T = \frac{V}{n_{ig}} \cdot dp_i \qquad (2.3)$$

and substituting V/n_i with RT/p_i, the following would be defied (2.4)

$$(d\mu_i)_T = \frac{RT}{p_i} \cdot dp_i \,. \qquad (2.4)$$

In order to gain a measure of μ_i it is necessary to define a standard value for the chemical potential μ_{ig}^0 by defining a standard $p_i = p_i^0$ (1 bar) and a n_i^0 (2.5, 2.6):

$$\int_{\mu^0{}_{ig}}^{\mu_{ig}} (d\mu_{ig})_T = RT \int_{p_i^0}^{p_i} \frac{1}{p_i} dp_i \text{ , yielding at } \mu_{ig} = \mu_{ig}^0 RT \cdot \ln(p_i - p_i^0) \qquad (2.5,\ 2.6).$$

This happens with ideal gases.

With real gases though the intermolecular forces between particles may not be neglected, and they influence the partial pressure of the chemical, but not its quantity n_i (mol). This real pressure is called fugacity.

In contrast with the ideal gas partial pressure, the fugacity is not only a function of the amount of substance and temperature, but also of the composition of the gaseous system and of the total pressure. It is anyway closely related to the partial pressure of the compound. Assuming θ_{ig} as a fugacity coefficient accounting for a non ideal gas (2.7),

$$f_{ig} = \theta_{ig} \cdot p_i \,. \qquad (2.7)$$

Since under typical environmental conditions gas densities are very low, conventionally it can be set θ_{ig}=1 bar, i.e. any compound will exhibit ideal behavior. Hence if in a mixture of gaseous compounds the partial pressure p_i is defined as $p_i = x_{ig}p$ and $x_{ig} = \frac{n_{ig}}{\sum_j n_{jg}}$ is the mole fraction of i, and $\sum_j n_{jg}$ is the total number of moles present in the gas, and p is the total pressure, equation 2.8 would be obtained:

$$f_{ig} = \theta_{ig} x_{ig} p \cong p_i \qquad (2.8).$$

Fugacity, meaning escaping tendency, has hence dimension of pressure. For a given amount of chemical in a two-phase system equilibrium is reached when fugacities of the compounds are equal t one other in both phases. Hence, fugacity is an equilibrium criterion, as the chemical potential, and it is directly proportional to concentration by a proportionality constant Z defined as "fugacity capacity" ($mol/(Pa\ m^3)$), as indicated in equation 2.1:

$$C = f \cdot Z \qquad (2.9)$$

From the ideal gas law, Z for air is defined as $1/R \cdot T$ where R is the ideal gas constant and T is absolute temperature. When an equilibrium partition coefficient is defined between air and another compartment x, then Z for the x compartment can be calculated. Definitions of Z for environmental compartments are shown in Figure 2.2 Mackay, 2001).

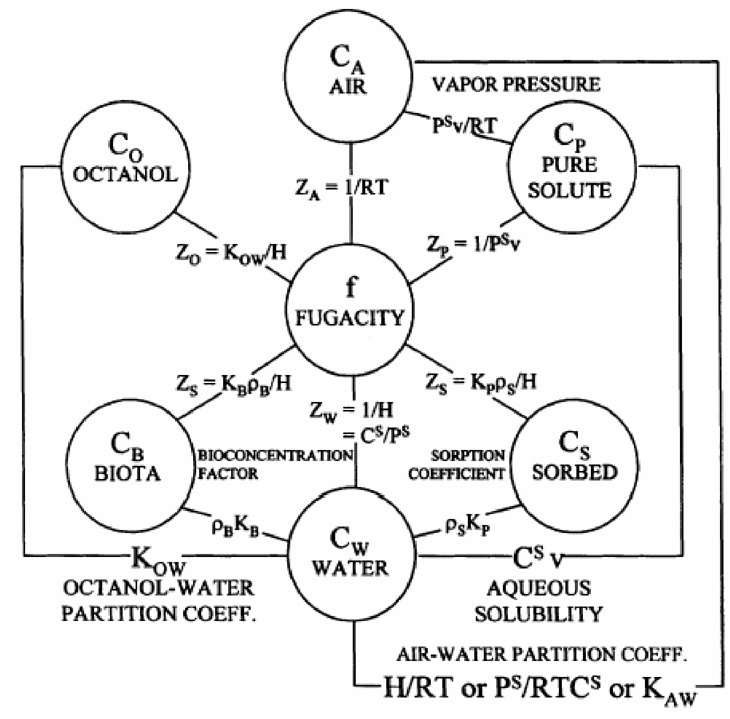

Figure 2.2. Relationship between Z and the partition coefficients (from Mackay, 2001).

Rates of chemical transport and transformation are described using D values defined as described as it follows (2.10):

$$rate = G \cdot Z \cdot f = D \cdot f \qquad (2.10),$$

where G (m^3/h) is the flow rate of the medium under consideration. D rates are expressed as mol/(Pa·h), and are analogous to first order rate constants. D values can represent a variety of processes including chemical reaction, advection in a moving phase, and diffusive exchange between phases.

2.5.4 *Steady state, equilibrium and levels of complexity*

There is frequent confusion on the terms 'equilibrium' and 'steady state'. It is very important not to consider these terms as synonyms, because they are not. *Equilibrium* implies that phases have concentrations such that they experience no tendency for net transfer of mass. *Steady state* instead implies constancy with time. In the real environment a complex assembly of phases are observed, in which some are (approximately) in steady state, others in equilibrium, and still others in both steady state and equilibrium.

Considering the fugacity approach, depending on the equilibrium and on the time-dependence of a system, there are four levels of model complexity, defined as follows.

The simplest fugacity calculation is referred to as "Level I", and describes equilibrium partitioning of a fixed number of moles (M) of chemicals in a closed system of well mixed environmental compartments of known Z values and volumes (V):

$$M = V_1 \cdot C_1 + V_2 \cdot C_2 = V_1 \cdot Z_1 \cdot f + V_2 \cdot Z_2 \cdot f = f \cdot (V_1 \cdot Z_1 + V_2 \cdot Z_2) \qquad (2.11)$$

Where C stands for the concentration (mol/m^3) in each environmental compartment. In general, the solution is (2.12):

$$f = M \Big/ \sum_i V_i \cdot Z_i \qquad (2.12).$$

Level I fugacity models simply show the relative equilibrium partitioning of a conserved (i.e. non-reacting) chemical in a multimedia setting. They assume equilibrium and steady-state to apply in this closed system.

"Level II" models include degrading reactions and advective loss, assuming steady state conditions where emissions (E, mol/h) are balanced by removals. The total D value for removals is calculated (D_i) as the sum of the D values that remove chemical from the phase. Therefore (2.13):

$$f = E \Big/ \sum_i D_i \qquad (2.13).$$

Level II models assume equilibrium and steady-state to apply in an open system with inputs and outputs. Mode-of-entry is irrelevant because the chemical immediately establishes equilibrium upon introduction to the system.

"Level III" models allow non-equilibrium conditions between compartments in the system, but each compartment and the overall system is at steady-state i.e. chemical emissions are balanced by removal processes; conditions are constant with time but compartments are not at equilibrium and different fugacities apply to each medium. Rates of intermedia transport are calculated. A separate mass balance equation including emissions (E_i) and transfer from other compartments ($D_{i,j} \cdot f_j$) and removal processes (transport and transformation) from each compartment ($D_i \cdot f_i$) is written for each environmental compartment (2.14):

$$E_i + D_{i,j} \cdot f_j = f_i \sum_i D_i \qquad (2.14).$$

Hence, for a system defined by n compartments, a system of *n* equations and n unknown fugacities is to be solved.

"Level IV" fugacity models are dynamic or unsteady-state. They are most often used to determine how long it will take for concentrations to change as a result of changing rates of emission. Equations that relate the emission rate to each compartment (E_i) to fugacity have the following general form (2.15):

$$d(V_i, Z_i, f_i)/dt = E_i + \sum_{i,j} D_{j,i} \cdot f_j - f_i \sum_i D_i \qquad (2.15).$$

For a system defined by *n* compartments, a system of *n* equations and *n* unknown fugacities is to be solved. Solutions for chemical fugacity in each medium as a function of time can be deduced by explicitly solving the system of equations, or by approximation using numerical integration.

Each increasing level of complexity provides additional insight into the behavior of chemicals in the real environment and introduces new environmental chemistry concepts.

In this thesis level III multimedia models will be mainly approached, except in one case (in the model evaluation exercise presented in chapter 4) where a dynamic treatment will be presented in order to evaluate the model capability to reproduce the temporal variability of observed data.

CHAPTER 3 INTRODUCING AN INTEGRATED CLIMATE CHANGE PERSPECTIVE IN POPs MODELING, MONITORING AND REGULATION

This chapter presents a review on the implications of climate change on the monitoring, modeling and regulation of persistent organic pollutants (POPs). Current research gaps are also identified and discussed.

Long-term datasets are essential to identify relationships between climate fluctuations and changes in chemical species distribution. Reconstructing the influence of climatic changes on POPs environmental behavior is very challenging in some local studies, and some insights can be obtained by the few available dated sediment cores or by studying POPs response to inter-annual climate fluctuations. Knowledge gaps and future projections can be studied by developing and applying various modeling tools, identifying compounds susceptibility to climate change, local and global effects, orienting international policies.

Long term monitoring strategies and modeling exercises taking into account climate change should be considered when devising new regulatory plans in chemicals management.

3.2 Introduction

As it was introduced earlier (in chapter 2), never in the past changes have been as rapid as those which are experienced in modern times, and there is now strong evidence that this is due to human influence (Solomon et al., 2007). Because climate change may be the greatest challenge that humankind currently faces, most countries joined international agreements on future perspectives and policy, e.g. the Kyoto protocol (1997, http://unfccc.int/kyoto_protocol/items/2830.php), and the United Nations Framework Convention on Climate Change (UNFCCC, 1994, http://unfccc.int/2860.php).

Like climate change, environmental contamination caused by Persistent Organic Pollutants (POPs) is a global concerning issue. POPs are defined in the UNECE (United Nations Economic Commission for Europe) Convention on Long-Range Transboundary Air Pollution (CLRTAP). POPs accumulate in living organisms and subsequently in humans via food. Because of an increasing concern about these contaminants, international treaties were signed at international level: the United Nations Environmental Program (UNEP) Stockholm convention signed by 127 countries in 2001 is an important example of the worldwide attention focused on POPs, and also the UNECE Protocol for the selection of new POP substances in 1998 demonstrates the international consideration of POPs contamination issues (OECD, 2004).

As the environmental behavior of POPs depends on the complex interaction of many factors, any significant environmental alteration is likely to affect their distribution and fate. Temperature plays an important role in affecting POPs mobility but also several other parameters are key factors in influencing POPs behavior and should therefore be taken into account. Some examples are given by wind and oceanic current patterns, precipitations distribution, land cover characteristics and so on. The alteration of any of these factors will in turn influence the parameters controlling the environmental distribution and fate of POPs, such as reaction rate constants (i.e. partitioning and degradation rates), the release rates from secondary sources (e.g. contaminated soil), uptake rates, bioaccumulation dynamics.

To date, only few studies focused on the existing interactions between climate change and POPs behavior and distribution (Eisenreich, 2005; Dalla Valle et al., 2007; Jenssen, 2006; Macdonald, 2005). Some information is available for specific case studies, in particular about the Arctic environment, undoubtedly the most vulnerable and affected area with respect both to POPs contamination and climatic changes (e.g. Macdonald et al., 2003, 2003b and 2005). However, many uncertainties and challenges have to be still addressed and there is also paucity of experimental data and scientific background information, from which to evaluate the real significance of climate change influence on POPs behavior and fate. Suitable data for a better understanding on the influence of climate change on the cycling of POPs in the environment are certainly not enough or covering time span that is not long enough to study long term phenomena. Such a gap could be covered by collecting more soil and sediment core samples, thus allowing the study of contamination trends depending both on climate conditions as well as on emissions history.

The main objective of this chapter is to identify the implications of climate change for POPs monitoring and modeling, and for regulation and policy perspectives, as it is summarized in Table 3.1 The most relevant research gaps are also discussed.

Table 3.1. Implications of climate change on POPs monitoring, modeling and regulation.

Climate change	Effects on POPs behaviour	Actions		
		Monitoring	Modeling	Regulation
Wind speed	POPs atmospheric distribution	The representativeness of environmental monitoring is less reliable in a climate change perspective: monitoring programs for all compartments need to be more representative of short periods of time More studies on dated environmental cores would help in identifying relationships between climate and POPs benavior in the past Hystorical emissions inventories are needed for modeling studies	Higher spatial and temporal Resolution Better evaluation of chemical-physical parameters Identification of climate-sensible chemicals Long-term simulations taking intoaccount climate change Estimation of future emission dynamics	There is the need to implement climate change into existing regulations REACH regulation should clearly include climate change issues WFD should explicitly take climate change into account Monitoring programs should be carried out more often because of the representativity decreases in consideration of occurrung climate change
Temperature	POPs degradation rate, emissions			
Salinity	POPs adsorption on suspended particulate matter			
Precipitation	POPs atmospehric wet deposition flux			
Oceanic currents	POPs marine spatial distribution			
Snow rate	POPs atmospheric deposition			
Dry period	POPs volatilisation			
Ice cover	POPs release from ice			
Organic Carbon Content	POPs adsorption/release			
Sediment deposition	POPs deposition rate (in water)			
Sediment resuspension	POPs re-circulation			
Population dynamics	POPs ad- and ab-sorption			
Vegetation mass	POPs adsorption on vegetation biomass			

REACH: Registration, Evaluation, Authorization and Restriction of Chemical substances; *WFD* : Water Framework Directive.

3.3 POPs and climate change

3.3.1 Direct and indirect impacts of climate change

As a definitive distinction between direct and indirect climate change impacts on the environment is still missing, in the present study a distinction is made between “direct” and “indirect” climate change impacts on POPs environmental behavior. “Direct” climate change impacts are primarily driven by temperature rise (i.e. change in ice coverage, marine and atmospheric temperature, sea level rise, precipitation amounts and the related extreme events, water vapor, marine salinity, wind and current patterns). “Indirect” climate change impacts are derived by the former, and affect aspects related to a change in ice coverage, compartments temperature, sea level rise (i.e. the temperature-directly related climate change effects). Land use change, change in medium properties, modification of human activities, release of volatile chemicals may be defined as indirect impacts of climate change. Such impacts are listed in Figure 3.1.

Significant indirect impacts can result from direct impacts of climate change on environmental processes, having a remarkable influence on human activities. For instance, agriculture is thought to be one of the most vulnerable human activities in a climate change perspective (Thomson et al., 2006), in fact agricultural production is dependent on solar radiation and is strongly affected by changes in temperature and precipitation regimes. In Europe, this is relevant both for the Northern (temperature limited) and Southern (moisture-limited) regions (Trenberth et al., 2007). In turn, changes in land use (i.e. agricultural land use in the Arctic) may enhance the introduction of pests and diseases in new exploited areas, and possibly trigger alterations in the food web structure. Such imbalance could drive towards an increased use of banned pesticides that would enhance the bioavailability of toxic and bioaccumulating chemicals in the environment, hence worsening the quality of the ecosystem (Eisenreich, 2005; Macdonald et al., 2005).

3.3.2 Climate change influence on POPs behavior and fate

As discussed in the previous paragraphs, the main consequence of climate change probably lies in the increase of global temperature in both the oceanic and terrestrial environments. Several mechanisms are known to influence the distribution of POPs in the environment, since their environmental behavior strictly depends on: the capacity of the environmental compartments to degrade or accumulate POPs, the atmospheric circulation patterns, the spatial and temporal evolution of primary and secondary sources, and on the kinetics of the air-surface exchange (Dalla Valle et al., 2007). Secondary emissions can be also influenced by climate change, as global warming may enhance the release of volatile contaminants from soil (Dalla Valle et al., 2007, Eckhardt et al., 2007), and changes in wind and precipitation patters can alter the way chemicals are redistributed in the environment.

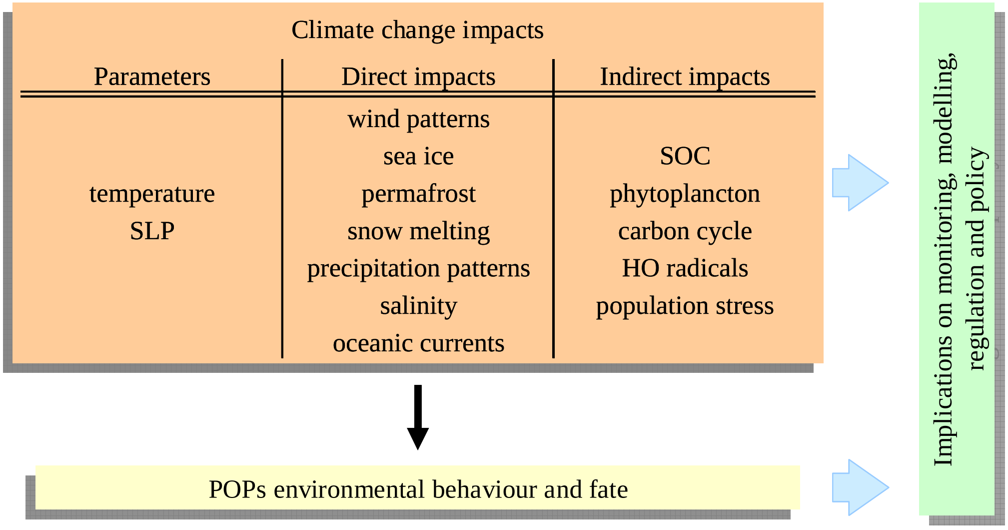

Figure 3.1. Direct and indirect impacts of climate change on POPs behavior and fate and subsequent consequences on monitoring, modeling and environmental policy. SLP: Sea Level Pressure; SOC: Suspended Organic Carbon.

Surface temperature over land has increased at a faster rate than it has over the oceans in both hemispheres (about 0.27 °C vs. 0.13 °C per decade), and the warming trend was observed to be greatest at higher northern latitudes (Trenberth et al., 2007). Temperature is thought to be one of the main climate drivers in determining POPs global distribution (Bloomfield et al., 2006) as it influences emission rates from primary and secondary sources, gas-particle partitioning, reaction rates (photolysis, biodegradation, oxidation), air-surface exchange (volatilization), major hydroxyl radical formation, etc.

Furthermore, temperature is correlated with sea level pressure, which is a key factor in regulating cyclones and anticyclones, and associated wind patterns. Accordingly, it is well documented that the changes in both temperature and the large-scale wind system are associated with changes in POPs circulation patterns (Ma et al., 2004; Macdonald et al., 2005), and that they are a relevant issue to be considered both at the global and local scale, (Daly and Wania, 2005).

The state of the cryosphere is important since it stores about 75% of the world freshwater, and variations in ice amount play a crucial role in freshwater availability (Lemke et al., 2007). Currently, ice permanently covers 10% of the land surface, and approximately 7% of the oceans (as annual mean). In winter snow covers approximately 49% of the land surface in the northern hemisphere (Zhang et al., 2003). As a consequence of the current trend of temperature increase, the biggest ice-mass losses contributing to sea level rise come mainly from the ice cap of Alaska (Raper and Braithwaite, 2005), and second is the contribution by the Arctic glaciers (Comiso et al., 2003).

Permafrost and seasonally frozen ground in most regions also displayed large changes in recent decades: in the northern hemisphere the maximum area covered by seasonally frozen ground decreased by about 7% from 1901 to 2002, with a drop off in spring of up to 15% (Zhang et al., 2003). Decreases in snowpack extent have also been documented in several regions worldwide by studying annual time series of mountain snow water equivalent and snow depth measurements (Mote et al., 2005). For all these reasons, sea ice can be well considered an indicator of climate change. Sea ice is also a significant POPs reservoir, and influences the contaminant dispersion through the sea ice trajectories (Wania et al., 1999). The loss of permafrost alters the existing biological processes in the top 1 m soil layer where almost all ecological processes occur. Permafrost destruction allows a more efficient transport of contaminants into ponds and lakes or re-mobilization of contaminants stored in tundra soils (Macdonald et al., 2005).

Snow melting is also thought to be important as a driving factor in POPs cycling, but there is only a rudimentary understanding of this process, and the capability of expressing quantitatively its influence on POPs behavior is limited (Meyer and Wania, 2007). Abundant snow deposition in high-latitude regions may lead to a large contaminant release during snowmelt. Hence, there is a high potential for revolatilization and runoff, especially where rocky soils and lack of vegetation prevail, like in mountain regions. This is of particular concern because contamination of snow and lake water in mountain regions may have the potential to impact drinking and agricultural water supplies (Daly and Wania, 2005).

As mentioned above, temperature increase may lead to an increase of water vapor atmospheric concentration, and this in turn will influence precipitation patterns. In fact an increase in heavy precipitation events and in floods has been recently observed while the total amount of precipitation was unchanged or decreasing (Easterling et al., 2000).

Precipitation and runoff are important factors in interpreting and predicting the environmental behavior of POPs: changes in duration and intensity in seasonal precipitation may lead to changes in the spatial and temporal distribution of POPs wet deposition and their degradation products (Breivik et al., 2006; Daly and Wania, 2005). Furthermore, it is important to consider whether precipitations occurs as snow or rain, and the duration of snow cover in controlling POPs interactions with the environment (Daly and Wania, 2005; Macdonald et al., 2005). Floods are also important in determining POPs environmental dissemination as contaminated sediments may be redistributed on large uncontaminated soil areas (Hilscherova et al., 2007).

In addition, ice melting and increased evaporation rates influence ocean salinity, which affects in turn organic chemicals solubility. An increase in salinity leads to a decrease in POPs solubility (Schwarzenbach et al., 2003; Alaee et al., 1996). This effect is known as salting-out effect, and increases exponentially with increasing salt concentrations. Normal sea water salinities (0.5 M) would affect POPs concentrations by a factor of 1.5-3, but in environments characterized by higher salt concentrations salting-out will be substantial (Schwarzenbach et al., 2003). Climatological studies showed that salinity increased in evaporative regions, while it decreased at northern latitudes. This freshening is due to increased northern precipitation amounts, faster ice melting and increased water runoff (Häkkinen, 2002). In turn, salinity in conjunction with wind patterns influence oceanic currents (Lohmann et al., 2006, 2007), which are important in determining POPs cycling. In fact the turbulent flux of the water column strengthens the upward diffusion of sediment entrained contaminants and determines the extent to which inputs from the atmosphere mix into the water column (Jurado et al., 2007). However comprehensive studies of how these changes may affect contaminant pathways have not been conducted yet and little is known about the importance of marine currents on POPs cycling in the environment.

Secondary climate change effects may also interfere with POPs behavior. Once a persistent pollutant is released to air, water and soil, it undergoes different transport pathways, eventually reaching the biota, and each step is potentially influenced by climate change. Climate change may for instance affect wind patterns or oceanic currents, and the partitioning or the degradation rate of the released chemicals, thus influencing the pollutants persistence and environmental distribution.

Climate change may affect also population dynamics, including that of phytoplankton, which plays an important role in controlling the biogeochemical cycles in the marine environment. Dachs and co-workers (1999) developed an air-water-phytoplankton exchange model with the aim of describing the existing interactions between air-water exchange and phytoplankton uptake. This model was based on the assumption that air-water exchange dynamics are influenced by phytoplankton biomass and growth rate (Dachs et al., 2000; Jurado et al., 2004). In particular, phytoplankton biomass shows an important spatial and seasonal variability affecting the long term fate of POPs and plays a key role in determining the storage capacity of surface waters, because POPs are adsorbed or absorbed to the phytoplankton organic carbon surfaces (Jaward et al., 2004; Jurado et al., 2004). In turn, this partitioning affects the net air-water exchange flux, by controlling dissolved phase concentrations and hence the fugacity gradient with the atmospheric gas phase. Finally, phytoplankton also affects the migration of POPs from the surface water to deep water because of the plankton seasonal transfer into deep water (Dachs et al., 2000; Jaward et al., 2004).

The alteration of the carbon cycle by climate change is another relevant aspect to be considered when studying the effects of climate change on POPs behavior. As it was argued before, indirect impacts consist in an alteration of medium properties, and are caused primarily by temperature trends that can lead, for example, to a variation in soil organic carbon content. Fang et al. (2005) found that different types of soil organic matter will respond to global warming with accelerated decomposition trends. It is worth noting that even minor changes in long term processes such as paedogenesis should not be ignored because these have potentially important implications for long-term agricultural land use and are often irreversible (Bloomfield et al., 2006).

Another environmental parameter influencing POPs behavior is radiative forcing, which depends on many factors as long lived greenhouse gases, clouds, aerosol, ozone, volcanic eruptions, etc. Radiative forcing is following an increasing global trend (Nozawa et al., 2005; Takemura et al., 2005), and this may indirectly affect POPs distribution, since HO· driven reactions are the dominant POPs loss-process in the atmosphere. In fact solar radiation promotes the photolysis of precursor oxidants into hydroxyl radicals (HO·), which play an important role in POPs degradation in air (Mandalakis et al., 2003). The HO· concentration depends on solar radiation (Macleod et al., 2007) and on the presence of other gases in the atmosphere. In fact HO· is expected to decrease with increasing carbon monoxide and methane, whereas it is expected to rise with NOx and ozone increase. Since both these gases are expected to change in atmospheric concentration, it is difficult to get effective future projections of the state of $HO^{\cdot}$, whose concentration depends on both the emission and climate change scenarios (Denman et al., 2007). Accordingly, Lelieveld et al. (2004) showed that global $HO^{\cdot}$ levels have changed little in the past century, but regional changes have been substantial.

Finally, it is important to emphasize that climate change is likely to pose additional stress to individuals, thus, when taking into consideration POPs impact on the ecosystem, it must be remembered that the combination of the presence of pollutants and climate change may be detrimental for mammals and seabirds. However, Ishibashi et al. (2001) showed that there is always temperature dependence in contaminants driven effect on goldfish, when one chemical is considered. Brian et al. (2008) showed that the effect of temperature on the response of fish to a defined mixture of estrogenic chemicals containing also environmentally relevant chemicals is not evident when chronic exposure is the endpoint, but the biological response to chemicals was induced more rapidly at higher temperatures. There is clearly the need for further research on the synergic effects of multiple stressors (natural or anthropogenic, one chemical or mixture, chemical or non chemical) on wildlife (Jenssen, 2006), especially experiments that enable to explain the way in which temperature exerts its effects at the molecular and physiological level are likely to be of relevance in improving the understanding of the impacts associated to climate change.

3.4 Implications for monitoring

Providing experimental evidence of changes in POPs distribution and fate due to global warming is extremely challenging, as long term monitoring data is needed for different environmental compartments. The difficulty to discern how much of the observed changes can be ascribed to climate variations and not to changes in production and use of the chemicals themselves is also to be taken into account when dealing with such a complex problem.

It is well known that temperature and other climate related parameters (e.g. precipitations and wind patterns) are extremely influential in shaping the patterns of chemical cycling in the environment, therefore an effort towards the collection and study of historical records should be encouraged. Long term datasets can be obtained by soil, ice or sediment cores, sampled from undisturbed media, possibly from remote areas to minimize the influence of local sources of contamination. These datasets should also encompass a large range of regions in order to appreciate the spatial variability in the response of ecosystems to climate change. Such datasets are unfortunately rare (Eisenreich, 2005), since monitoring activities are often sparse and time series are not long enough (Macdonald et al., 2005).

However, for the study of long term trends existing monitoring programs are available, which started during the eighties and are still carried out by the European Monitoring and Evaluation Program (EMEP, www.emep.int), the Arctic Monitoring and Assessment Program (AMAP, www.amap.no), the Integrated Atmospheric Deposition Network (IADN, http://www.msc-smc.ec.gc.ca/iadn/index_e.html), and the Northern Contaminants Program (NCP, http://www.ainc-inac.gc.ca/nth/ct/ncp/index-eng.asp). Furthermore, the reconstruction of the historical trends based on dated sediment or soil cores and other environmental archives are reliable data in order to have a long time-trend description (e.g. Dalla Valle et al., 2005, 2005b; Zhu and Hites, 2005; Baker and Hites, 2000; Rose et al., 2004; Wagrowski and Hites, 2000; Macdonald et al., 2000; Muir et al., 2002; Lockhart 1994, 1996, 1997; Rawn et al., 2001; Lockhart et al., 1995, 1997).

Ice and snow cores are an important proxy for climate change effect on POPs environmental distribution (Macdonald et al., 2005), but only a few studies in this field have been developed, i.e. ice cores are useful in identifying POPs historical trends because they show the influence of long range transport and of local transport patterns (Villa et al., 2003; Garbarino et al., 2002; Matthews, 2001; Jaffrezo et al., 1994; Peters et al., 1995; Vehviläinen et al., 2002).

Monitoring programs should also consider spatial variability, since it plays a crucial role in modulating climate variability and hence in understanding POPs distribution trends. The Article 16 of the Stockholm Convention stipulates that comparable monitoring data should be provided in order to assess the effectiveness of the convention through a global monitoring program (Harner et al., 2006; Pozo et al., 2006). For instance, lake sediments can provide data on spatial and temporal variability of atmospheric inputs of hydrophobic POPs to lakes and terrestrial surfaces: sediment data may thus provide information suitable for evaluating model predictions of the POPs characteristic travel distance (Breivik et al., 2006). According to the Stockholm Convention, some studies are focused on local contaminants distribution in soils and sediments. This information is useful in order to localize the contaminants distribution in sediment (i.e. Kiss et al., 1997; Fattore et al., 1997; Hildebrandt et al., 2006; Kishida et al., 2007), but this does not help in identifying past distribution trends in the environment. A global monitoring campaign was also made for soil by Meijer et al. (2003), who collected PCBs concentrations in soils in 1998.

Furthermore, the collection of emission and global concentration data is very important in order to understand which are the consequences of climate change on POPs global distribution, namely on POPs LRAT, which is influenced by climate change (Beyer et al., 2003). Li (1999) made a first step in drawing a comprehensive global POPs distribution inventory, focusing on the estimation of HCHs at a global scale. Mass balance applications followed this study, e.g. Wania et al. (1999c) applied a global multimedia distribution model assuming the emission estimates by Li (1999). Breivik et al. (2007) made another step in drawing a comprehensive global PCBs distribution inventory, focusing on estimations of global emissions for 22 individual congeners. This work provided useful information for subsequent studies in POPs global distribution trends and it is desirable that similar studies will be conducted for other chemical classes. PCBs however could well be considered as marker compounds to study climate change induced changes in distribution patterns. This because they are no longer produced and their cycling is therefore mainly driven by transport processes and primary emissions (Lohmann et al., 2007). In addition the presence of spatially resolved emission trends at the global scale could prove to be extremely useful in future modeling exercises.

3.5 Implications for modeling

As discussed in the previous paragraphs, shifts in environmental conditions due to climate change, together with changes in human activities, can significantly affect the behavior and fate of chemicals in the environment. It should be taken in mind, as an example, how our planet has been modified by humans over the last century, to realize how much the current landscape is likely to be radically transformed in the future. Therefore, in order to predict the fate of chemicals in response to environmental changes, the evolution of environmental conditions should be taken into account in modeling exercises, especially in long term projections of POPs future concentrations. Obviously, the understanding and ability of making long term predictions on global change scenarios is limited and affected by many sources of uncertainty. However, such long term predictions are relevant in POPs contamination study because these chemicals are intrinsically bound to reach remote regions and contaminate the environment for decades after their release.

3.5.1 Modeling POPs

POPs behavior and environmental fate in a climate change perspective can be simulated either by fugacity based multimedia models or by General Circulation Models (GCMs) coupled with a chemical module (Ilyina et al., 2006). GCM are used for simulating realistic atmospheric circulation and they are usually very complex models because of their high spatial and temporal resolution, and the motion equations, hence their output is sometimes difficult to interpret (Stewart, 2004). On the other hand, multimedia environmental models are relatively simplified models used for studying processes where the environment is represented as a set of spatially homogeneous boxes (Mackay et al., 2001). These models are particularly suitable for (i) explaining differences in environmental fate and transport between chemicals in a defined environment and (ii) exploring the influence of variable environmental factors on chemical fate and transport (Macleod et al., 2005). Table 3.2 shows the main characteristics of the models considered in the present paragraph, and their suitability to analyze climate change effects on POPs environmental behavior.

Table 3.2. List of the multimedia fate and transport models cited in this chapter.

Model	Description	Advantages in climate change perspective studies
BETR Global	Level III-IV model. Latitudinal and longitudinal resolution, 288 regions. Seven environmental compartments are considered (two atmospheric layers, soil, vegetation, coastal water, freshwater and sediments).	It can identify impacted regions with a longitudinal and latituinal resolution.
Globo-POP	Level IV Latitudinal resolution up to 10 regions. It takes into account 9 compartments (freshwater and sediment, four vertical atmospheric layers, upper ocean layer, cultivated and uncultivated soils).	This model can be used for evaluating climate change effects on POPs distribution assuming a latitudinal-resolved world. Including ice cover it is suitable for climate change studies.
CliMoChem	Level IV model. Latidudinal resolution, up to 20 regions. It takes into consideration four environmental compartments (coastal water, soil, vegetation, atmosphere). The version by Stocker et al. (2007) takes into account also snow-related processes.	This model can be used for assessing the POPs fate and transport assuming also the ice melting and the change in snow precipitations.
G-CIEMS	Level IV fugacity model. GIS-based models. Six environmental compartmens are assumed in this model (atmosphere, fresh water - rivers and lakes, coastal water, sediments, soil).	It could be used for calculating the fate of persistent pollutants in a climate change perspective especially at high spatial resolution for the dry land areas, where this model allows to easily distinguish different environments.

Several compartment-based multimedia models are user friendly and they do not require a huge amount of data, which is instead requested for GCMs models. On the other hand, GCMs are becoming more prominent for describing the fate of POPs concerning climate change. GCMs simulate climate using mass, energy, and momentum conservation equations that are integrated over connected atmospheric, land, and ocean volumes. GCMs have high temporal and spatial resolution and can be structured to fit detailed air and water flow patterns (e.g Lammel, 2004). They can be adapted to simulate the fate and transport of POPs by adding equations to describe degradation, deposition, revolatilization from surfaces, partitioning to sorbed phases etc. However, they are mathematically complex and require a great amount of computational time (Stewart, 2004).

Efforts in considering how climate conditions influence POPs environmental distribution have been conducted by applying different types of mass balance models (see Table 3.2). For example, the Berkley-Trent Global Model (BETR-Global) is a global scale mass balance model developed on the basis of steady state (level III) or unsteady state (level IV) scenarios (Macleod et al., 2005). It has been applied also for local scale simulations, and on this case it demonstrated how temperature, atmospheric stability (i.e. wind speed and mixing height) and concentration of photochemically generated hydroxyl radicals are sufficient to explain the observed patterns of PCB atmospheric concentration under different environmental conditions (Macleod et al., 2007). This model (see Table 3.2 for some more details) is suitable for studies focusing on global change effects on POPs distribution because it is also longitudinally resolved.

Other multimedia models do not have longitudinal resolution, for instance Globo-POP is a multimedia mass balance model developed by Wania and Mackay (1995), based on 10 latitudinal zones. The Globo-POP seasonal resolved inputs are temperature, ice cover and HO radicals concentration (Meyer and Wania, 2007); additional non temporal resolved input parameters are considered by the model (e.g. organic carbon fraction, aerosol fraction, suspended solids, etc.). Furthermore, Climochem (Scheringer et al., 2000) is a level IV model with no longitudinal resolution. Each zone is described by the land-to-water ratio, annual temperature and compartmental volumes. The version by Stocker et al. (2007) implements also the ice and snow compartments, which would allow a complete mass balance in a climate change perspective, since the ice compartment is relevant in climate change issues.

Another possibility for POPs fate modeling is given by the use of a spatially resolved and geo-referenced dynamic multimedia environmental fate model, G-CIEMS (Grid-Catchment Integrated Environmental Modeling System) that was developed on a geographic information system (i.e. GIS; Suzuki et al., 2004). This model consists of a basic fugacity formulation (Mackay, 2001) following a level IV calculation, referred to each geo-referenced cell, divided into six compartments (air, freshwater-rivers and lakes, sediments, forest, seawater, soil); advective transport is considered through adjacent cells. This model was used to predict the POPs concentrations in coastal areas and it was observed that approximation associated to this model is better than the estimate given by the traditional multimedia fate and transport model (Suzuki et al., 2004). This model allows the distinction between different environments because it can reach high resolutions in particular for the mainland where rivers are exactly traced. Local case study could be hence studied following this approach.

These are just some examples of models applied for the study of POPs environmental behavior and fate and therefore the list is not exhaustive, other models have been proposed for similar purposes (e.g. Breivik et al., 2006; Wei et al., 2008).

An additional complication in the study of organic chemicals fate in a changing environment results from the interaction with living organisms. In particular, bioaccumulation and biomagnification processes can be altered by changes in climate and environmental conditions thus triggering changes in bioconcentration that are magnified along the food chain. In addition, the consequences for organisms at the top of the food chain, especially in cold climates, can be amplified because of synergic effects with thermal stress or other stresses that result from changes in environmental conditions (Jenssen, 2006).

3.5.2 Temporal variability approach in understanding Climate Change consequences on POPs behavior

A useful exercise aimed at considering the effects of climate change on POPs behavior can be represented by the study of the influence of inter-annual and seasonal climate variability. This could provide valuable information on the sensitivity of chemicals behavior to climate variations. Short and medium term fluctuations of climate conditions can be very significant and they can have a great influence in controlling the environmental fate of chemicals. Inter-annual climate variability includes oscillations in precipitations and temperature (Su et al., 2007) that easily exceed the medium and long term trends. Such variations can be considered as a proxy of climate change, providing experimental evidence of what could happen in long term dynamics. Becker et al. (2008) imputed the oscillation in historical trends in atmospheric γ-HCH concentration to climate variability associated to the Arctic Oscillation (AO) through the application of dynamic harmonic regression (DHR), a statistical technique used to provide long term trend information.

Paleoclimatic studies show that the terrestrial climate had always been changing, and had always been characterized by high intrinsic variability. In order to have a better understanding of climate change, the extent of natural variability needs to be studied in detail, bearing in mind that climate variability is characterized by a wide spectrum of temporal and spatial scales. Some recent studies, for example, have pointed out how the POPs LRAT is remarkably affected by inter-annual and seasonal climate oscillations (Ma et al., 2004, Macleod et al., 2005; Macdonald et al., 2005), especially when secondary emissions are the main source for the chemicals.

Recently, increasing attention has been given to global circulation patterns of climate variability, in particular NAO (Northern Atlantic Oscillation) and ENSO (El Niño Southern Oscillation) account for the highest variations in weather and climate around the world (Stenseth et al., 2002). For instance, Macleod et al. (2005) evaluated the influence of inter-annual variability in the North Atlantic Oscillation (NAO) on atmospheric concentrations of PCBs. This study showed that there is a correlation between NAO index and PCB 28 atmospheric concentrations especially during autumn and winter in the Northern Hemisphere. The same authors investigated also on how the daily atmospheric concentration cycle of PCBs can be described by a simple model that takes into account only 3 factors changing over the 24 hours (diel cycle): the air boundary layer thickness, air temperature and the concentration of OH radical (Macleod et al., 2007). This study shows different correlations between the mentioned factors and PCBs atmospheric concentrations for the single local studies. Stable environmental conditions are a key factor in determining the interpretability of model results.

However, despite the relevance of temporal variability in influencing POPs distribution, the link between inter-annual changes in atmospheric POPs concentrations and climate variability has not yet been studied extensively. This is primarily due to the lack of continuous atmospheric POPs measurements before the 1980s, and to the difficulty of discerning if and when climate fluctuations may have dominated the observed seasonal cycles of atmospheric concentration (Ma et al., 2004). Diurnal and seasonal variability result directly from the temporal variation of solar radiation. For instance, during the warm season the thick atmospheric mixed layer is not easily modified through alteration of radiative forcing, whether during winter time at the high latitudes the atmospheric layer is thinner and readily altered by changes in atmospheric thermal radiation. This phenomenon influences different processes, from POPs degradation up to precipitation distribution. In general short term climate variability is important in predicting climate impacts on POPs environmental distribution and fate, in particular taking into account that diurnal and seasonal fluctuations exceed temperature range expected by the Special Report on Emission Scenarios (SRES) provided by the IPCC: is it then worth being concerned about e.g. a 0.4º C long term temperature increase when the daily gradient is around 20º C? For this reason, it is worth studying the relevance of both temporal and spatial variations of environmental properties in order to fully understand POPs behavior. This can be done by comparing monitoring data (i.e. spatial variability) with temporal variability.

3.5.3 Future perspectives

Models used to predict the behavior and distribution of POPs and organic chemicals rely on very simplified assumptions concerning the physical environment they study. This certainly simplifies the analysis of the environmental processes involved and makes the calculations faster and easier, but, if the influence of climate and its variability (e.g. daily and seasonal temperature fluctuations, the temporal distribution of precipitations) are not taken into account, spurious results can be obtained (Meyer and Wania, 2007; Wania and Mackay, 1999). For example, an average precipitation rate is commonly assumed, which is equivalent to assume a light, constant rain over the whole year, an approach that has proven to produce artifacts in modeling simulations compared to a more realistic assumption of intermittent rain (Hertwich, 2001). Furthermore, normally it is not specified whether precipitations occur in form of rain or snow (Beyer et al., 2003), which is instead a key information for the estimation of atmospheric scavenging.

In summary, except for some targeted exercises, so far multimedia models have not been extensively applied to predict the possible effects of climate change on the distribution of chemicals in the environment. Modeling simulations could help identifying the chemical classes that could be more sensitive to climate change, on the basis of their physical-chemical properties (Macleod et al., 2007b). Similarly, modeling simulations can be used to estimate the LRAT potential, or the characteristic travel distance (Breivik et al., 2006) and simulate how those may be affected by changing climate conditions. More site specific simulations could be conducted for the regions of interest, applying different future scenarios (Breivik et al., 2006, 2007; Meyer and Wania, 2007; Wegmann et al., 2006) on the basis of climate change assumptions.

Modeling can be of great help to policymakers for taking decisions about the most suitable chemical management practices and regulations at the national and international level in many ways (Wania and Mackay, 1999). The detailed understanding of the processes controlling long-term global concentrations of POPs is necessary especially to support effective international actions (Macleod et al., 2007) and organizations like the Strategic Approach to International Chemicals Management (SAICM) or the International Panel on Chemical Pollution (IPCP; Scheringer et al., 2006).

In climate change modeling it is also necessary to consider the consequences related to irreversible events to take place. Such events, because of the high uncertainty regarding climate unpredictability (i.e. abrupt climate change, or rapid events; Schneider, 2004), are typically excluded from standard climate change scenarios, although the nonlinearity of the climate system may lead to abrupt phenomena. Some possible abrupt events may be represented by a dramatic shift of the Atlantic thermohaline circulation, rapid deglaciation and massive melting of permafrost or increases in soil respiration leading to fast changes in the carbon cycle. Others may be truly unexpected, resulting from a strong, rapidly changing forcing of a nonlinear system (Le Treut et al., 2007). The consequences of such events on the Earth system, and in particular on POPs cycling should also be investigated.

The simulation of long term fate of chemicals requires both an estimation of future emission dynamics (both with temporal and spatial detail), and the prediction of environmental changes. These come from the combination of changes in climate conditions and in socio-economic evolution.

A more complex study could provide a global scale long term prediction, coming from the coupling of a chemical module to a global circulation model, thus enabling the description of long term dynamics of several classes of chemicals. This is certainly an ambitious task but it is technically feasible and its application could provide very useful information on the ultimate fate of POPs taking into account the high variability of meteorological and transport conditions (Wania, 1999). A study in this direction was made by Gong et al. (2007) and Huang et al. (2007), who considered a Global Environmental Model coupled with an aerosol model and with a chemical module in order to develop the GEM/POPs model which was developed in order to evaluate the POPs atmospheric deposition patterns and budgets. Longer simulations and more processes are to be taken into account to study historical global fate.

In multimedia fate and transport modeling, an improvement on the model parameterization is desirable. In particular more realistic degradation rates are needed, together with a more detailed description of the vegetation biomass seasonal fluctuation, which has proved to be a significant factor in controlling the global fate of POPs (e.g. Dalla Valle et al., 2005c; Gouin et al, 2004). Other parameters should be allowed to vary over time, and precipitations should be described as intermittent and not constant during the whole year (Breivik et al., 2006).

3.6 Implications for regulation and policy

National and international treaties and laws on chemicals management and pollution control do not take adequately into account climate change or more in general the possibility that the environment will undergo some significant changes over time. If global warming will occur, higher temperatures will enhance the mobility and the LRAT potential for chemicals, thus potentially increasing the environmental concentrations of some pollutants in already vulnerable areas. In addition, those areas may be already affected by other climate change related stresses, making their ecosystems more vulnerable, generating a synergic effect (e.g. Jenssen, 2006). On the other hand, temperature rise would increase degradation rates and therefore the net result is difficult to predict, as it depend on processes that respond in opposite ways to temperature changes.

Climate change became an international issue of concern in 1994, when 191 nations subscribed the United Nations Framework Convention for Climate Change (UNFCCC), in order to discuss possible ways of tackling global warming at the international level. A few years later a number of nations approved an additional treaty, the Kyoto Protocol (signed in 1997 by 173 nations, and entered into force in 2005), which adopted more legally binding and restrictive measures. In 1988 the World Meteorological Organization (WMO) and UNEP established the Intergovernmental Panel on Climate Change (IPCC) with the aim of assessing on a comprehensive basis the scientific, technical and socio-economic information relevant in understanding the scientific basis of risk of human-induced climate change, its potential impacts and options for adaptation and mitigation.

The EU member states have shown great attention to environmental pollution issues over the last few decades and most of them readily signed both the CLRTAP protocol and the Stockholm Convention. Furthermore, as an attempt to avoid past errors and to have a unique regulatory framework for chemicals, the REACH directive (Registration, Evaluation, Authorization and Restriction of Chemicals), which entered into force on 1st June 2007, has been launched. REACH concerns the regulation of chemicals in the UE with the main aim to improve the protection of human health and the environment through the better and earlier identification of the properties of chemicals (http://ec.europa.eu/environment/chemicals/reach). However, this regulation is focused on the identification of risks caused by chemicals and on the risk management by chemicals manufacturers and importers, but there is no reference to the possible influence of climate change on the risks posed by chemicals production or usage (Verdonck et al., 2007). Climate change should instead be taken into account when describing the exposure scenarios for persistent chemicals in the Chemical Safety Report required by REACH regulation.

Despite the fact that climate change is considered a worldwide controversial issue, introducing climate change into a regulatory framework is still an open question. Climate change could directly impact water industry asset performance, such as sewage treatment plants and sewage networks, or indirectly impact diffuse pollution, as it in the case of POPs environmental behavior. This is why the contribution of climate change to the overall risk should be considered. Unfortunately, whilst allowances are beginning to be made (i.e. in the case of flood risk and water resources management through the Water Framework Directive, WFD 2000/60/EC), some issues (i.e. diffuse pollution) have yet to be climate-proved. This is why it is necessary to deal with climate change thorough regulation issues (Wilby et al., 2006).

Additionally, climate change may influence monitoring activities’ performance, compromising their implementation. In fact climate change could lead to a higher variability in measured parameters, with a consequent reduction in the statistical power of monitoring programs (Crane et al., 2005). This happens for instance with chemical standards, which are often used as a tool directed at the protection of human health and of the environment. In fact, many regulatory agencies are responsible for developing and monitoring human health and environmental chemical standards. Many standards are enforceable numerical limits, whether others are not mandatory, but are still considered in guidelines. Since it is clear that many complex interactions between climate change and chemicals may occur (Breivik et al., 2007, 2006; Bytnerowicz et al., 2007; Macleod et al., 2005, 2007), monitoring activities may be adversely affected by climate change, i.e. the current monitoring system would not allow to detect breaches of environmental standards with the current degree of confidence (Crane et al., 2005).

In summary, one of the most concerning policy challenges in climate change is how to develop a decision making process considering long term climate variability and change (Wilby et al., 2006). In fact climate change is linked to uncertainty and variability, which are not easily implemented at the regulatory level. Moreover, since implementing climate change into regulations may cause a reduction in the statistical power of monitoring programs (Crane et al., 2005), including global change issues in a regulating perspective is a concerning topic and still an opened issue. Increasing variability is likely to arise in river system and in fluid media; Crane et al. (2005) showed that many more samples may be needed to maintain the current levels of confidence in chemicals standards. A possible solution could be the adoption of a statistical modeling approach aimed at planning monitoring programs taking into account climate change influences. In particular, such statistical modeling approach should be adopted by regulatory agencies in order to evaluate the statistics of each chemical standard currently in use, the influence of climate change on the ability of current monitoring programs to continue to detect compliance to the same degree of confidence, and the identification of the predictions to particular model components (Crane et al., 2005). Furthermore although well known records standing for the effectiveness of climate change were reported (Trenberth et al., 2007), regulations do not explicitly consider risks posed by climate change and its consequences on chemicals behavior and distribution (Bloomfield et al., 2006). Because these issues are complex and linked together, the regulation tool should aim at integrating the different environmental aspects related to climate change and POPs behavior and providing a predictive framework for climate change risk evaluation.

3.7. Conclusions to chapter 3

In this chapter a series of possible effects of climate change on the distribution and fate of POPs has been illustrated, in particular to discuss the implications of climate change on monitoring, modeling and regulation issues of this class of chemicals. Providing experimental evidence of changes in POPs fate due to global warming is extremely challenging, as long term monitoring data is needed for each environmental compartment. Furthermore, the difficulty to discern how much of the observed changes can be ascribed to climate variations and not to changes in production and use of the chemicals themselves is also to be taken into account when dealing with such a complex problem. For this, the identification of a specific representative compound could be useful to study the effects of climate evolution on POPs distribution and behavior. In order to discern the influence of climate change from that of usage and production patterns, a chemical no more produced or used is more suitable. PCBs could be a good example and an extremely useful exercise could be that of estimate how much of this class of chemicals that are currently stored in ice, soil and sediment compartments may be released because of climate change or changes in the environmental compartments that are climate driven. Moreover inter-annual and seasonal climate variability could provide valuable information on the sensitivity of chemicals behavior to climate variations, since short and medium term fluctuations of climate conditions can be very significant and they can have a great influence in controlling the environmental chemicals fate.

A decision-making process taking into account climate change could be developed through the adoption of a statistical modeling approach aimed at planning monitoring programs. Regulatory agencies should take into account such modeling approach in order to evaluate the statistics of each chemical standard currently in use, the influence of climate change on the ability of current monitoring programs to continue to detect compliance to the same degree of confidence (Crane et al., 2005).

Because these issues are complex and interconnected, the regulatory tools should aim at integrating the different environmental aspects related to climate change and POPs behavior and providing a predictive framework for climate change risk evaluation. Monitoring efforts should be made in order to verify the current environmental POPs distribution trends, and modeling exercises on temporal variability should be done in order to accurately predict climate change consequences on POPs distribution. Regulatory tools should be developed also considering the existing linkage between the issues of monitoring, modeling and regulation, and take into account the inherent uncertainty related to future global change.

PART 2: Methodological part

Introduction to Part 2 of this thesis

In the second part of the thesis I will present two applications of the methods introduced in chapter 2 in order to reach the objectives presented in chapter 1 and in light of the issues discussed in chapter 3.

Both case studies presented in this section follow the same approach in analyzing the effect of a climate change scenario on POPs environmental distribution. Because PCBs are no longer produced as I explained in the conclusions to chapter 3, and because they are priority chemicals as introduced in chapter 2, these chemicals were chosen as representatives for the analysis of climate change effects on POPs environmental distribution.

Fugacity models were set up in order to reproduce the environmental under the present climate scenario (referred to as 20CE in the following chapters), defining the present status of PCBs environmental distribution and a future climate change scenario as defined by the SRES report.

The model capability to represent the real state of the environmental PCBs concentration was evaluated through the comparison of modeled outputs from the 20CE set up with observations, and finally the 20CE modeled results are compared with the output from the climate change scenario set up

In chapter 4 BETR Global, a level III-IV fugacity model, was parameterized to represent the 20CE and A2 climate scenarios, and the results of the climate change scenarios are compared to the present climate scenario results in terms of PCBs atmospheric concentrations. This chapter is structured into two parts:

1. model evaluation: the present climate scenario output is compared to observed atmospheric PCBs concentrations;
2. climate scenarios comparison: the 20CE climate scenario is compared to the A2 climate scenario in terms of atmospheric PCBs concentrations.

In chapter 5 instead I will introduce a new level III fugacity model, which was created ad hoc for the present study. In this case, the chapter is structured in three parts:

1. model development: environmental parameters and chemical physical properties needed for the model parameterization are presented;
2. uncertainty and sensitivity analysis: an uncertainty analysis is presented and output variance is defined; also a sensitivity analysis is carried out;
3. climate change analysis: the environmental distribution of PCBs under the future climate A1B scenario is compared with the fugacity under the 20CE climate scenario.

Conclusions regarding all the activities carried out in this thesis are then discussed in chapter 6.

CHAPTER 4: MODELLING THE GLOBAL LEVELS AND DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN AIR UNDER A CLIMATE CHANGE SCENARIO

In this chapter the multimedia chemical fate model BETR Global was used in order to evaluate changes in the global distribution of two polychlorinated biphenyls, PCB 28 and PCB 153, under the influence of climate change. This was achieved by defining two climate scenarios based on results from a general circulation model, one scenario representing the last twenty years of the 20th century ("20CE scenario") and another representing the global climate under the assumption of strong future greenhouse gas emissions ("A2 scenario"). The two climate scenarios are defined by four groups of environmental parameters: 1) temperature in the planetary boundary layer and the free atmosphere, 2) wind speeds and directions in the atmosphere, 3) current velocities and directions in the surface mixed layer of the oceans, and 4) precipitation rate and geographical pattern. As a fifth parameter in the climate scenarios, the effect of temperature on primary volatilization emissions of PCBs was considered. Comparison of dynamic model results using environmental parameters from the 20CE scenario against historical long-term monitoring data of concentrations of PCB 28 and PCB 153 in air from 16 different sites shows satisfactory agreement between modelled and measured PCBs concentrations. The 20CE scenario and A2 scenario were compared using steady-state calculations and assuming the same source characteristics of PCBs. Temperature differences between the two scenarios are the dominant factor that determines the difference in PCB concentrations in air. The higher temperatures in the A2 scenario drive increased primary and secondary volatilization emissions of PCBs, *and enhance mobility from temperate regions to the Arctic. The largest relative increase in concentrations of both PCB congeners in air under the A2 scenario occurs in the high Arctic and the remote Pacific Ocean. Generally, higher wind speeds under the A2 scenario result in more efficient inter-continental transport of PCB 28 and PCB 153 compared to the 20CE scenario. This modelling indicates that, in a future impacted by climate change, increased volatilization emissions and increased mobility of persistent organic pollutants with properties similar to those of PCBs can be expected.*

4.1 Introduction

The term “climate change” is defined by the Intergovernmental Panel on Climate Change (IPCC) as a change in the climate condition that can be identified by changes in the mean value or variability of a climate property that persist for an extended time, typically decades or longer (Bernstein et al., 2007). Evidence of climate change has been observed at both global and local scales. It includes changes in surface temperatures and ice cover in the Arctic, widespread changes in precipitation pattern and amounts, ocean salinity, wind patterns and incidents of extreme weather including droughts, heavy precipitation, heat waves and intensity of tropical cyclones (Trenberth et al., 2007).

The scientific community has focused considerable attention on developing modelling tools to forecast global climate conditions. In 1980, the World Climate Research Programme (WCRP) was established with the goal to determine how predictable the climate is, and to assess the effect of human activities on climate. The WCRP, together with the Program for Climate Model Diagnosis and Intercomparison (PCMDI), provides technical support for modelling studies initiated by the IPCC. Recently, climate model output from simulations of the past, present and future up to the year 2100 was collected by the PCMDI as the third phase of the Coupled Model Intercomparison Project (CMIP3). This collection of modelling results is being used by the IPCC in the preparation of its Fourth Assessment Report and has been made publicly available to support scientific research about the potential effects of climate change.

Like climate change, environmental contamination by persistent organic pollutants (POPs) is an issue of global concern that is addressed by international agreements such as the Stockholm Convention (UNEP, 2001). Researchers studying POPs have developed global-scale mass balance models that are appropriate for explaining differences in environmental fate and transport between chemicals and for exploring the influence of environmental parameters on the environmental fate of chemicals (McKone and MacLeod, 2003).

To date, only a few studies have examined interactions between climate change and the environmental distribution of POPs (McKone et al., 1996; Dalla Valle et al., 2007; Macdonald et al., 2005; MacLeod et al., 2005; Ma et al., 2004; Becker et al., 2008). Information that is available is mostly focused on the Arctic, a region of particular interest to scientists studying both global warming and contamination by POPs.

Here the Berkeley-Trent global multimedia mass balance model (BETR Global) was used (MacLeod et al., 2001; MacLeod et al., 2005), together with information from the WCRP CMIP3 multi-model dataset, to model the fate of two archetypal POPs, PCB 28 and PCB 153, in the global environment. These substances were selected for this study because they are among the best characterized POPs in terms of physical chemical properties and emissions estimates. Attention was focused on the atmosphere because atmospheric transport largely determines source-to-receptor relationships for POPs (Stroebe et al., 2004) and because PCB 28 and PCB 153 have been the subject of long-term monitoring programs that characterize concentrations in the atmosphere. These time-resolved emissions and measurement data were used to evaluate modelled concentrations of these chemicals against measurements for the base-case climate scenario, i.e. the 20CE scenario as defined later in this chapter.

The environmental behaviour of PCBs and other persistent semi-volatile substances depends on complex interactions between many factors within an open environmental system. Therefore a comprehensive and predictive assessment of interactions between POPs and climate change is not technically feasible. The approach taken to address this problem is to only consider a manageable sub-set of possible changes in climate conditions in the model scenarios considered in this study, and to systematically explore the effects of those changes on modelled concentrations in air. In particular, the climate scenarios used here are defined by differences in 1) temperature, 2) atmospheric circulation patterns, 3) ocean circulation patterns and 4) precipitation rate. In addition, the effect of temperature differences between the climate scenarios on the rate of primary volatilization emissions of PCB 28 and PCB 153 were considered here, since this has been identified as the dominant mechanism of release of PCBs to the atmosphere (Breivik et al., 2007). Steady state model experiments that assume a fixed source profile for PCBs was used to explore the interactions between these selected aspects of climate change and the major processes that govern the global distribution of these two substances.

4.2 Materials and Methods

4.3.1 The model and its parameterization

BETR Global has a spatial resolution of 15° latitude x 15° longitude, or 288 grid cells that each define a model region. Each of these regions consists of up to 7 bulk compartments (ocean water, fresh water, planetary boundary layer –PBL, free atmosphere, soil, freshwater sediments, and vegetation). The model represents advective transport between the regions in air and water and inter-compartment transport processes like dry and wet deposition and reversible partitioning (MacLeod et al., 2005). To model degradation of PCBs in the gas phase, the version of BETR Global applied in this study uses spatially and temporally resolved concentrations of OH radicals in the global atmosphere derived from Spivakovsky et al. (2000).

BETR Global uses prescribed meteorological and oceanic data with a monthly time resolution. Precipitation rates, temperature fields and fluxes of air and ocean water across region boundaries are required as model inputs. In this project, these data were derived from the output of ECHAM5/MPI-OM (Roeckner et al., 2003), an atmosphere-ocean general circulation model (AOGCM). The datasets were obtained from the WCRP CMIP3 multi-model database, and are representative of the forecasts of the ensemble of models included in the IPCC's 4th Assessment Report (AR4) (Meehl et al., 2007). To evaluate the influence of a climate change scenario on the environmental distribution of POPs, two different climate scenarios are used: one scenario representing current climatic conditions ("20CE") and one representing a possible future climate in the year 2100 ("A2").

The 20CE-scenario is based on the AOGCM output for the years 1981 to 2000 of the CMIP3-"climate of the 20th century experiment" (20C3M). The A2-scenario is based on the output for the years 2080 to 2099 of the CMIP3-"SRES A2 experiment". The SRES (Special Report on Emission Scenarios) A2 scenario is the most extreme one among the four "marker scenarios" that were considered in AR4 with respect to assumed cumulative greenhouse gas emissions and consequently also with respect to predicted temperature change until 2100 (Nakicekovic et al., 2007; Bernstein et al., 2007).

From the AOGCM datasets, monthly averages over a 10-year period were calculated for 1) atmospheric temperature fields, 2) wind fields, 3) ocean current fields in the surface mixed layer, and 4) precipitation rates. These datasets were then re-gridded to match the spatial resolution of BETR Global, yielding a representative year of climatic conditions for each scenario that can be used to drive dynamic model calculations. The data were also averaged over the year to arrive at two steady state climate scenarios that can be used in steady state model calculations. The differences in these four environmental parameters between the two steady-state climate scenarios are illustrated in Figures A1-A5 in the Appendix A. In general, temperature in the planetary boundary layer is higher throughout the world under the A2 scenario, particularly in the Arctic. Wind speeds are also higher in the A2 scenario, particularly in the west-to-east direction at middle and high latitudes in both hemispheres. Ocean currents are faster in the west-to-east direction in the A2 scenario compared to the 20CE scenario, particularly at latitudes near the Antarctic and at high latitudes in the Northern Hemisphere in the Atlantic Ocean. Precipitation increases under the A2 scenario, particularly in the Equatorial areas.

4.3.2 Physicochemical properties and emission scenarios for PCB 28 and PCB 153

Partitioning properties of PCB 28 and PCB 153 from Schenker et al. (2005), and internal energies of phase change recommended by MacLeod et al. (2007b) are used in this study. Pseudo-first order degradation half-lives in air were calculated from second-order hydroxyl radical reaction rate constants extrapolated from data presented by Anderson and Hites (1996) and spatially and temporally resolved concentrations of OH radicals in the global atmosphere specified in the model; degradation half-lives in other compartments were estimated based on information in Wania and Daly (2002) and the generic half-life classes recommended by Mackay et al. (2006). These properties are shown in Appendix A in Table A1.

Breivik et al. (2007) estimated the yearly global emissions of 22 PCB congeners for the period 1970-2100 using a mass balance approach that estimates production, use, disposal and accidental spills of PCBs over their life-cycle. Because of the high uncertainties associated with these emission estimates, Breivik et al. (2007) presented “max”, “default” and “min” emission estimates.

The information in 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. This is important for this modelling study because the strength of primary passive volatilization sources depends on temperature according to equation 4.1:

$$\frac{E_2}{E_1} = \exp\left[\frac{\Delta U_\mathrm{A}}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \qquad (4.1)$$

where (E_2/E_1) is the ratio of the emission rates by passive volatilization at temperatures T_2 and T_1, ΔU_A is the internal energy of vaporization of the PCB congener, and R is the gas constant. Equation 4.1 was applied to model the intra-annual variability in PCB emissions in response to the seasonal cycle of temperature in the dynamic model runs used for the model evaluation. These results will be presented in the next paragraph. In addition, since temperature is one of the key variables in the two climate scenarios, Equation 1 was used to estimate the increase in primary PCB emissions associated with increased temperature under the A2 scenario relative to the 20CE scenario. The rate of secondary revolatilization of PCBs from water, soils and vegetation is also temperature dependent, but this is accounted for in the basic model structure of BETR Global.

4.3.3 Model performance evaluation

As a prerequisite to compare the fate of PCBs under the two climate scenarios, selected emission scenarios, physicochemical properties and environmental fate model were verified to provide together a reasonable representation of PCBs in the global environment. To this end, dynamic model calculations were conducted to evaluate the performance of the model when it is run under the conditions of the 20CE scenario. Then, steady-state calculations for two model experiments were performed (described further below), where the 20CE and the A2 scenarios are compared.

To evaluate the model, modelled concentrations of PCB 28 and PCB 153 are compared under the 20CE climate scenario with PCB concentrations measured in air at 16 monitoring stations located in 9 different model regions (see Table A2 in Appendix A). Dynamic model results for the two PCB congeners were calculated for both the “max” and “default” emission scenarios from Breivik et al. (2007) for the entire 170-year period from 1930-2100. This evaluation improves on the one reported earlier by MacLeod et al. (2005) by (i) applying a new parameterization and new version of the model with improved treatment of degradation in the atmosphere and the intra-annual variability of primary volatilization emissions, and by (ii) considering more monitoring stations and additional monitoring data that has become available since the previous model evaluation.

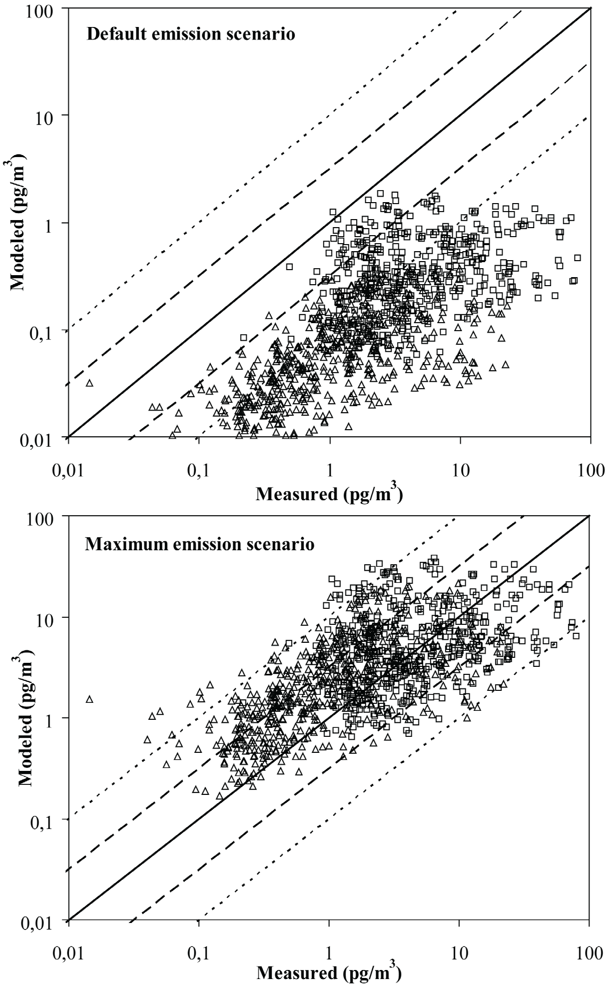

FIGURE 4.1. Comparison of seasonal average measured and modelled concentrations of PCB 28 (□) and PCB 153 (Δ) in air for the default and the maximum PCB emission estimates from Breivik et al. (2007). Measurement data are from the 16 monitoring stations located in 9 different BETR regions and seasonal averages are for 3-month periods beginning in January. Diagonal lines indicate perfect agreement, and agreement within factors of $10^{0.5}$ and 10.

Figure 4.1 compares modelled and measured seasonal (3-month) average concentrations of the two PCB congeners in air at the 16 monitoring stations for the two emission scenarios. Included in Figure 4.1 are data points for the period from 1990 to 2007, for which measured concentrations are available. Diagonal lines representing perfect agreement and agreement within factors of $10^{0.5}$ (= 3.16) and 10 are shown for comparison. Concentrations are clearly under-predicted with the default emission scenario. With the maximum emission scenario, 64% of the modelled concentrations are within a factor of 3.16 of the measured concentrations, and 96% are within one order of magnitude of the 1:1 line. This agreement between measured and modelled concentrations is viewed as satisfactory. Because the maximum emission scenario provides better agreement with field data, this one was used in the steady state calculations to compare the two climate scenarios.

Figure A6 in Appendix A illustrates the same data as Figure 4.1, but as time series of modelled and measured concentrations of PCB 28 and PCB 153 at the different monitoring sites. At most sites, the model provides a reasonable description of the intra-annual variability and the inter-annual trends in the monitoring data.

4.3.4 Model experiments

Two model experiments were performed to compare the fate of PCB 28 and PCB 153 under the two climate scenarios. In the first experiment modelled concentrations of PCBs under the 20CE and A2 scenarios are compared, then several sub-scenarios based on the 20CE scenario are parameterized, where one of the five groups of parameters that differ between the two climate scenarios is replaced, i.e. temperature, atmospheric circulation, oceanic circulation, precipitation or emissions with parameter values from the A2 scenario. This model experiment is designed to identify the effect of individual groups of environmental parameters on PCB distribution. In this experiment, spatial distribution of PCB emissions corresponding to the maximum emission scenario was assumed.

The second experiment is performed in order to identify the effect of climate change on the distribution of PCBs released from different source regions. Five hypothetical emission scenarios were considered as follows: North America, Europe, Asia, and South America, respectively, are the only primary source regions for PCBs, and the results between the 20CE and A2 parameterizations of the model are then compared. According to the information reported by Breivik et al. (2007), emissions are from the Great Lakes region and the United States north-east coast in the North America scenario, from central and eastern Europe in the European scenario, from the east coast of China and northern Japan in the Asia scenario and from southern Brazil in the South America scenario assumed in this study.

In both model experiments steady-state concentrations of PCB 28 and PCB 153 in the global environment are computed, using annual average climate conditions. Volatilization sources of PCBs were distributed to each region according to total estimated emissions during the 170 year long maximum emission scenario estimated by Breivik et al. (2007) and are the same in both climate scenarios. However, the emission rate to the atmosphere from these sources is adjusted for temperature as described above. To highlight the changes in levels and distribution attributable to differences in climate, these model experiments do not consider the large reductions in sources of PCBs that are expected to occur during the 21st century (Breivik et al., 2007). Instead, two alternative climate scenarios were compared, assuming that source characteristics of PCBs are the same in both scenarios and model results are then analysed for the two PCB congeners in terms of global and hemispheric concentration levels and source-to-receptor relationships, with a focus on concentrations in the planetary boundary layer.

4.4 Results

Results of the model experiments are presented in Figures 4.2 (first experiment) and 4.3 (second experiment) as the ratio of concentration of PCBs in the planetary boundary layer in the A2 climate scenario to concentration in the 20CE scenario. Figures A8 and A9 in the Appendix A show the same information as the difference in modelled concentrations in the planetary boundary layer between the 20CE and the A2 scenarios.

Figure 4.2A shows the ratio of modelled concentrations of PCBs at steady state in air in the planetary boundary layer under the A2 climate scenario to the concentrations under the 20CE scenario. For both congeners, concentrations in air are higher everywhere in the global atmosphere under the A2 scenario. The spatial pattern of increased concentrations is similar for PCB 28 and PCB 153 but the increase is more pronounced for PCB 153, up to a factor of 2.5, compared to a factor of 1.8 for PCB 28. Areas of notable increase in modelled concentrations are the Arctic and the equatorial Pacific Ocean.

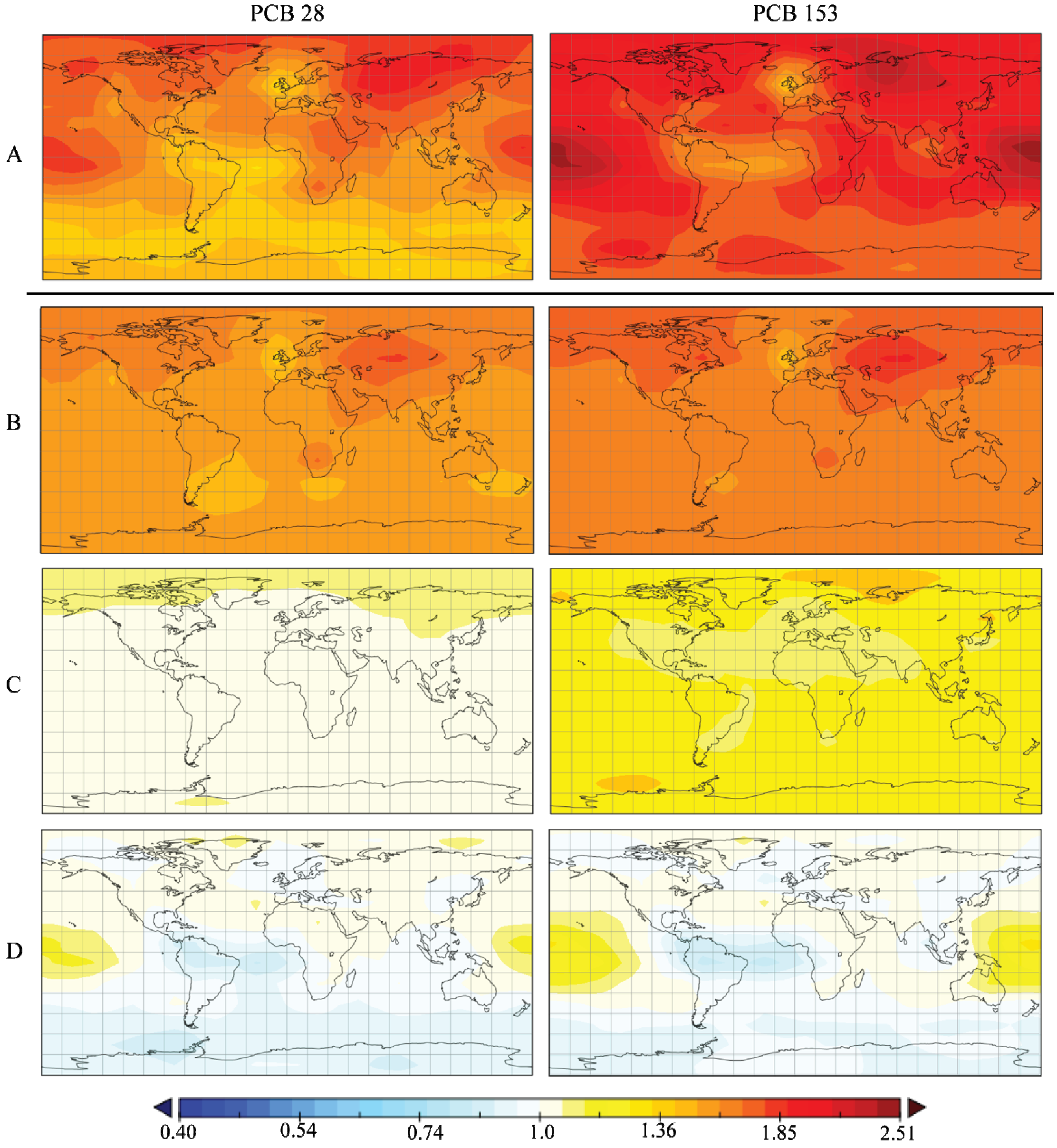

FIGURE 4.2. Ratio of modelled concentrations of PCBs at steady-state in the planetary boundary layer of the atmosphere under hypothetical climate conditions to modelled concentration under 20th century (20CE) conditions for PCB28 (left) and PCB153 (right). The hypothetical climate conditions are: (A) the A2 climate change scenario; (B) the 20CE scenario with primary emission rates adjusted to reflect temperature in the A2 scenario; (C) temperature fields from the A2 scenario (excluding temperature influence on primary

emissions), other parameters as in 20CE, and; (D) wind fields from the A2 scenario, other parameters as in 20CE.

The other panels of Figure 4.2 show results from the first model experiment, where hypothetical climate scenarios were built taking one climate parameter from the A2 climate scenario and all other parameters from the 20CE scenario. Shown are the three parameters with the strongest influence on the concentration patterns in air. These are temperature effects on emissions (panel B), temperature effects on dynamic re-partitioning and degradation (panel C) and wind speeds (panel D). The other two environmental parameters, oceanic currents and precipitation, lead to much smaller changes in environmental behaviour of PCBs in lower air (Figure A7).

Figure 4.2 shows that different parameters contribute to the overall difference between the A2 and 20CE scenarios at different locations. The effect of temperature on primary emissions (Figure 4.2B) results in a general increase in concentrations throughout the globe that is stronger for PCB 153 than for PCB 28. This increase is strongest over central Asia, which is caused by increased primary volatilization emissions in eastern Europe and Russia. The effect of higher temperatures under the A2 scenario on environmental partitioning and degradation of PCBs results in higher concentrations globally, especially in the Arctic and, to a lesser extent, the Antarctic (Figure 4.2C). The changes in atmospheric circulation patterns account for higher concentrations of both congeners in the equatorial Pacific, and lower concentrations in the equatorial Atlantic and over Antarctica (Figure 4.2D).

Figure 4.3 shows results for the second model experiment, in which the A2 climate scenario is compared to the 20CE scenario for emissions only in North America, Europe, Asia, and South America. For PCB 28, regardless of emission location, the modelled concentrations in air in the hemisphere where emissions occur increase, and there is a slight decrease in the other hemisphere, reflecting that the average half-life of PCB 28 in air is not long enough for efficient inter-hemispheric mixing. Furthermore, modelled concentrations of PCB 28 are higher in the direction “downwind” (i.e., eastward) of the source regions under the A2 scenario, and are in some cases lower immediately “upwind” (i.e., westward). This trend implies an increased potential for inter-continental transport and transport into the Arctic, and is most obvious for emissions in Europe, but is also apparent for emissions in North America and Asia. For PCB 153, modelled concentrations in air increase in both hemispheres under the A2 scenario compared to the 20CE scenario. The pattern of higher concentrations downwind from source regions under the A2 scenario is again evident, implying increased inter-continental transport and transport to the Arctic. In all scenarios, the modelled PCB concentrations in equatorial regions over the Pacific Ocean are higher under the A2 scenario than under the 20CE scenario.

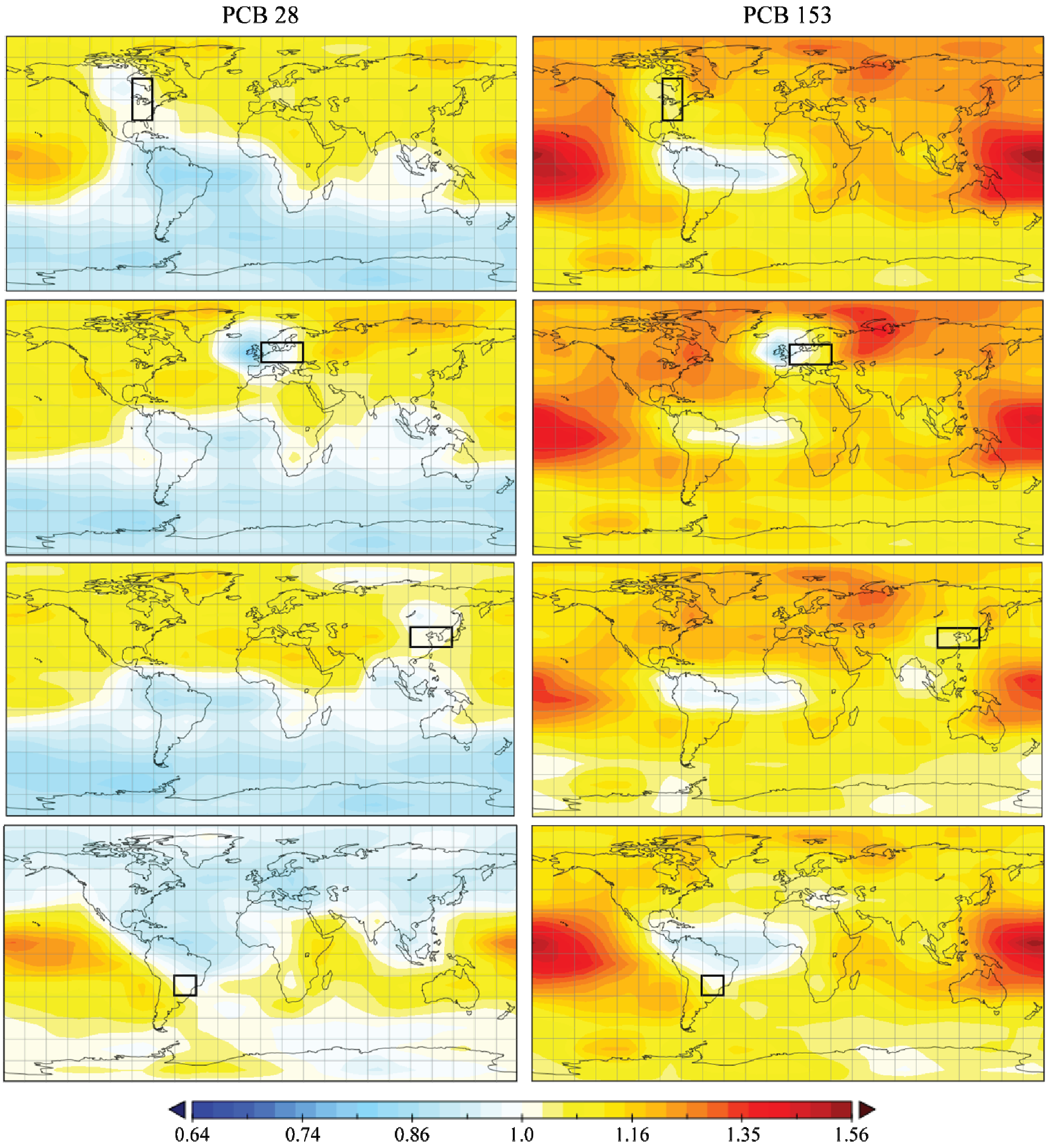

FIGURE 4.3. Ratio of modelled PCB concentration at steady state in the planetary boundary layer of the atmosphere under the A2 climate scenario to modelled concentration under the 20CE scenario for PCB28 (left) and PCB 153 (right) for emission in North America, Europe, Asia and South America (top to bottom).

4.5 Discussion to chapter 4

First, a model evaluation of BETR Global is reported, where modelled concentrations for PCB 28 and PCB 153 are compared to field data. The agreement between measured and modelled concentrations (Figure 4.1 and Figure A6 in Appendix A) demonstrates that, under the 20CE scenario, the model can account for much of the variability in monitoring data between sites and over time. The dynamic version of the model was used for the model evaluation, whereas the effect of the climate change scenario was examined using steady-state calculations. Dynamic calculations were used to evaluate the model against recent monitoring data because PCBs are not currently near steady-state in the global environment. However, steady-state concentrations were selected to evaluate the effect of the A2 climate scenario because they reflect the long time-scale associated with POPs, and the steady-state concentration is a surrogate for cumulative environmental exposure, regardless of the temporal pattern of emissions (von Waldow et l., 2008). Therefore, this modelling exercise does not predict concentrations of contaminants in the atmosphere in the future, but rather analyzes changes relative to a base case scenario under a climate change scenario.

Second, results from the first model experiment identified temperature and atmospheric circulation patterns as the climate parameters affecting the PCB distribution in the planetary boundary layer most strongly. The increase of primary volatilization emissions as a result of higher temperature in the A2 scenario is the single most influential effect of climate change on the modelled concentrations of both PCB 28 and PCB 153 in air. The effect of increased temperature on the strength of primary volatilization emissions of POPs has not been explicitly characterized in earlier modelling studies (McKone et al., 1996; Dalla Valle et al., 2007; MacLeod et al., 2005), which focused on the impact of changes in atmospheric circulation, rainfall, and the effect of temperature on secondary re-emission from soils and vegetation. However, results demonstrate that the more efficient mobilization of POP-like substances from primary sources in a future impacted by global-scale warming may dominate all other effects of climate change on global-scale pollutant dynamics. The larger absolute value of the internal energy of vaporization (ΔU_A) of PCB 153 (−91.6 kJ/mol) relative to PCB 28 (−77.6 kJ/mol) accounts for the stronger effect of temperature on emissions of PCB 153.

Thirdly, the results in Figure 4.2C demonstrate that higher temperatures in the A2 scenario result in higher modelled concentrations of both PCB congeners in air, even when emissions are held constant. This is the net result of two competing parameters, (i) increased volatilization from secondary sources, which is determined by ΔU_A, and (ii) increased degradation in surface media, which is determined by the assumed activation energies for degrading reactions (30 kJ/mol for all compartments except the atmosphere, where the degradation rate constant is only a function of hydroxyl radical concentrations). Modelled concentrations in air due to secondary volatilization are higher in the warmer A2 scenario because volatilization rate is more temperature dependent than degrading reactions in surface media. However, the overall persistence in the multimedia environment is lower under the A2 scenario (PCB 28: 2.7 years in the A2 scenario versus 3.8 years in the 20CE scenario; PCB 153: 8.7 years versus 10.9 years). Therefore, model results suggest that substances with properties similar to those of PCBs are less persistent in the environment, but more efficiently transported in the global atmosphere under the A2 scenario compared to the 20CE scenario.

Shindell et al. (1999) used results from a GCM to argue that a future impacted by anthropogenic climate change would be characterized by a persistent shift towards positive values of the North Atlantic Oscillation (NAO) index. Two earlier modelling studies have used historical data to examine relationships between positive NAO index and global-scale pollutant transport in the atmosphere (Shindell et al., 1999; MacLeod et al., 2005). Both of these studies found increased transport of pollutants to the Arctic under positive NAO conditions. The findings reported in this chapter are consistent with these earlier studies in that the modelled transport of PCBs to the Arctic is higher in the A2 climate change scenario. In addition, the finding that transport of pollutants from European sources to the Arctic is more enhanced in the A2 scenario than transport from sources in North America or Asia is consistent with the results reported by Eckhardt et al., 2003.

The model results presented here provide some initial estimates of the possible effects of climate change on the environmental distribution of POPs, and this activity can be considered as a first step in answering the questions put forward by the UNECE (2008) on this topic. Overall, this model assessment forecasts that under the influence of climate change the world may, in effect, “become smaller”, i.e., enhanced volatilization emissions of POPs can be expected to be more efficiently transported across national boundaries and into remote areas. However, it should be recognized that this work is not a comprehensive assessment. Only four environmental parameters are considered in the climate scenarios, and these do not cover the full spectrum of phenomena that may result from climate change.

CHAPTER 5: MODELING THE INFLUENCE OF CLIMATE CHANGE ON THE MASS BALANCE OF POLYCHLORINATED BIPHENYLS IN THE ADRIATIC SEA

Climate forcing by greenhouse gasses is forecasted to influence the Adriatic Sea region in a variety of ways, including temperature, wind speeds, oceanic currents, precipitation and water salinity. The Adriatic Sea is intensively developed with agriculture, industry, and port activities that introduce pollutants to the environment. Here, a new Level III fugacity model is developed and applied 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 PCB 52, 138 and 153 against measured concentrations in the region using the 20th Century (20CE) climate scenario described in the Special Report on Emission Scenarios (SRES) by the IPCC, and using Monte Carlo uncertainty analysis. Modeled fugacities of PCBs in air, water and sediment of the Adriatic are in good agreement with observations under the assumption that atmospheric deposition is the main source of PCBs to the Sea. Model experiments are used to assess the influence of the forecast future changes in (1) atmospheric temperature, (2) wind speed, (3) precipitation, (4) oceanic currents, (5) oceanic temperature, and (6) particulate organic carbon on the mass balance of PCBs under the IPCC A1B climate scenario. Modeled fugacities of PCBs in the Adriatic Sea under the A1B climate scenario are higher for a set emission scenario because higher temperatures reduce the fugacity capacity of air, water and sediments. Higher bioconcentration factors in homeotherms is a possible implication of this finding.

5.1. 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, port activities 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 system 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).

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, occurrence of extreme weather events etc. (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 Environmental Program (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 (see chapter 4, and some other studies: Becker et al., 2008; Ma et al., 2005; Dalla Valle et al., 2007, MacLeod et al., 2005).

Although the mass budget of PCBs in the Venice Lagoon and the Western Mediterranean have been studied, a detailed knowledge about the occurrence and behavior of these chemicals 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, especially in a climate change perspective. Projections of the extent of future climate changes in the Adriatic Sea based on simulations of climate models provide forecasts for several climate variables such as temperature, wind speeds, oceanic currents, precipitation, salinity, water temperature. 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 some understanding of the influence of a climate scenario on the fate of pollutants in the aquatic and atmospheric environment of the Adriatic Sea.

In this study climate projections for the Mediterranean area developed in a recent intensive study (SIMTA, Gualdi et al., 2008) are used 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: PCB 52, 138 and 153. The influence of variation in seven 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 is estimated. The seven environmental parameters are: (1) atmospheric temperature, (2) wind speed, (3) precipitation, (4) oceanic currents, (5) oceanic temperature, (6) temperature effect on emissions (7) particulate organic carbon (*POC*) content in marine water.

5.1.2. The study area

The major axis of the Adriatic Sea is oriented in the northwest-southeast direction. The northern section is very 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., 1997a). 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).

5.2. Methods

5.2.1. Model development

On the basis of its physical (Artegiani et al., 1997a, b), biological (Zavatarelli et al., 2000) and oceanographic characteristics, the model of the fate of PCBs in the Adriatic Sea divides it into three sub-regions: the North Adriatic Sea (NAS), the Central Adriatic Sea (CAS) and the South Adriatic Sea (SAS), as it is shown in Appendix B of this thesis, in Figure B1.

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 in air, degradation by OH· reaction in air, and degradation in water and sediment are considered as intermedia and intramedium processes in the model presented here. Figure 5.1 represents graphically the processes taken into account by the model.

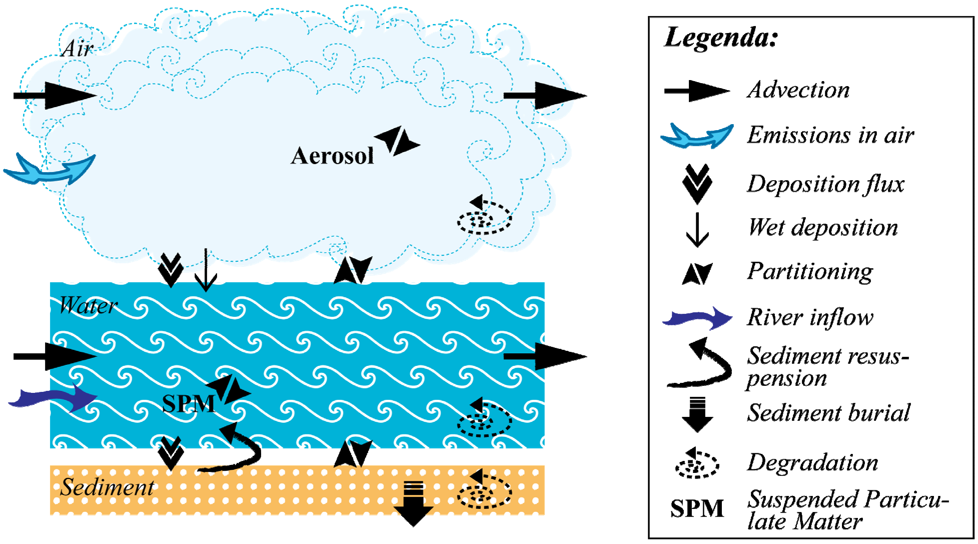

Figure 5.1. Processes taken into account in the Adriatic Sea level III fugacity model presented in this project.

The model has been applied 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.

5.2.2. *Model parameterization*

Partitioning properties for the selected chemicals were taken from Schenker et al. (2005), internal energies of phase change are recommended by MacLeod et al. (2007b). 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 B1.

Model input values for environmental parameters are defined for the Adriatic Sea according to Table B2. 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 (20th century scenario, 20CE), and the 21st century scenario under the A1B scenario as described in the Special Report on Emission Scenarios by the IPCC in the year 2100 (Nakicenovic et al., 2000). These data and the related estimates of uncertainty used in the Monte Carlo analysis are reported in tables B3-B7.

5.2.3. Uncertainty analysis

This model simulation is based on selected input parameters describing environmental properties, chemical properties, chemical release rates and background concentrations. Inputs uncertainties have been estimated as confidence factors (*Cfs*), where 95% of possible values lie between *Cf* times the median and the median divided by *Cf* (MacLeod et al. 2002). The *Cfs* for climate variables were calculated from the EBU POM output database, as it is shown in tables B3-B7 (*Cfs* in parentheses); the variability in other properties were estimated based on uncertainty analysis studies in the literature (MacLeod et al., 2002). The parameters for compartmental dimensions were assumed to be fixed values and marked with *Cf=1*. For background concentrations the uncertainty is defined by previous model experiments (see chapter 4).

Propagation of variance in inputs into the model results was evaluated through a Monte Carlo analysis. Uncertainty analysis in this study was meant to estimate the total variance in model output and to identify parameters that are most important in determining the variance of the outputs. The Crystal Ball™ software package was used to provide a contribution to variance analysis for individual parameters, and to estimate uncertainty in model outputs due to uncertainty in all input parameters.

5.2.4 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, the same emission is assumed 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 primary volatilization. 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. In the A1B climate scenario, the variation in emission related only to the difference in temperature (ΔT) between the 20CE and the A1B scenario was considered as a sixth varying parameter under the A1B scenario (see equation 4.1, reported also here):

$$\frac{E_{20CE}}{E_{A1B}} = \exp\left[\frac{\Delta U_A}{R} \cdot \left(\frac{1}{T_{20CE}} - \frac{1}{T_{A1B}}\right)\right] \qquad (4.1)$$

where ($E_{\mathrm{20CE}}/E_{A1B}$) 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), and R is the gas constant.

5.3. Model experiments

First, as a prerequisite to compare the fate of PCBs under the two climate scenarios, confidence was built on that the selected emission scenario, physicochemical properties, and environmental fate model together provide a reasonable representation of PCBs in the Adriatic Sea environment. To this end, the model calculations from the 20CE model scenario were compared against measurements from the real environment to evaluate the performance of the model. For the atmosphere, data from Monodori et al. (2006) and Klanova et al. (2007, 2007b) were used to estimate concentrations in the NAS and CAS. For the coastal water environment measures from Ferrara and Funari (2004) were used. 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 solid density of 2550 $\mathrm{Kg \cdot m^{-3}}$ (Frignani et al., 2005).

Second, several model experiments were performed to compare the fate of PCB 52, 138 and 153 under the 20CE and the A1B climate scenarios. In a first experiment modeled concentrations and fugacities of all three PCBs under the 20CE and A1B scenarios are compared. Then, several sub-scenarios are parameterized based on the 20CE scenario, where one of the six factors that differ between the two climate scenarios were replaced with parameter values from the A1B scenario, i.e. (1) atmospheric temperature (T_A), (2) atmospheric emissions (T_{EMISS}), (3) coastal water temperature (T_W), (4) atmospheric circulation ($u,v_{(AIR)}$), (5) marine circulation ($u,v_{(SEA)}$), (6) precipitation (*rain*). A change in (7) POC (*POC*) was also considered, and 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. A factor of change, F, the ratio of model results under the alternative scenario and 20CE scenarios was used in order to compare the different scenarios.

5.4. Model results

5.4.1. Model evaluation

The model is evaluated 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 directly proportional to concentration (C, mol/m^3). The proportionality constant between the two is the fugacity capacity (Z, Pa m^3/mol), thus, ($C=f\cdot Z$). 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. Fugacity is considered 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.

Figure 5.2 shows fugacities calculated from measured concentrations of PCBs in air, water and sediment in the Adriatic compared to modeled fugacities (Pa). 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 an apposite review of monitoring studies. The comparison is possible for 8 of the 9 modeled compartments; no measured data for the comparison 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 (Figure 5.2). 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 are model results outside of a factor of 3.16 of the measurements (see Figure 5.2.b).

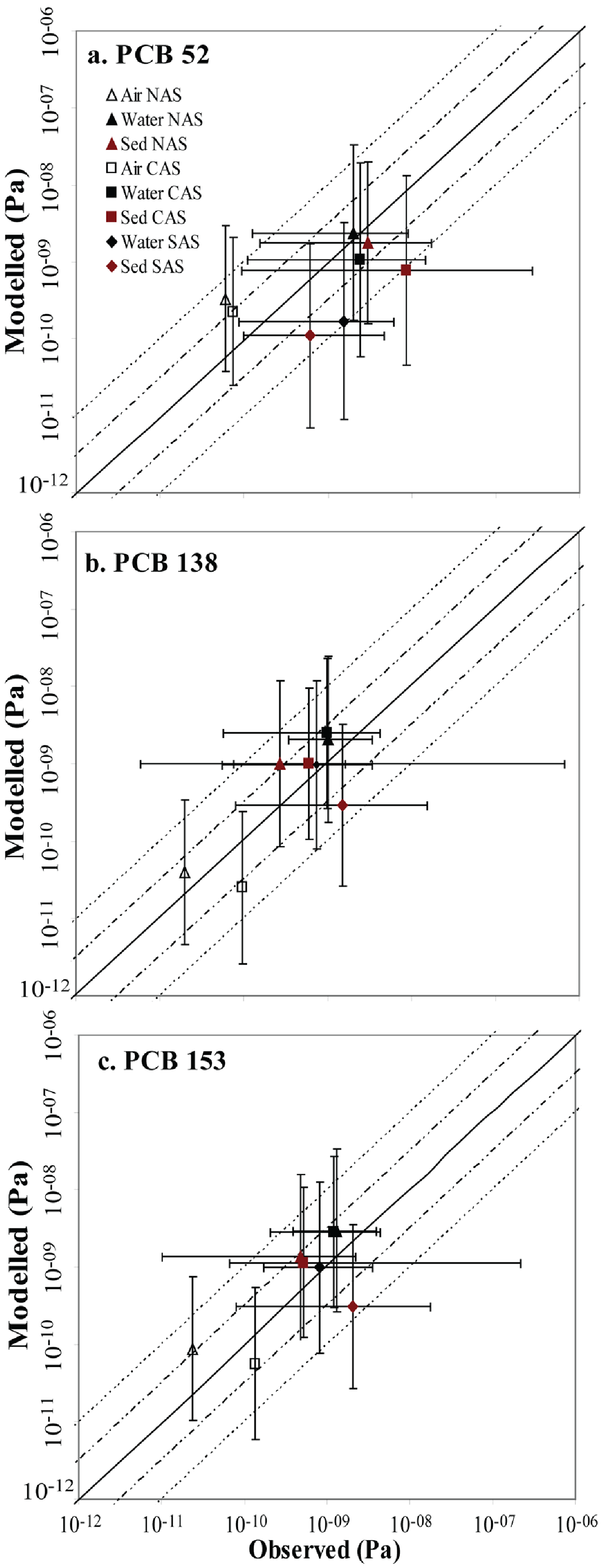

Figure 5.2. Comparison of measured and modeled concentrations of a. PCB 52, b. PCB 138 and c. PCB 153 in air, water and sediment. Diagonal lines indicate perfect agreement, and agreement within factors

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 the Monte Carlo uncertainty analysis.

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. 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 suspended particulates to the sediment.

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 lays within one order of magnitude for both regions. Mass balances for the three PCB congeners are shown in Figure B2 where fluxes are reported as mol/h. 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 2.05, 20.34 and 11.53 years. The longer residence times of PCB 138 and PCB 153 are due to higher hydrophobicity and longer degradation half-lives in all compartments.

5.4.2 Sensitivity and Uncertainty analysis

Sample results of the sensitivity and uncertainty analysis for PCB 153 are shown in Figure 5.3 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 octanol-air partition coefficient (K_{OA}) in all compartments, reflecting the importance of deposition from the atmosphere in determining the level of PCBs in the system. The background concentration of PCBs in air and aerosol concentration in air and deposition rate are influential in determining the modeled fugacity in air.

In water, temperature and K_{OW} play an important role and half-life in sediment is more prominent in determining the uncertainty associated to the output sediment fugacity. Figures B3 and B4 in the Supplementary Material show the sensitivity results for PCBs 52 and 138. The uncertainty analysis allowed us to estimate the output uncertainty for fugacity in all the different compartments. For the lower chlorinated PCB 52 K_{OA}, degradation half-lives and OH· reaction constant play an important role as chemical parameters in determining the results. For the highly chlorinated PCBs 138 and 153 degradation is less important, and K_{OA} and K_{OW} are important in determining the results. Environmental parameters playing an important role are solids fraction in aerosol, density of solids and sediment, and organic carbon content for PCBs 138 and 153, which are more hydrophobic and hence have a higher affinity for the solids fraction in the different media. Among considered climate variables, model outputs are most sensitive to water temperature and marine currents. These parameters are also defined under the two climate scenarios, and this is reflected also in the trend of $F_{U,V(SEA)}$ and F_{TW}, which are important in driving the F_{A1B} (see Figure 5.4).

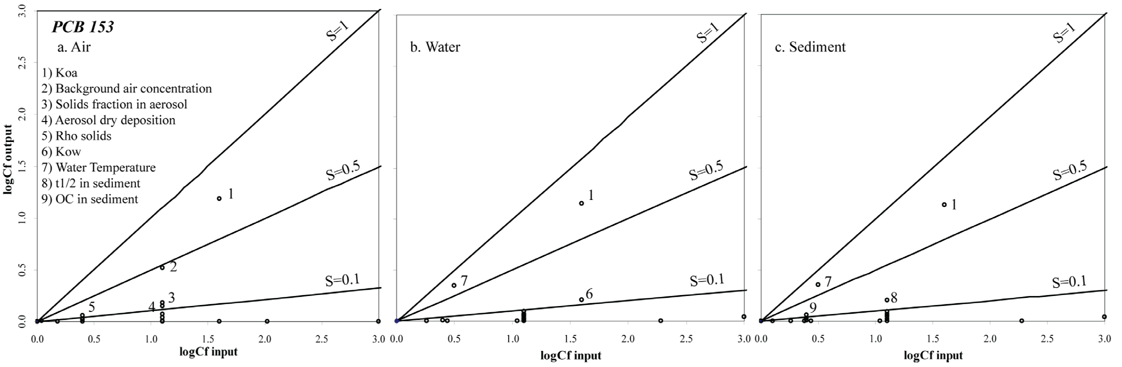

Figure 5.3: Graphical analysis of contribution to uncertainty in steady state fugacity of PCB 153 in the CAS. Analysis for a. atmosphere, b. water and c. sediment. The most important individual input parameters in terms of contribution to uncertainty in total steady state fugacity of PCB 153 are K_{OA} for all compartments, and background air concentration and aerosol solids fraction and dry deposition are important in determining the output fugacity for air, whereas for water and sediment temperature, K_{OW}, OC content and sediment half-life are more influential. Lines corresponding to sensitivity S=1, 0.5 and 0.1 are shown.

5.4.3. Model results for climate scenario experiments

Figure 5.4 shows the factor F – the ratio of modeled fugacity (f), fugacity capacity (Z), or concentration (C) in the alternate climate scenario to the fugacity in the 20CE scenario – for model experiments for PCB 153. F_{A1B} represents the ratios under the A1B and the 20CE climate scenarios. To understand which environmental variables within the ones defined under a climate change scenario are more important in determining a different environmental behavior, $F(f)$, $F(Z)$ and $F(C)$ are calculated also for the single-parameter climate scenarios, and compared the results with the F_{A1B}. F_{TA}, $F_{U,V(AIR)}$, F_{EMISS}, F_{RAIN}, F_{POC}, F_{TW}, $F_{U,V(SEA)}$, are factors of change for, respectively atmospheric temperature, wind speeds, temperature effect on emissions, precipitation, POC, sea temperature and marine currents.

Under the A1B scenario, modeled fugacities of PCB 153 are between a factor of 1.5 and 2.5 higher than under the 20CE scenario (white squares in Figure 5.4.a). Because $C=fZ$, 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 1.2 of values for the 20CE scenario (white squares in Figure 5.4.c), and it is evident that higher fugacities under the A1B scenario are primarily a result of lower fugacity capacities (white squares in Figure 5.4.b). Figure B6 shows the same information for PCB 138, which behaves very similarly to PCB 153.

F(f) calculations for PCB 52 fall in the range 1.5-2.0, this means that modeled fugacities for this congener are between a factor of 1.5 and 2 higher under the A1B scenario compared to the 20CE climate scenario (white squares in Figure B5.a). Modeled concentrations under the A1B climate scenario are within a factor of 0.7 and 1.2 of values for the 20CE scenario (see white squares in Figure B5.c), hence it is clear that the higher fugacities under the A1B scenario for PCB 52 are also primarily a result of lower Z (Figure B5.b, white squares).

Furthermore, the comparison of Figures 5.4, B5 and B6 shows that an increase in concentration is expected only in atmosphere for PCB 52, whereas a decrease is observed in water and sediment, where the chemicals tendency to escape is enhanced under the A1B climate scenario.

Figure 5.4.a shows that the modeled fugacity of PCB 153 is higher under the A1B scenario in all compartments. Figure 5.4.a, 5.4.b and 5.4.c show cases were $F(f)_{A1B}>1$ is

attributable to both a $F(Z)_{A1B}$<1 (as it can be observed for F_{TW}, F_{TA}, F_{A1B}), or an increase in concentration C ($F_{U,V(SEA)}$). From the comparison for the other F, it can be observed that $F(f)_{TA}>1$ and $F(f)_{TW}>1$ are explained by the $F(Z)_{TA}<1$ and $F(Z)_{TW}<1$ (see Figure 5.4.b). POC and wind velocities do not strongly affect Z, in fact from Figure 5.4 it is evident that $F(f)_{POC}$ and $F(f)_{U,V(SEA)}$ are determined almost entirely by $F(C)_{U,V(SEA)}$ and $F(C)_{POC}$.

Figure 5.4 shows that the most influential environmental variables for modeled fugacity of PCBs are T_A, T_W, $u,v_{(SEA)}$, and POC. Precipitation and effect of temperature on emissions do not play an important role in determining the environmental fugacities under the A1B scenario. This may be due to the fact that precipitation was underestimated in the 20CE climate scenarios (likely this may happen also under the A1B scenario), and the change between the two climate scenarios was very low (the highest expected variation is 0.31 mm/y in the central Adriatic Sea under the A1B scenario, see Table B5). Also the effect of temperature on volatilization from primary sources does not account much for the increase in fugacities in the future, in fact the fugacity ratio is always closed to 1. Previous studies showed that under a climate change scenario the temperature effect on primary volatilization of PCBs would increase concentrations everywhere (see the case study presented in chapter 4 of this thesis), thus background concentration would be higher everywhere. In the present study only the temperature effect on primary local emissions have been considered, and this is why the temperature effect on emissions is low.

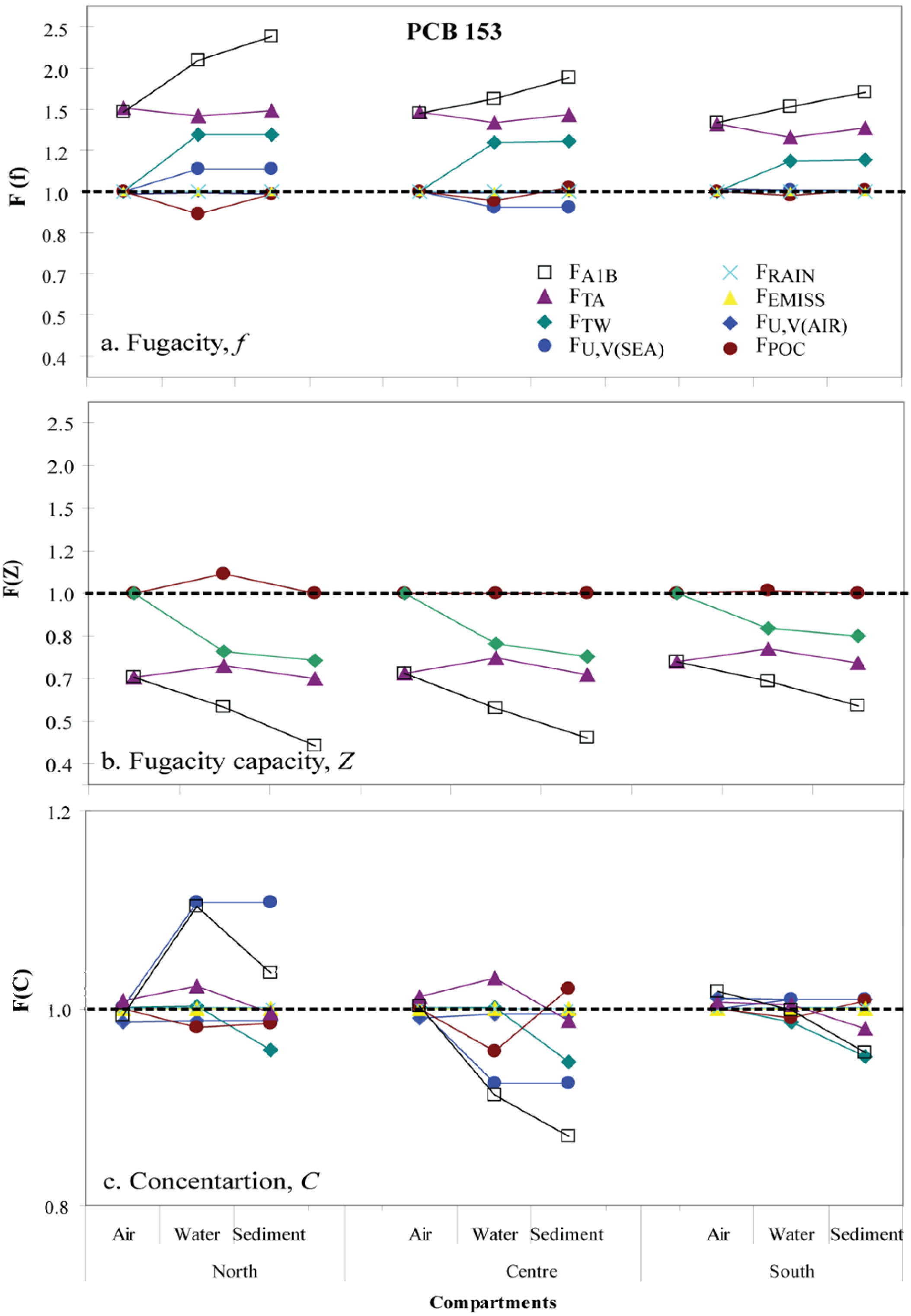

Figure 5.4. Experiments results are shown here for PCB 153. a: here the F – factor of change – for fugacities in the different compartments and regions is shown; b: the F values for Z are shown (only T_A, T_W and $u,v_{(SEA)}$ and POC contribute to determine a change in Z); c: F for concentration in 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_{EMISS}*,* F_{RAIN}*,* F_{POC}*,* F_{Tw}*,* $F_{U,V(SEA)}$*, stand respectively for atmospheric temperature increase, air velocity, temperature effect on emissions, precipitation, POC, sea temperature and sea currents factor of change. The increase in F for fugacity can be explained either from a decrease in Z or by an increase in C.*

5.5. Discussion of the results presented in chapter 5

A new mass balance for PCBs 52, 138 and 153 in the Adriatic Sea is reported in this chapter. The agreement between measured and modeled fugacities shown in Figure 5.2 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. This 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. 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. This mass balance indicates that in the Adriatic, the main input of PCBs comes from atmospheric deposition and sediment resuspension rather than from emissions to water.

Furthermore, from the mass balance presented in this study it can be observed that OH· reaction is important for PCB 52 (in Figure B3), but the influence of this parameter is much lower for PCB 138 and 153 (Figures B4 and 5.3 respectively). A mass balance of the Eastern Mediterranean (Mandalakis et al., 2005) reported that the main depletion pathway of PCBs from atmosphere was OH· reaction for PCBs with up to 6 Chlorines, whether for higher chlorinated PCBs the main depletion pathway was deposition from atmosphere; the model output is in fact sensitive to aerosol deposition ($S>0.1$ in Figures 5.3 and B4).

Results from the model experiments for the climate change scenarios show that PCB concentrations in the environment do not change significantly in the A1B scenario in response to changes in environmental conditions, when emissions are kept constant. However, fugacities are expected to increase by a factor of 1.5-2.5 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 this study was focused on the abiotic environment, it can be noted that lower fugacity capacities of the environment could have implications for bioconcentration potential of pollutants. Homeotherms maintain a constant body temperature, thus under a climate change scenario, the fugacity capacity of their bodies would not change as the environment warms. Thus Chemicals that have an enhanced tendency to escape from air, water and sediment (Figure 5.4.a) under a A1B climate change scenario, may have enhanced potential for bioaccumulation into homeotherms.

The model experiments for the A1B climate change scenario identified temperature, marine currents and POC as the climate and environmental parameters affecting the distribution and fugacity of PCBs in the case study area, whereas precipitation, wind speeds and effect of temperature on primary emissions were less influential in changing modeled fugacities in the future climate scenario (Figure 5.4 and B5 and B6). These results are consistent with the sensitivity analyses that showed low sensitivity of the model to these climate variables.

It should be stressed here that this work is not a comprehensive assessment. Only a subset of environmental variables that may be affected by climate forcing was considered, and the watershed has not been explicitly considered so far in this 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. This 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.

CHAPTER 6: CONCLUSIONS

This thesis was triggered by the need of clarifying the climate change interactions on POPs environmental behavior at both the global and regional scales. In the first part of the thesis, a review about the implications of climate change on POPs monitoring, modeling ad regulation is presented. As a result from the assumptions made in chapter three, PCBs were chosen as chemicals which may be suitable for climate change studies, because they are not produced any more, hence the change in environmental levels can be ascribed to climate variability and to environmental degradation only, and not to changes in production and use of these chemicals. A further reason why PCBs have been selected for the applications presented in chapters 4 and 5 is that they are among the best characterized POPs in terms of physical chemical properties and emissions estimates.

In particular, in chapters 4 and 5 a series of model exercises have been applied to several PCBs congeners (PCB 28, 52, 138 and 153) in analyze the climate change effects on PCBs environmental distribution considering a specter of congeners with low to high degree of chlorination.

In the two case studies attention was driven on the effect of a given set of climate variables on the environmental distribution of PCBs under a climate change scenario. The model calculations under the 20CE climate scenario (i.e. the current climate scenario) have been compared to observed data in order to evaluate the model agreement between model results and measured data. Finally, the future climate scenario was compared to the present one in order to investigate the difference in environmental PCBs distribution in both case studies under a future climate change scenario.

The model exercise at the global scale presented in chapter 4 showed that temperature and atmospheric circulation patterns are the climate parameters affecting PCBs environmental distribution more strongly in atmosphere, in particular the increase in primary volatilization emissions as a result of higher temperatures under the climate change scenario is the single most influential effect of climate change on the modeled concentration of both PCB 28 and 153 in air. Furthermore results by this case study show that under the A2 scenario the transport of PCBs from European countries to the Arctic is higher, and that transport of POPs-like substances from European sources to the Arctic is more enhanced under the A2 scenario than transport from sources in North America or Asia. This model exercise shows that under a climate change scenario the world may “become smaller” in terms of enhanced volatilization emissions of POPs that can be expected to be more efficiently transported across national boundaries and remote areas.

The model exercise at the regional scale consisted first of all in building a new mass balance for PCBs 52, 138 and 153 in the Adriatic Sea. The 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 pollutants’ concentrations in the Adriatic Sea, and that in the region the main input of PCBs comes from atmospheric deposition and sediment resuspension rather than from emissions to water. Results from the regional model experiments for the climate change scenario show that PCBs concentrations in the environment do not vary significantly under the climate change scenario in response to changes in environmental conditions, when emissions are kept constant. However, fugacities are expected to increase by a factor of 1.5-2.5 in air, water and sediment under the assumed climate change 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 this study was focused on the abiotic environment, it should be noted that lower fugacity capacities of the environment could have implications for bioconcentration potential of pollutants. Homeotherms maintain a constant body temperature, thus under a climate change scenario, the fugacity capacity of their bodies would not change as the environment warms. Thus chemicals that have an enhanced tendency to escape from air, water and sediment under a climate change scenario, may have enhanced potential for bioaccumulation into homeotherms.

This model experiment identified temperature, marine currents and POC as the climate and environmental parameters affecting the distribution and fugacity of PCBs in the case study area, whereas precipitation, wind speeds and effect of temperature on primary emissions were less influential in changing modeled fugacities in the future climate scenario. These results are consistent with the sensitivity analyses that showed low sensitivity of the model to these climate variables.

The model results presented in this thesis provide some initial estimates of the possible effects of climate change on the fate and transport of PCBs. The model experiments presented in chapter 4 and 5 demonstrate that more efficient mobilization of POP-like substances from primary sources in a future impacted by global scale warming may dominate all other effects of climate change on pollutants dynamics, and that the most influential parameter in determining this behavior is increasing temperature.

However it should be said that this work is not a comprehensive assessment. In both case studies only a subset of environmental variables that may be affected by climate forcing was considered, and only a limited set of pollutants. In the regional scale case study, only a few amount of data was available for the atmospheric environment, and for the water compartment no data were accessible, hence measurement of concentration in marine biota as a proxy to water concentrations have been considered. Samples distribution have not allowed a higher resolution than the one adopted in the case study.

Further developments in this field consist in considering a larger set of climate variables, and estimates for pollutants future environmental emissions. For the Adriatic Sea a similar study on the effect of climate change on the bioaccumulation of PCBs and other chemicals could be a further step, associated with environmental monitoring campaigns, which appeared to be scarce from the data collection carried out within this thesis.

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Appendix A

A.1 Differences between the four environmental parameters between the two scenarios

Figures in this section (A1-A5) show the difference between the environmental parameters (wind fields in free atmosphere and planetary boundary layer, current velocities in the oceanic mixed layer, surface temperature and precipitation rates) between the two climate scenarios (A2 and 20CE).

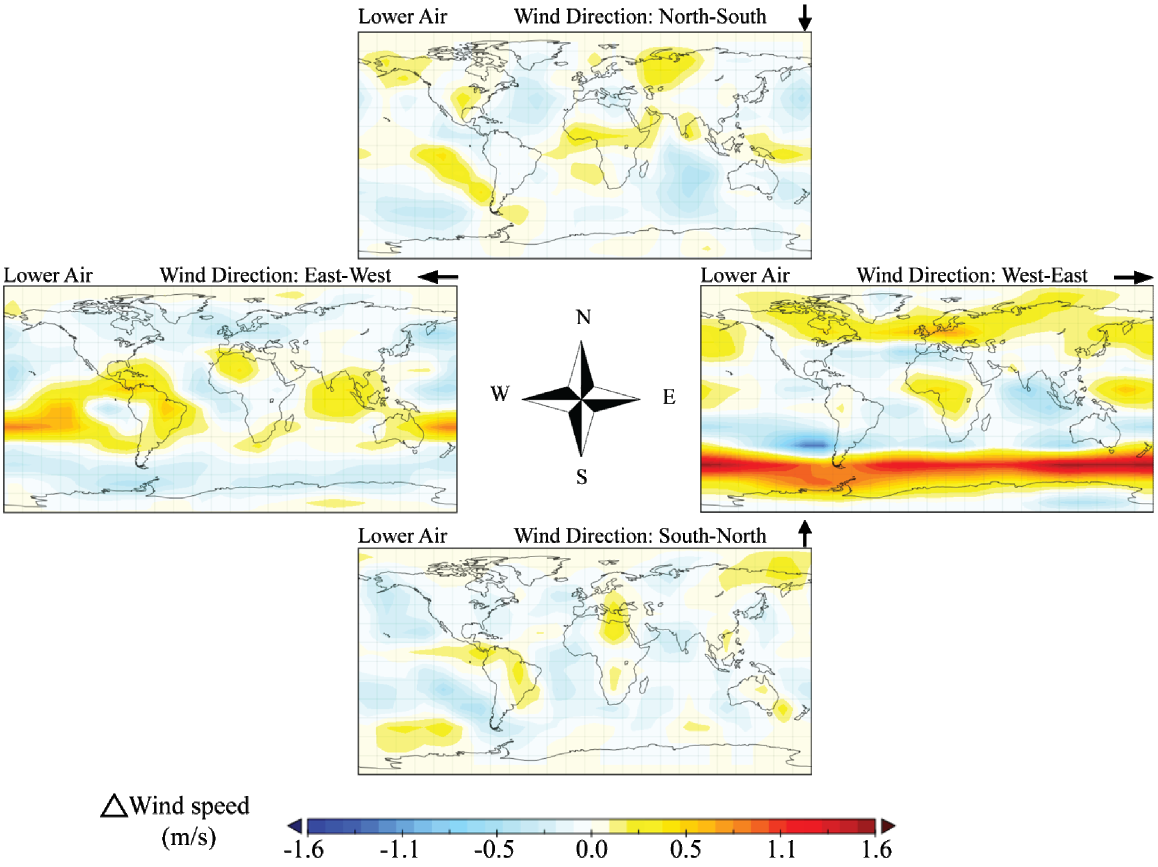


Figure A1: Difference (Δ) in average annual wind speed across regional boundaries in the planetary boundary layer (lower air) compartment between the A2 and the 20CE climate scenarios in each of the four possible directions. Highest wind speed increases are associated with west-to-east winds in the mid-latitudes of both hemispheres.

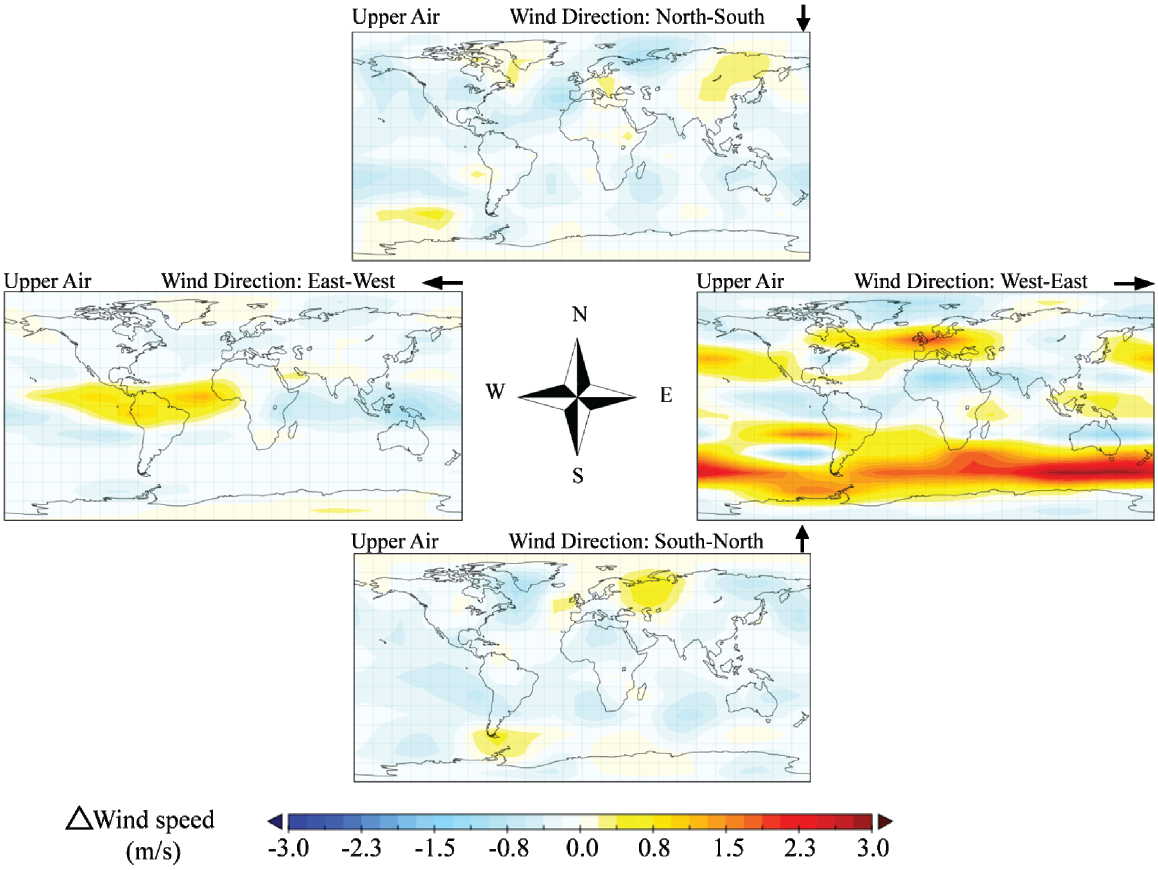


Figure A2: Difference (Δ) in average annual wind speed across regional boundaries in the free atmosphere (upper air) compartment between the A2 and the 20CE climate scenarios in each of the four possible directions. As for the planetary boundary layer, highest differences in wind speed are in the west-to-east direction in mid-latitudes.

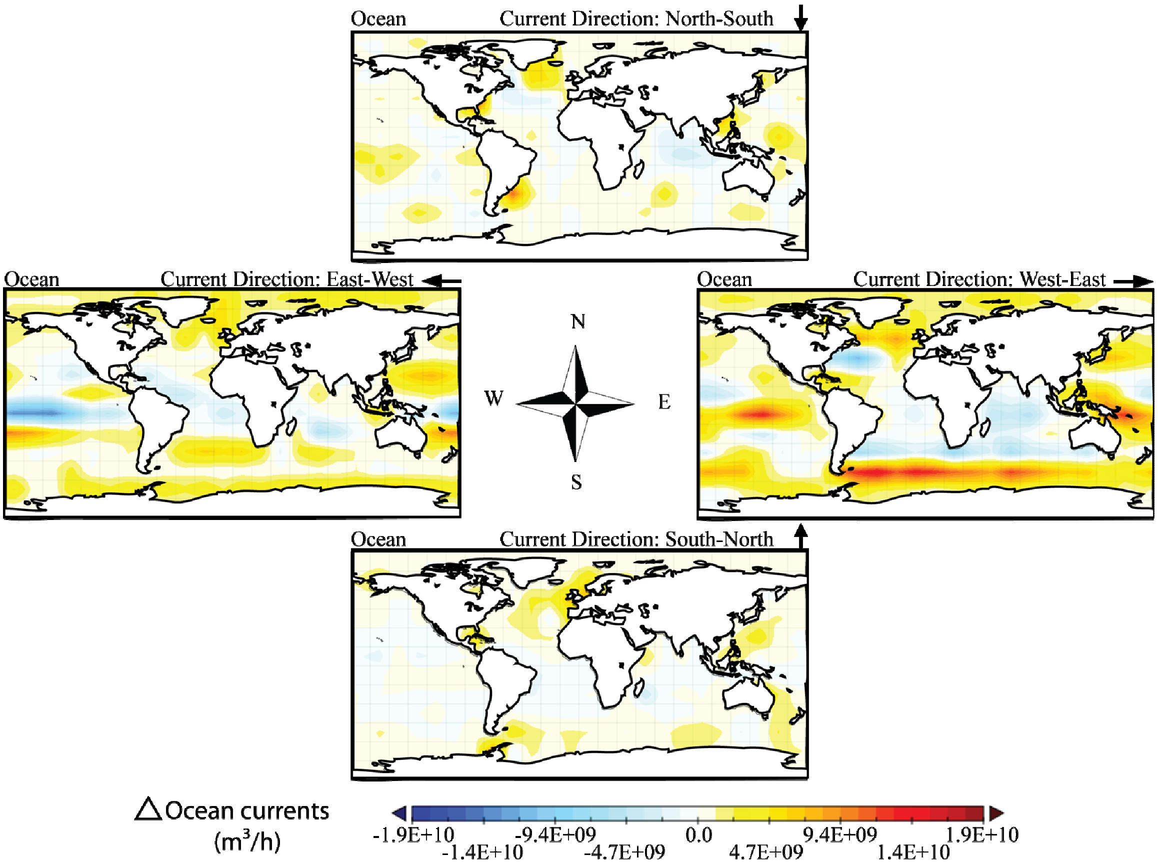


Figure A3: Difference (Δ) in average annual flux of ocean water across regional boundaries between the A2 and the 20CE climate scenarios in each of the four possible directions. Largest differences are associated with the Antarctic Circumpolar Current and the Southern Equatorial current.

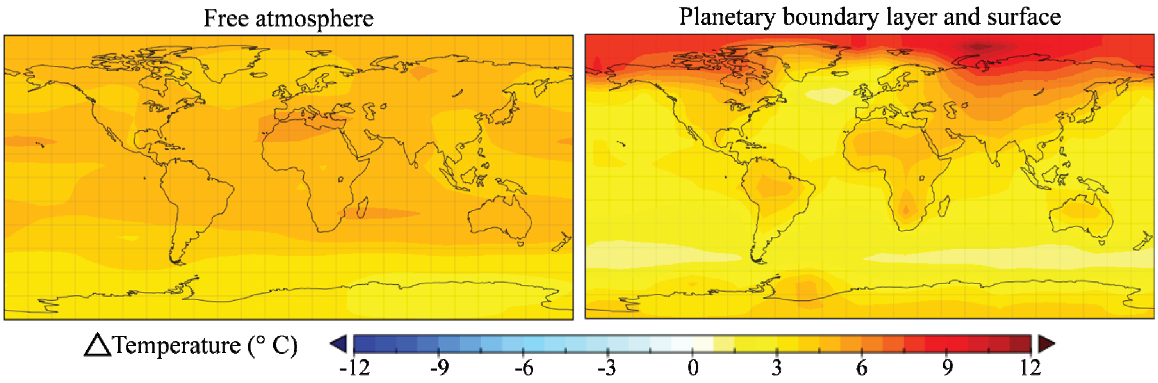


Figure A4: Difference (Δ) in average annual temperature between the A2 and the 20CE scenario in the free atmosphere (left panel) and the PBL and the surface compartments (right panel).

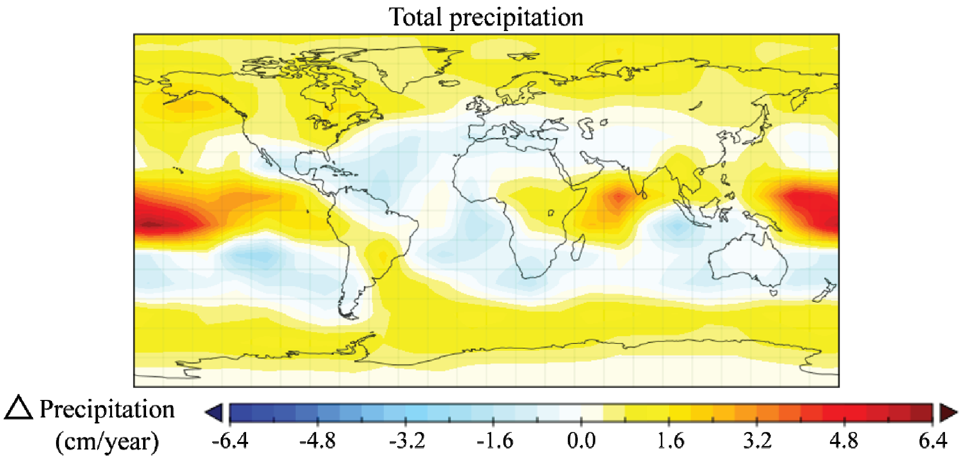


Figure A5: Difference (Δ) in average annual total precipitation between the A2 and the 20CE scenario. The total precipitation is higher over the majority of the world under the A2 scenario, with peaks in the Tropics.

A.2 Physical chemical properties of PCB 28 and PCB 153

In Table A1 the physical chemical property data used in the model runs are presented.

	PCB 28	***PCB 153***
Partition coefficients[1]		
log K_{oa}	7.86	9.45
log K_{ow}	5.92	7.31
log K_{aw}	–1.93	–2.13
Internal energies of phase change[2]***:***		
octanol-air, ΔU_{oa}	–77.6	–91.6
octanol-water, ΔU_{oa}	–20.0	–20.0
Degradation half-lives[3] ***(h) in:***		
air[4]	550	5 500
vegetation	5 500	55 000
fresh water	5 500	55 000
coastal water	5 500	55 000
soil	10 000	550000
sediment	10 000	550000
Activation energy of degradation reactions (kJ/mol) in:		
air	0	0
vegetation	30	30
fresh water	30	30
coastal water	30	30
soil	30	30
sediment	30	30

1: partitioning properties by Schenker et al. (2005); 2: internal energies extrapolated by MacLeod et al. (2007b); 3: degradation half lives from Wania and Daly (2002); 4: Half-life quoted here is extrapolated from Anderson and Hites (1996) assuming global average OH radical concentrations. Modeled half-lives in each region are calculated monthly during dynamic model runs based on OH radical concentration data from Spivakovsky (2000).

A.3 Model evaluation

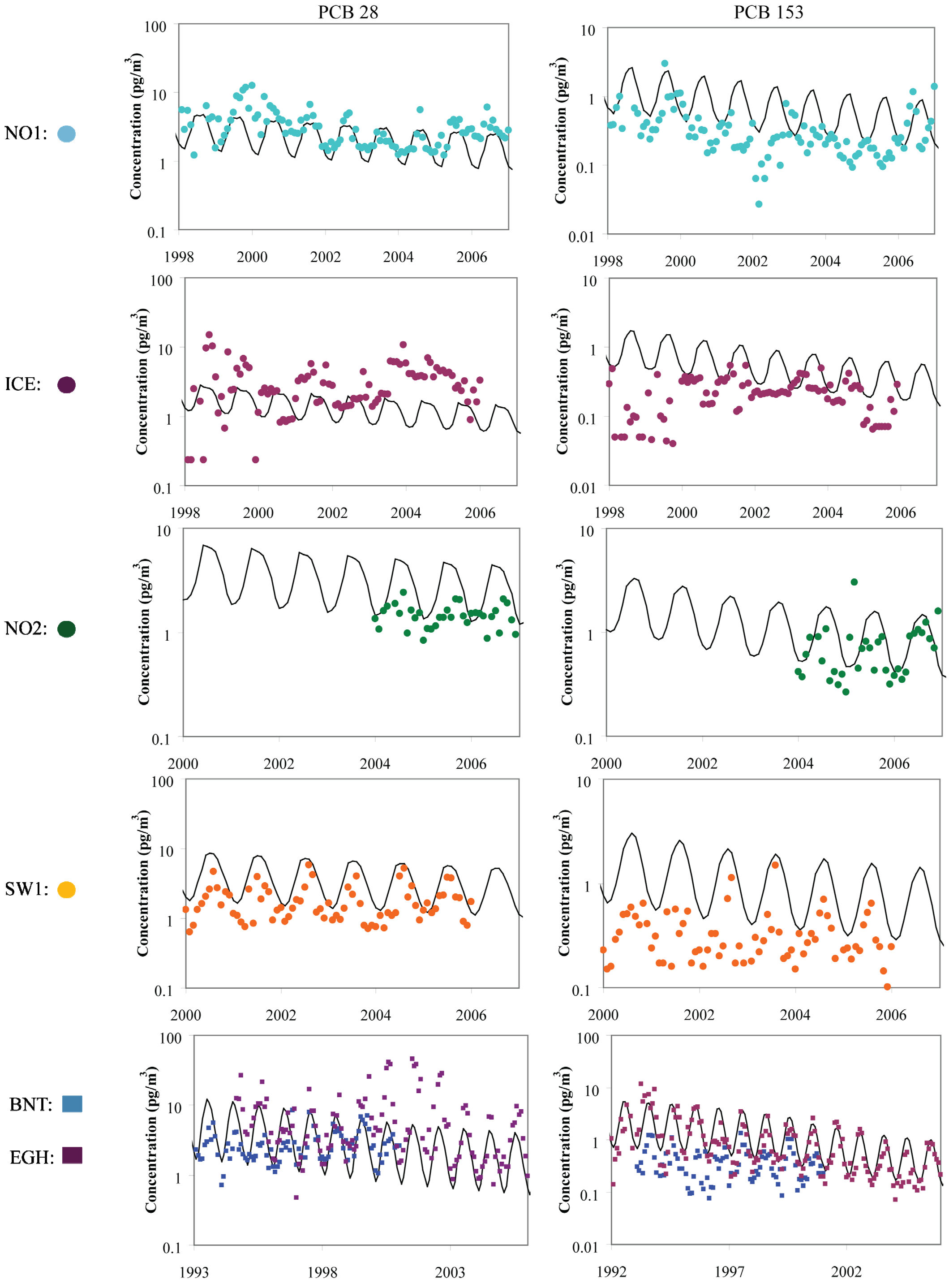
The model performance was evaluated through a comparison with measurement data from monitoring stations listed in Table A2. Data are provided by the European Monitoring Environmental Program (EMEP, available at http://tarantula.nilu.no/projects/ccc/emepdata.html), by request to the Integrated Atmospheric Deposition Network (IADN, http://www.msc-smc.ec.gc.ca/iadn/index_e.html) and by request to Dr. Robert G. M. Lee, Institute of Environmental and Natural Sciences, Lancaster University.

TABLE A2. Sources for Long-term Monitoring Data of Atmospheric PCB Concentrations

Abbreviation		Site name and Location	Latitude	Longitude	BETR Global model region	Data period used in the analysis	Data availability
1	NO1	Zeppelin station, Norway	78° 54' 00" N	11° 53' 00" E	13	1998-2006	a
2	ICE	Storhofdi, Iceland	63° 24' 00" N	20° 17' 00" W	35	1995-2005	a
3	NO2	Birkenes, Norway	58° 23' 00" N	08° 15' 00" E	37	2004-2006	a
4	SW1	Pallas, Sweden	68° 00' 00" N	24° 9' 00" E	38	2003-2005	a
5	BNT	Burnt Island, USA	45° 49’ 42" N	82° 56’ 53" W	55	1992-2006	b
6	EGH	Eagle Harbor, USA	47° 27’ 47" N	88° 08’ 59" W	55	1990-2005	b
7	GB1	High Muffles, Great Britain	54° 20' 04" N	00° 48' 27" E	60	2004-2005	a
8	GB2	Hazelrigg Station, Lancaster, England	54 ° 01' 00" N	02° 46' 03" W	60	1994-2003	c
9	SW2	Rorvick, Sweden	57° 25' 00" N	11° 56' 00" E	61	1994-2002	a
10	SW3	Rao, Sweden	57° 23' 38" N	11° 54' 50" E	61	2002-2006	a
11	CRP	Kosetice Observatory, Czech Republic	49° 35' 00" N	15° 00' 05" E	62	1999-2005	a
12	SW4	Aspreveten, Sweden	58° 48' 00" N	17° 23' 00" E	62	1995-2005	a
13	SBD	Sleeping Bear Dunes, Michigan	44° 45’ 40" N	86° 03’ 31" W	79	1991-2005	b
14	STP	Sturgeon Point, New York	42° 41’ 35" N	79° 03’ 18" W	79	1991-2005	b
15	PPT	Poin Peter, Ontario, Canada	43° 50’ 34" N	77° 09’ 13" W	79	1990-2005	b
16	CLV	Cleveland, Ohio, USA	41° 29' 31" N	81°40' 42" W	79	2003-2005	b

a: Data provided by European Monitoring Environmental Program, EMEP, available at http://www.nilu.no/projects/ccc/emepdata.html; b: By request to Integrated Atmospheric Deposition Network, IADN, http://www.msc-smc.ec.gc.ca/iadn/index_e.html; c: By request from Dr. Robert G. M. Lee, Institute of Environmental and Natural Sciences, Lancaster University.

In Figure A6 graphs showing concentration versus time for all the sampling stations considered in this study are reported. Each line shows model results in one BETR region, obtained on the basis of the maximum emission scenario proposed by Breivik et al (2007) .


PCB 28
PCB 153
NO1: ●
ICE: ●
NO2: ●
SW1: ●
BNT: ■
EGH: ■
Concentration (pg/m^3)
100
10
1
0.1
0.01
1998
2000
2002
2004
2006
1993
2003
1992
1997

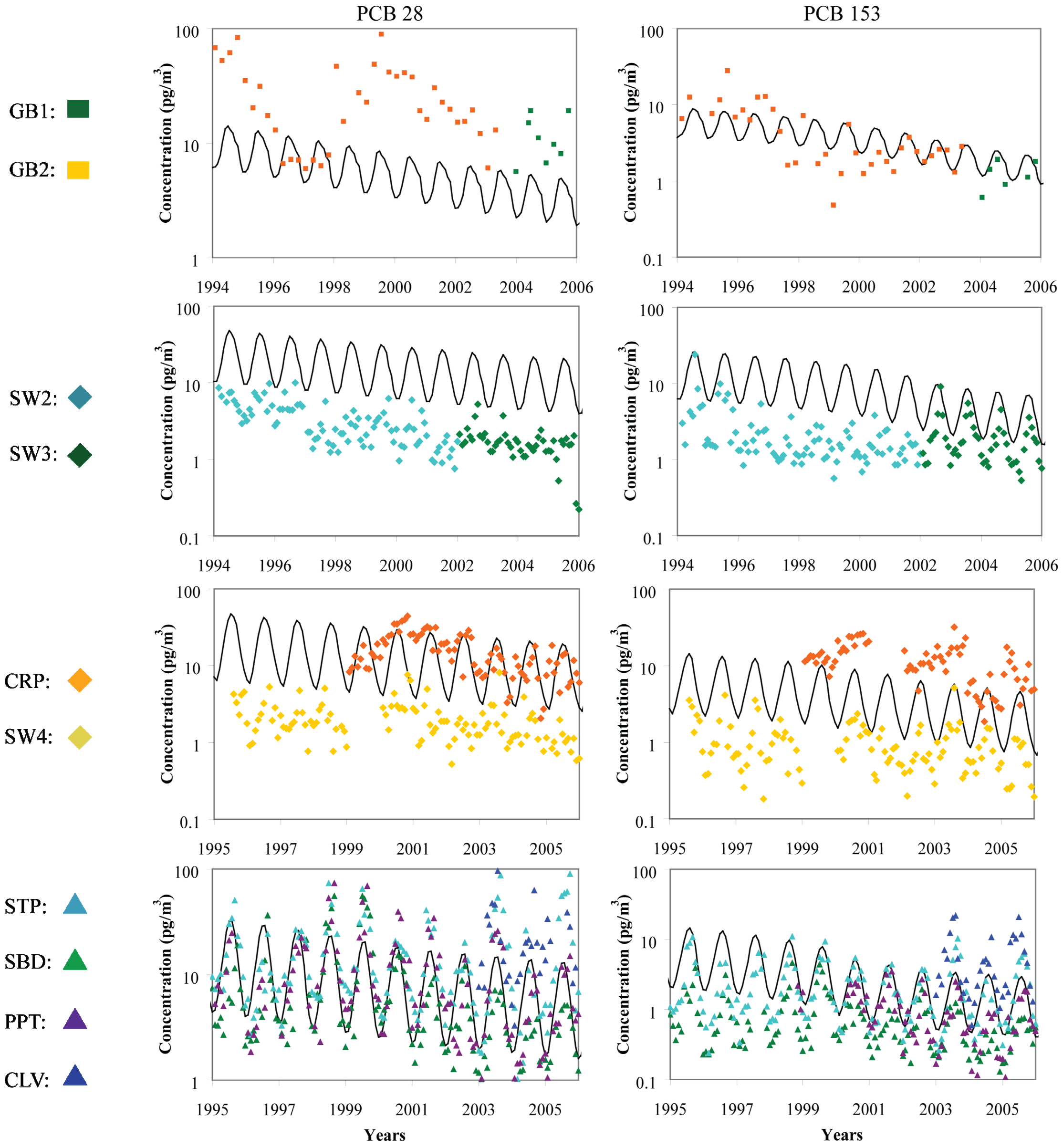


Figure A6: Time series for modeled concentrations in (pg/m^3) (line) and monitoring data in (pg/m^3) at the different stations listed in Table S2 for PCB 28 (left column) and PCB 153 (right column). The model results are based on the maximum emission scenario.

A.4 Additional model results from experiment 1

Besides considering the three environmental parameters shown in Figure 4.2 (B, C, D) in chapter 4, also the oceanic currents and precipitation patters were considered as varying parameters in the two climate scenarios.

Figure A7 represents the results of the first model experiment which consisted in assuming a change in oceanic currents only (Figure A7.E) and in precipitation patterns only (Figure A7.F).

In Figure A7 it is shown that the change in oceanic currents in the A2 scenario causes a slight increase in atmospheric concentration of both PCBs congeners in both hemispheres, with a slightly higher increase along the South American Pacific coast. For PCB 28 an increase also in the Arctic is predicted (Figure A7.E).

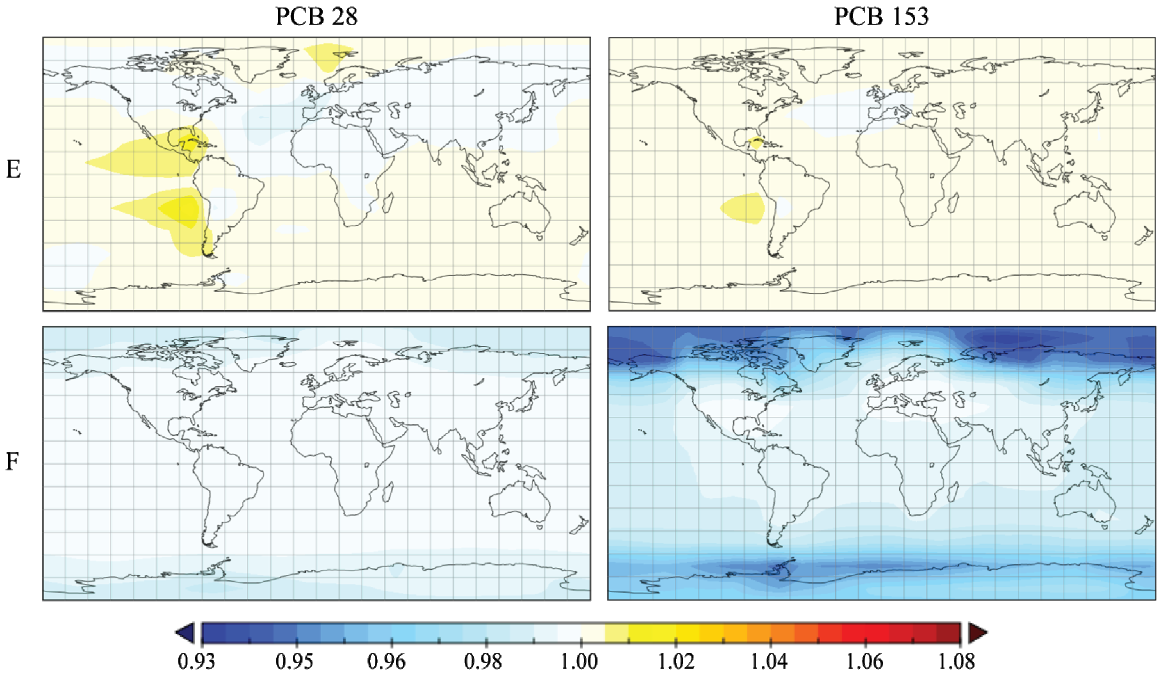


Figure A7: Ratio of modeled PCB concentrations at steady state in the planetary boundary layer under the single A2 parameter scenario to the modeled concentrations under present day conditions for PCB28 (left column) and PCB153 (right column). The single parameter A2 scenarios are: ocean currents from A2, other parameters from 20CE (E); precipitation patterns from A2, other parameters from 20CE (F).

The change in precipitation under the A2 scenario results in a decrease in atmospheric concentration of both PCBs congeners in both hemispheres, in particular for PCB 153 at high latitudes in the north hemisphere. However, the lower air concentration remains unchanged at equatorial latitudes for both congeners under this scenario (Figure A7.F).

Through the comparison of Figure 4.2 and Figure A7 it is verified that both changes in oceanic currents and precipitation patterns do not contribute to the patterns highlighted in the total A2 scenario (Figure 4.2.A). Hence precipitation patterns and oceanic currents are much less important in influencing the overall changes in concentrations of PCBs in lower air in the A2 scenario compared to the 20CE scenario.

A.5 Linear plots for experiment 1 and 2

Figure A8 and A9 show the same information as Figure 4.2 and 4.3 plotted on a linear scale as absolute differences. It was chosen to plot the ratio of the values in the two climate scenarios in chapter 4 to show small differences at the global scale that are not evident in Figures A8 and A9.

Figure A8 can be compared to Figure 4.2 and represents the differences between the absolute concentration values of PCB 28 (left column) and PCB 153 (right column) in the planetary boundary layer (u.m.: mol m^{-3}) in the different climate scenarios on a linear scale.

In Figure A8.A it is shown that for both congeners concentrations in air are higher in the Northern hemisphere under the A2 scenario. The spatial pattern of increased concentrations is similar for PCB 28 and PCB 153. Areas of notable increase in modeled concentrations are North America and Europe, which are areas of PCB sources. The other panels of Figure A8 show results from the first model experiment, where hypothetical climate scenarios were constructed from one climate parameter taken from the A2 climate scenario and all other parameters from the 20CE scenario. These are temperature effects on emissions (panel B), temperature effects on dynamic re-partitioning and degradation (panel C) and wind speeds (panel D). The effect of temperature on primary emissions (Figure A8.B) results in a general increase in concentrations throughout the Northern hemisphere. This increase is strongest over North America and Europe. The effect of higher temperatures under the A2 scenario on environmental partitioning and degradation of PCBs results in higher concentrations globally, but at this scale spatial trends are not detected (Figure A8.C). The changes in atmospheric circulation patterns account for higher concentrations of both PCBs congeners in the equatorial Pacific, and lower concentrations over Antarctica (Figure A8.D).

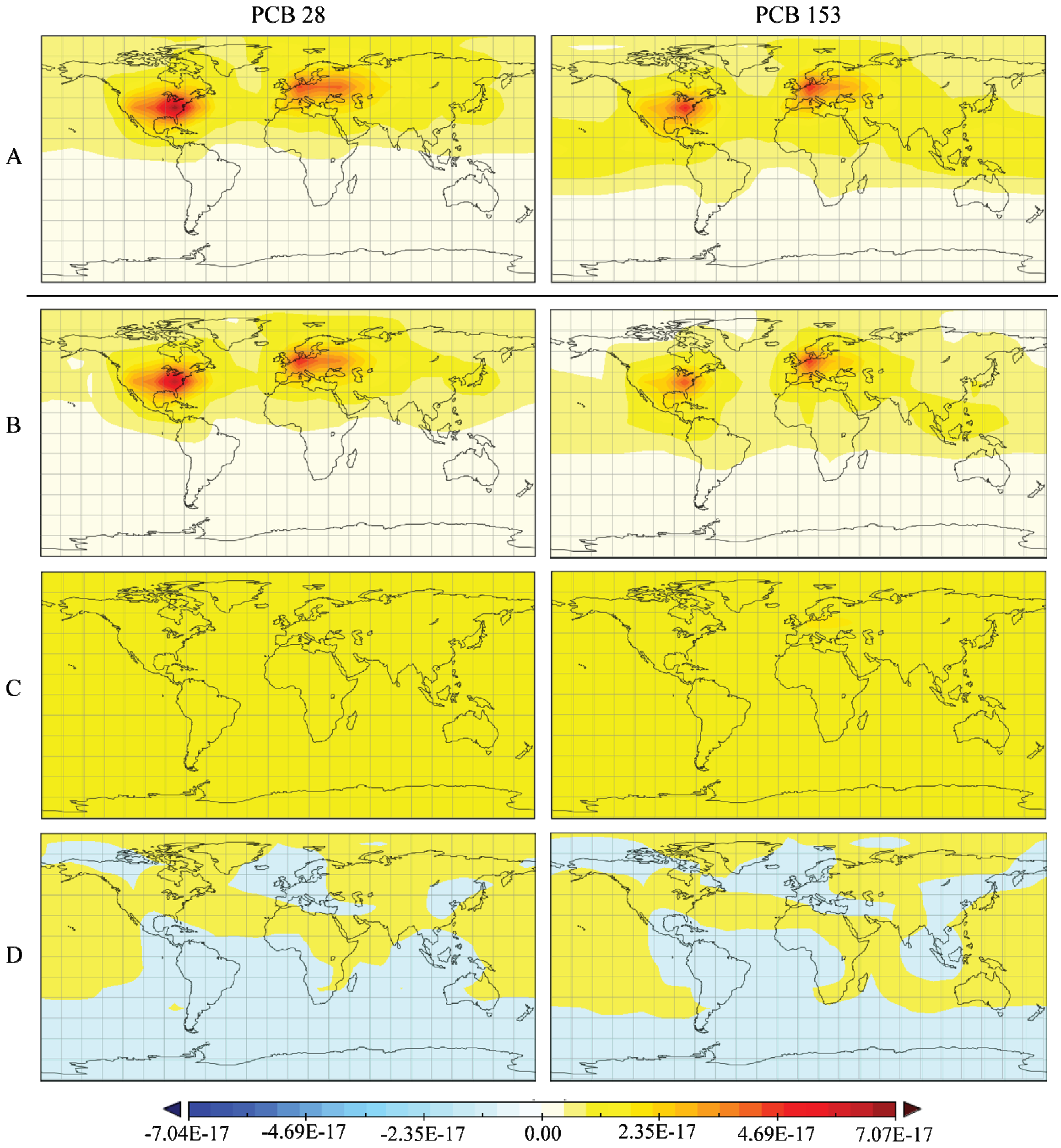


Figure A8: Difference in modeled PCB concentration (mol m^{-3}) at steady state in the planetary boundary layer under hypothetical climate conditions and modeled concentrations under the 20CE climate scenario for PCB 28 (left) and PCB 153 (right). The hypothetical conditions are: The A2 scenario (A); the 20CE scenario, where primary emission rates are adjusted to reflect temperature as in the A2 scenario (B); temperature fields from A2 (excluding temperature influence on primary emissions), other parameters from 20CE (C), and wind fields from A2, other parameters from 20CE (D).

Figure A9 shows results for the second model experiment, in which the A2 climate scenario is compared to the 20CE scenario for emissions only in North America, Europe, Asia, and South America. Here the linear difference in concentration between the two climate scenarios is shown.

This Figure can be compared with Figure 4.3 in chapter 4, as they show the same information on different scales. On the linear scale, the global trend of increasing relative concentrations in atmosphere for PCB 28 observed in Figure 4.3 is not detectable in Figure A9. Modeled absolute concentrations of PCB 28 are still clearly higher in the direction “downwind” (i.e., eastward) of the source regions under the A2 scenario, and are in some cases also lower immediately “upwind” (i.e., westward). This trend implies an increased potential for inter-continental transport and transport into the Arctic, and is most obvious for emissions in Europe, but is also apparent for emissions in North America. For PCB 153, modeled concentrations in air also increase in the hemisphere where emission occurs under the A2 scenario compared to the 20CE scenario. The pattern of higher concentrations downwind from source regions under the A2 scenario is again evident, implying increased inter-continental transport and transport to the Arctic. In all scenarios, the modeled PCB concentrations in equatorial regions over the Pacific Ocean are higher under the A2 scenario than under the 20CE scenario.

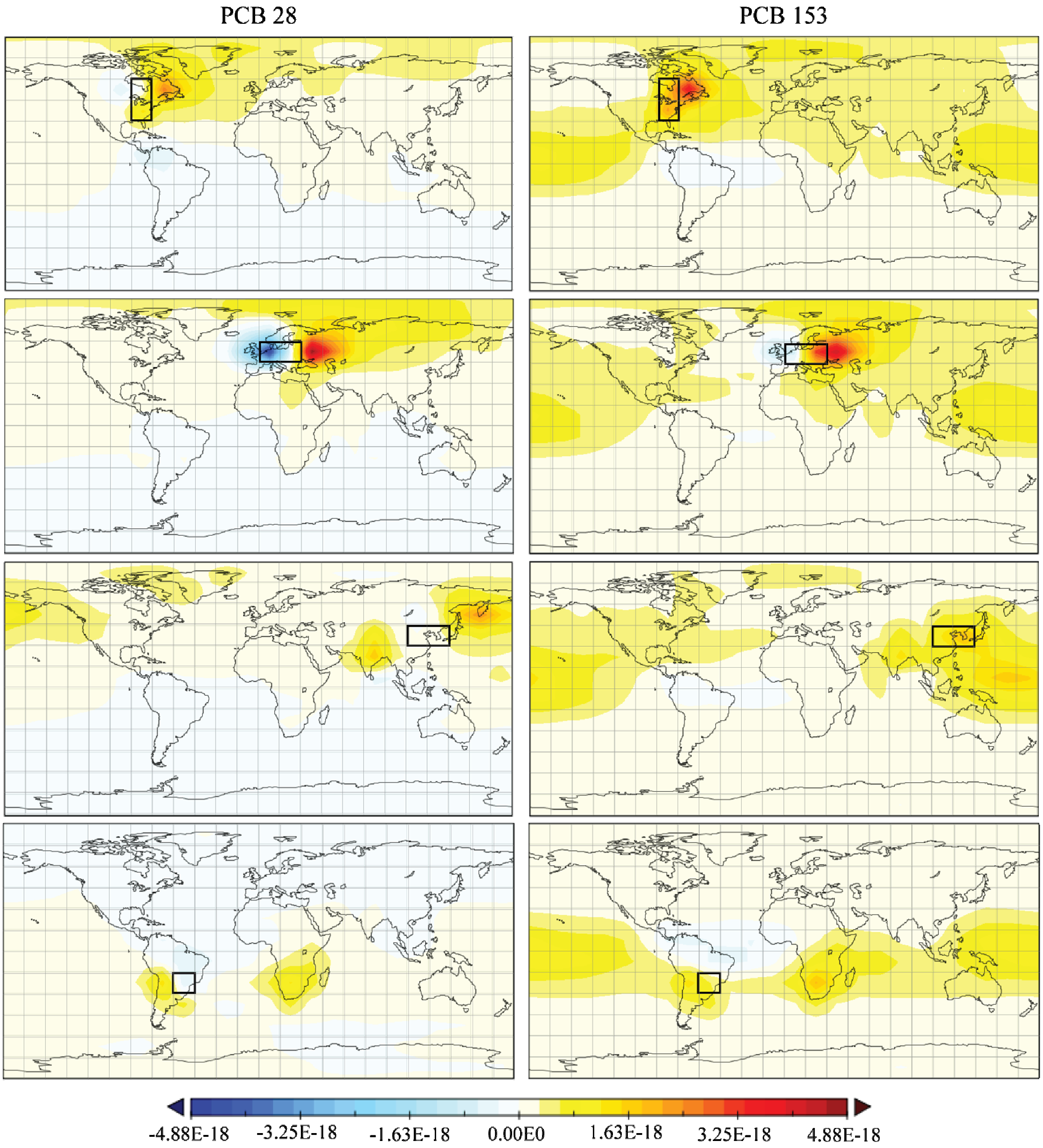


Figure A9: Difference in modeled PCBs concentration (mol m^{-3}) at steady state in the planetary boundary layer under hypothetical climate conditions and the modeled concentrations under the 20CE climate scenario for PCB 28 (left) and PCB 153 (right) for four emission regions, North America, Europe, Asia and South America (top to bottom). Emission regions are marked with black rectangles.

Appendix B

B.1 Model set up

Figure B1 shows the model domain and the three model regions. These model regions were defined taking into account the morphological characteristics of the Adriatic Sea and the data availability.

The three boxes divide the Adriatic Sea in north, central and south Adriatic Sea as it is shown in figure B1. These three regions are described as follows:

a. Region 1: ‘northern Adriatic Sea’, NAS in chapter 5. It includes the Gulf of Trieste, the Venice Lagoon and the Po delta, and covers the coastal areas corresponding to Friuli Venezia Giulia, Veneto, and Emilia Romagna. On the east coast the first box includes the Istria peninsula, corresponding to the Slovenian and Croatian coastal areas. The latitudes go from 45.53°N to 43.94°N and longitudes range from 12.05 to 14.98°E. An average depth of 35 m is assumed according to Artegiani et al. (1997a) and PCBs inputs are defined for the Venice Lagoon (Moret et al., 2004).

b. Region 2: ‘central Adriatic Sea’, CAS in chapter 5. It includes on the western coast the Marche, Abruzzo and Molise districts, and almost all the Croatian coastal area on the east border of the Adriatic Sea. This region ranges from a latitude of 44.81 to 41.92° N, and from a longitude of 12.79° E to 16.12° E. An average depth of 100 m was defined according to Artegiani et al. (1997a). No data were available for PCBs measurements in rivers and in air from the environmental agencies. Estimates of the total PCBs content in rivers and of rivers discharge for Croatia was available (Croatian Waters, data for the year 2007, personal communication).

c. Region 3: ‘southern Adriatic Sea’, SAS in chapter 5. It includes the coasts of the district Puglia on the Italian shores, and on the other side of the Adriatic Sea the box includes the coastal areas of both Albania and Montenegro. This is from a latitude of 43.27° N to 39.71° N and from a longitude of 15.08° E to 19.66° E. No information on PCBs content in rivers was given for this region.

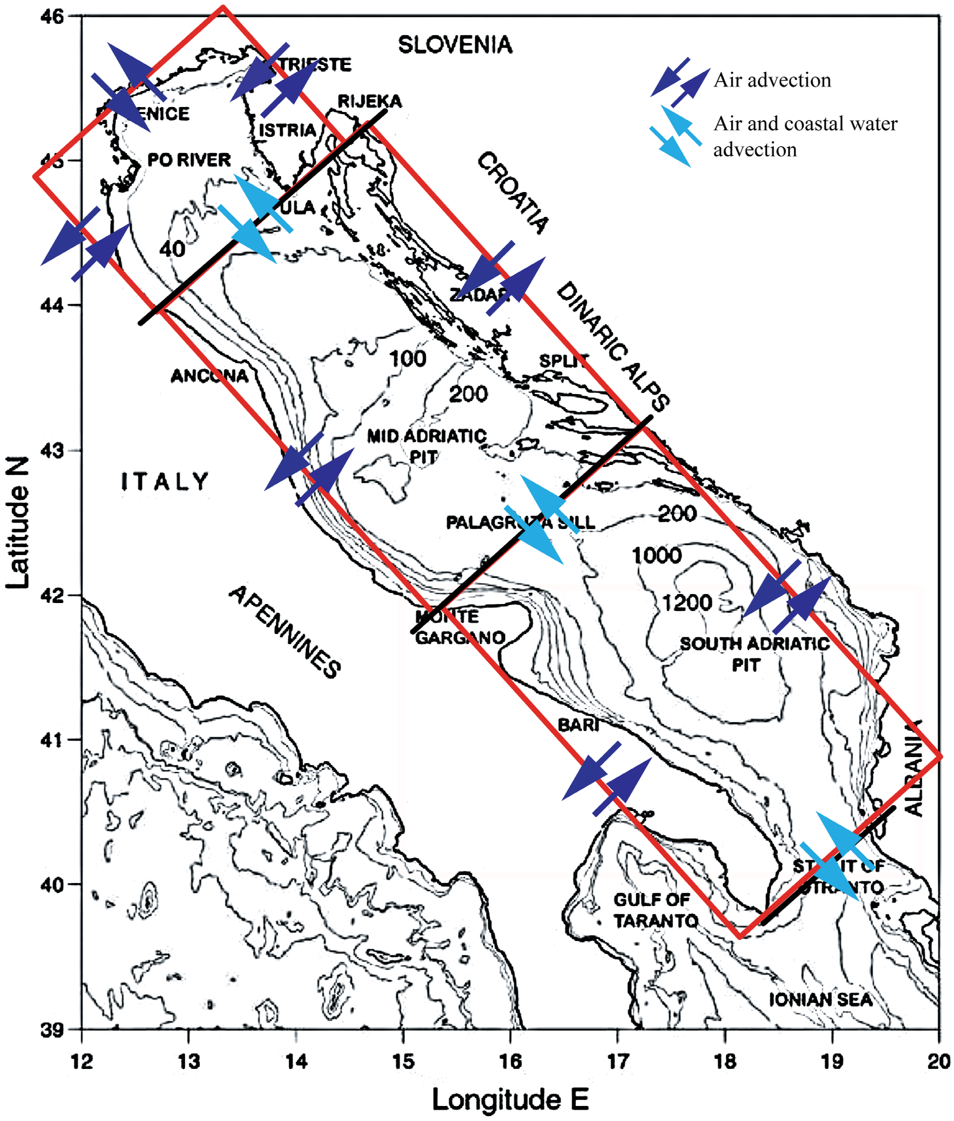


Figure B1. 3 boxes domain for the case study. The definition of the 3 boxes takes into account both the morphological characteristics of the Adriatic Sea and the PCBs concentration data availability.

A convenient way of estimating the state of the environment with respect to environmental contamination by POPs (in this case PCBs) is to compare fugacity values of a chemical among the different compartments for estimating the inter-compartmental fluxes (Mackay, 2001). The higher the fugacity, the higher the tendency of the chemical to transfer to another phase. Fugacity is related to concentration by a linear relationship B.1:

$$C = Z \cdot f \qquad \text{(B.1)}$$

where C stands for concentration in the environmental medium (mol·m^{-3}), Z is the fugacity capacity of the medium (mol ·Pa^{-1}·m^{-3}), and f is the fugacity (Pa).

Z is a proportionality constant which is dependent on the properties of a given environmental compartment, on temperature and on the physical-chemical properties of the chemical of interest.

Z values for the three environmental compartments considered in the model are defined as:

$$\left.\begin{array}{l} Z_{air} = \dfrac{1}{R \cdot T_{air}} \\ Z_{aer} = Z_{air} \cdot K_{QA} \end{array}\right\} \rightarrow Z_{bulk,a} = Z_{air} \cdot (1-aer) + Z_{aer} \cdot aer \qquad \text{(B.2)}$$

$$\left.\begin{array}{l} Z_{SPM} = Z_{water} \cdot K_{WP} \\ Z_{water} = \dfrac{1}{R \cdot T_{water} \cdot K_{aw}} \end{array}\right\} \rightarrow Z_{bulk,wat} = Z_{water} \cdot (1-SPM) + Z_{SPM} \cdot SPM \qquad \text{(B.3)}$$

$$Z_{sed} = Z_{water} \cdot K_{sw} \cdot \rho \cdot K_{OC} \cdot OC \qquad \text{(B.4)}$$

$$Z_{bulk,sed} = Z_{sed} \cdot sed + Z_{water} \cdot (1-sed) \qquad \text{(B.5)}$$

Where Z stands for the fugacity capacity in the various compartments (mol·Pa^{-1}·m^{-3}), and the subscripts *air, bulk,a, aer, water, SPM, bulk,wat, sed, bulk,sed* stand for atmosphere (gaseous phase), aerosol, whole atmospheric compartment, coastal water, suspended particulate matter water, bulk water compartment, sediment, bulk sediment compartment respectively.

K stands for the partition coefficients, and subscripts *WP, QA, aw, sw* stand for water-particle exchange, aerosol-air exchange, air-water and sediment-water exchange. K_{OC} (kg·m^{-3}) stands for the organic carbon-water partition coefficient, and OC is the organic carbon fraction. SPM stands for the volume fraction of suspended particulate mater in water (m^3/m^3), *sed* stands for the volume fraction of solids in the sediment (m^3/m^3), *aer* stands for the volume fraction of the aerosol, ρ stands for solids density in sediment (kg m^{-3}), R is the ideal gas constant (Pa·m^3·mol^{-1}·K^{-1}), T (°K) stands for temperature in the atmospheric compartment (subscript *air*) and in coastal water (subscript *wat*).

In order to calculate the steady state fugacities, a level III fugacity model was built. At the steady state it is assumed that total inputs and outputs are constant over time, and the inputs are equal to the outputs. Air, coastal water and sediment were defined as environmental compartments, and aerosol and suspended particulate matter in water were also considered as two sub-compartments. Aerosols and suspended matter are considered in equilibrium respectively with the gas phase in the atmosphere and with the coastal water solution phase.

The model was written in an excel file. The first step was the calculation of Z values for all the compartments and the sub-compartments. Then transport D values are calculated in terms of mol $\mathrm{Pa}^{-1}\mathrm{h}^{-1}$ according to Mackay (2001).

The model solves the following system of mass balance equations (B.6):

$$\begin{cases}
E_1 + D_{1,in} \cdot f_{1,in} + f_4 \cdot D_{4,1} + f_2 \cdot D_{2,1} = f_1 \cdot (D_{1,2} + D_{1,react} + D_{1,out} + D_{1,4}) \\
E_2 + f_1 \cdot D_{1,2} + f_3 \cdot D_{3,2} + f_5 \cdot D_{5,2} = f_2 \cdot (D_{2,1} + D_{2,react} + D_{2,5} + D_{2,3}) \\
f_2 \cdot D_{2,3} = f_3 \cdot (D_{3,react} + D_{3,2} + D_{bur}) \\
E_4 + D_{4,in} \cdot f_{4,in} + f_1 \cdot D_{1,4} + f_5 \cdot D_{5,4} + f_7 \cdot D_{7,4} = f_4 \cdot (D_{4,5} + D_{4,react} + D_{4,out} + D_{4,1} + D_{4,7}) \\
E_5 + f_4 \cdot D_{4,5} + f_6 \cdot D_{6,5} + f_2 \cdot D_{2,5} + f_8 \cdot D_{8,5} = f_5 \cdot (D_{5,4} + D_{5,react} + D_{5,2} + D_{5,6} + D_{5,8}) \\
f_5 \cdot D_{5,6} = f_6 \cdot (D_{6,react} + D_{6,5} + D_{bur}) \\
E_7 + D_{7,in} \cdot f_{7,in} + f_4 \cdot D_{4,7} + f_8 \cdot D_{8,7} = f_7 \cdot (D_{7,8} + D_{7,react} + D_{7,out} + D_{7,4}) \\
E_8 + f_7 \cdot D_{7,8} + f_9 \cdot D_{9,8} + f_5 \cdot D_{5,8} + f_{8,in} \cdot D_{8,in} = f_8 \cdot (D_{8,9} + D_{8,react} + D_{8,7} + D_{8,out} + D_{8,5}) \\
f_8 \cdot D_{8,9} = f_9 \cdot (D_{9,react} + D_{9,8} + D_{bur})
\end{cases}$$

Where E_1, E_2, … E_8 are emissions in air and water; $D_{1,in}$, $D_{2,in}$ and $D_{8,in}$ are the advection fluxes in air and water; $f_{1,in}$, … $f_{8,in}$ are the inflow fugacities in air and water (assuming both particulate and fluid inputs), $f_{1,\ldots}$ f_9, are the fugacities in air (subscripts 1, 4, 7), water (subscripts 2, 5, 8) and sediment (subscripts 3, 6 and 9); $D_{1,2}$, … $D_{9,8}$, are the D values for both inter-compartmental and advective transport in the system; $D_{1,react}$, … $D_{9,react}$, are the reaction D values for each compartment, D_{bur} stands for sediment burial (only in the sediment compartment, see Figure B2, where a schematic representation of the model and of the processes considered in it is given).

B.2 Physical chemical data

Table B1 shows the physical chemical data used in the model parameterization.

Table B1. Physical chemical properties used in the model parameterization.

	PCB 52	*PCB 138*	*PCB 153*
Partitioning properties [1]			
LogKoa	8.22 (1.1)	9.67 (1.1)	9.45 (1.1)
LogKow	6.26 (1.1)	7.7 (1.1)	7.31 (1.1)
LogKaw	-1.96 (1.1)	-1.97 (1.1)	-2.13 (1.1)
Internal energies [2]			
Octanol - Water, ?Uow (kJ/mol)	-20 (1.5)	-20 (1.5)	-20 (1.5)
Octanol - Air, ?Uoa (kJ/mol)	-8.14E+01	-9.38E+01	-9.38E+01
Degradation half-lives [3]			
Air Reaction half-life (h)[4]	3924	10807	10807
Coastal Water Reaction half-life (h)	10000 (3)	55000 (3)	55000 (3)
Sediment Reaction half-life (h)	17000 (3)	550000 (3)	550000 (3)

Cfs are reported in parenthesis. 1: partitioning properties by Schenker et al. (2005); 2: internal energies extrapolated by MacLeod et al. (2007); 3: degradation half lives from Wania and Daly (2002); 4: Half-life quoted here is extrapolated from Anderson and Hites (1996) assuming global average OH radical concentrations derived by Spivakovsky et al. (2000).

B.3 Environmental parameters

In Table B2 the environmental parameters applied in the model parameterization are presented.

The coastal water particle sinking velocity is taken from Frignani et al. (2005) and from Turchetto et al. (2007) taking into consideration the mass accumulation rates and the total mass fluxes defined for the western coast of the Adriatic Sea. Information on the organic carbon content comes from Alvisi (2009) for the North Adriatic, and is assumed similar in the central Adriatic. The values for the atmospheric total suspended matter are given for the Venice Lagoon and here these values are assumed to be consistent also for the Adriatic Sea. A site far from highly populated areas was chosen as a reference for this value (Rossini et al., 2005).

The suspended particulate matter (SPM) in coastal water was given by the 4-years monthly averaged sampling campaigns in the NAS held by the Environmental Regional Agency (ARPAV). In general there is a lack of information for the CAS and the SAS. The SPM and the OC fraction in inflow water (rivers fresh water) was estimated for the north region by Boldrin et al. (2005).

Finally, river discharges are estimated together with water runoff from Raicic et al. (1994) and the flux from the Venice lagoon was estimated from Bianchi et al. (2004).

Table B2. Environmental input parameters.

Parameter	Value	u.m.	Source
Water side air-water MTC	0.05 (3)	$m\ h^{-1}$	Berkeley-Trent Global model, (MacLeod et al., 2001).
Air side water-air MTC	5 (3)	$m\ h^{-1}$	
Sediment-wat diff MTC	0.01 (3)	$m\ h^{-1}$	
Scavenging ratio	20,000 (2)		Berkeley-Trent Global model, (MacLeod et al., 2001).
Aerosol dry deposition	10.8 (3)	$m\ h^{-1}$	General estimation assumed by Mackay (2001).
Sediment flows:			
resuspension rate	from 1.24 to 1.50 (3)	$g\ m^{-2}d^{-1}$	From Frignani et al. (2005) and Turchetto et al. (2007).
deposition rate	from 4.13 to 4.99 (3)	$g\ m^{-2}d^{-1}$	
burial rate	from 2.90 to 3.46 (3)	$g\ m^{-2}d^{-1}$	
Concentration of solids			
coastal water	6.86 (3)	$mg\ L^{-1}$	Estimated from ARPAV, available data upon request.
inflow water (fresh)	7.404 (3)	$mg\ L^{-1}$	Estimated from Boldrin et al., 2005.
Venice Lagoon inflow water	26.66 (3)	$mg\ L^{-1}$	Estimated from Bianchi et al., 2004.
aerosol	0.334 (3)	$mg\ L^{-1}$	Estimated from Rossini et al., 2005.
sediment	0.2 (3)	m^3/m^3	BETR Global model, MacLeod et al. (2001).
rho solids	2,550 (1.5)	$kg\ m^{-3}$	From Frignani et al. (2009)
OC fraction			
water (coastal)	From 0.005 to 0.05 (1.5)		From Frignani et al. (2007); Alvisi et al (2009); Turchetto et al. (2007).
sediment	0.02 (1.5)		Sampling campaigns by ARPA. De Lazzari et al. (2003) for the CAS.
inflow water	0.26 (1.5)		Estimated from Boldrin et al., 2005.
Venice Lagoon inflow water	0.24 (1.5)		Estimated from Bianchi et al., 2004.
resuspended sediment	0.2 (1.5)		BETR Global model, MacLeod et al. (2001).

Parameters used as input in the model. MTC: Mass Tranfer Coefficient; OC: Organic Carbon. *Cfs* are given in brackets.

B.4. Climate variables

In this paragraph the climate variables for the three model regions are shown, for both the 20CE and for the A1B climate scenarios. The difference between the A1B and the 20CE climate scenarios for each region and for each variable is also presented. The variables for the atmospheric compartment are presented first, and then come the variables for the marine compartment.

B.4.1 Atmospheric parameters

The values shown in the following tables (B3-B7) represent the average, maximum and minimum value for the year 1990 for the present climate scenario (20CE in the further text) and for the year 2100 for the A1B climate scenario, as 6 hours-average.

The variation in wind speeds (u.m. m/s) over the three regions of the domain is given in Table B3. The average, maximum and minimum values are given for the three regions of the geographic domain of the model for both climate scenarios (20CE and A1B). In the third column the difference between the A1B and 20CE values for the arithmetic mean, maximum and minimum values is presented.

Table B3.a,b show the values for the u component, and tables B3.c,d show the values for the v component of the vector describing the wind speed.

The u wind component is always directed northward in both the 20CE and A1B scenario, but there is an enhanced increase in wind speed southward in the A1B scenario (the increase in the u component directed southward is higher than the increase in the u component directed northward in all the three regions when the mean values are considered). The v component is instead always directed westward, this trend being enhanced in the A1B scenario.

Table B3. ***u*** **and** ***v*** **wind speed components are shown here for the 20CE and A1B climate scenarios defined by the University of Belgrade RCM. In the third column the difference A1B-20CE is shown for the arithmetic mean, maximum and minimum values. Units are m/s. Cf are given in parenthesis.**

Region	**Climate scenarios**						**Difference**		

a. From South to North, u component

	20CE			**A1B**			**A1B-20CE**		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	2.32 (1.41)	15.34	0.00	2.21	19.07	0.00	-0.109	3.731	0.000
CAS	2.27 (1.38)	18.49	0.00	2.20	20.31	0.00	-0.072	1.815	0.000
SAS	2.32 (1.45)	19.93	0.00	2.17	18.93	0.00	-0.149	-0.998	0.000

b. From North to South, u component

	20CE			**A1B**			**A1B-20CE**		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	1.69 (1.19)	14.18	0.00	1.82	17.35	0.00	0.132	3.165	0.000
CAS	1.72 (1.31)	16.70	0.00	1.82	20.21	0.00	0.091	3.513	0.000
SAS	1.74 (1.16)	18.77	0.00	1.84	18.20	0.00	0.108	-0.566	0.000

c. From West to East, v component

	20CE			**A1B**			**A1B-20CE**		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	1.83 (1.19)	17.52	0.00	1.75	18.21	0.00	-7.73E-02	6.83E-01	-7.34E-06
CAS	1.78 (1.53)	18.08	0.00	1.74	18.14	0.00	-4.79E-02	6.20E-02	1.12E-06
SAS	1.78 (1.56)	20.30	0.00	1.71	17.99	0.00	-6.15E-02	-2.31E+00	9.27E-06

d. From East to Wast, v component

	20CE			**A1B**			**A1B-20CE**		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	1.95 (1.29)	16.13	0.00	1.99	18.82	0.00	4.26E-02	2.69E+00	-1.85E-05
CAS	1.90 (1.19)	18.12	0.00	1.94	16.78	0.00	3.68E-02	-1.34E+00	9.25E-06
SAS	1.88 (2.80)	18.76	0.00	1.96	18.21	0.00	8.06E-02	-5.49E-01	9.87E-06

Table SM4. Atmospheric temperatures (u.m. °K) are shown here for the 20CE and A1B climate scenarios defined by the University of Belgrade RCM. In the third column the difference A1B-20CE is shown for the arithmetic mean, maximum and minimum values. Cfs are shown in parehthesis.

	20CE			**A1B**			**A1B-20CE**		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	286.7 (1.07)	331.0	249.5	289.6	335.5	261.0	2.9	4.5	11.5
CAS	287.5 (1.05)	331.0	241.4	290.2	334.0	251.8	2.8	2.9	10.4
SAS	287.6 (1.05)	322.3	252.1	290.0	330.1	259.9	2.3	7.9	7.7

In Table B4 the atmospheric temperature trend is shown for both the 20CE and A1B scenarios. The temperature increases everywhere under the A1B scenario, with a maximum increase in the SAS (with 7.85°K increase against a 2.95 for the central region and 4.46 °K for the northern region), and with the minimum value being up to 11.53°K lower in the A1B scenario in the NAS, whereas the minimum value decreases of 10.38°K in the CAS and 7.73°K in the SAS. Basically, the average temperature trend increases of around 2 °K in all the regions under the A1B climate scenario, especially in the NAS. The increase in the maximum temperature is expected to occur in the SAS under the A1B scenario (the difference is 7.85 °K higher temperatures in air in this region) and the also the minimum temperature increases of 11.53 °K in the NAS against 10.38 in the CAS and 7.73 in the SAS.

Table B4. Atmospheric temperatures (u.m. °K) are shown here for the 20CE and A1B climate scenarios defined by the University of Belgrade RCM. In the third column the difference A1B-20CE is shown for the arithmetic mean, maximum and minimum values. Cfs are shown in parehthesis.

	20CE			A1B			A1B-20CE		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	286.7 (1.07)	331.0	249.5	289.6	335.5	261.0	2.9	4.5	11.5
CAS	287.5 (1.05)	331.0	241.4	290.2	334.0	251.8	2.8	2.9	10.4
SAS	287.6 (1.05)	322.3	252.1	290.0	330.1	259.9	2.3	7.9	7.7

Regarding precipitation, Table B5 shows that it is increasing under the A1B scenario in the NAS and SAS. The increase is though not relevant since it is on the order of tens of μm (around 40.4 μm/y increased precipitation is expected in the north). The maximum values give instead a decrease of 1.62 cm/y in the NAS, and 2.8 mm/y in the CAS and an increase of the same order of magnitude in the SAS. Also the forecasts for the 20CE exhibit pretty low precipitation values over the Adriatic Sea. It is reported also in the final report about the EBU-POM simulations that the regional circulation model (EBU-POM, Gualdi et al., 2008) shows smaller precipitation all over the Mediterranean Sea, if compared with observations. The global model used for external forcing has actually better results (Gualdi et al., 2008).

Table B5. Atmospheric precipitation (u.m. m/y) are shown here for the 20CE and A1B climate scenarios defined by the University of Belgrade RCM. In the third column the difference A1B-20CE is shown for the arithmetic mean, maximum and minimum values. Cfs are shown in parenthesis.

	20CE			A1B			A1B-20CE		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	0.000368 (6.09)	0.0434	0.0000	0.0004	0.0272	0.0000	4.04E-05	-1.62E-02	0.00E+00
CAS	0.000441 (3.62)	0.0368	0.0000	0.0003	0.0339	0.0000	-1.31E-04	-2.87E-03	0.00E+00
SAS	0.000326 (24.2)	0.0285	0.0000	0.0003	0.0274	0.0000	1.21E-05	-1.12E-03	0.00E+00

B.4.2 Marine parameters

Table B6.a,b shows the average, maximum and minimum values for the *u* oceanic current component whereas tables B5c,d show the average, minimum and maximum values for the *v* currents component for the 20CE and the A1B climate scenarios. In the 20CE scenario the oceanic currents are directed northward, and in the A1B scenario this trend is enhanced in the NAS, CAS and SAS. Instead the *v* component is directed westward in the CAS and SAS, and eastward in the NAS in the 20CE climate scenario.

In the A1B climate scenario the *v* component is instead directed eastward in both the NAS, CAS and SAS.

Table B6. ***u*** **and** ***v*** **oceanic current components are shown for the 20CE and A1B climate scenarios. In the third column the difference A1B-20CE is shown for the arithmetic mean, maximum and minimum values. Units are m/s. Cfs are given in parenthesis.**

Region **Climate scenarios** **Difference**

a. From South to North, u component

	20CE			A1B			A1B-20CE		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	0.0029 (9.79)	0.0298	0.0000	0.0030	0.0161	0.0000	1.2E-04	-1.4E-02	0.0E+00
CAS	0.0028 (14.87)	0.0214	0.0000	0.0031	0.0157	0.0000	2.8E-04	-5.7E-03	0.0E+00
SAS	0.0026 (20.11)	0.0136	0.0000	0.0029	0.0105	0.0000	2.9E-04	-3.1E-03	0.0E+00

b. From North to South, u component

	20CE			A1B			A1B-20CE		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	0.0028 (15.38)	0.0196	0.0000	0.0029	0.0192	0.0000	3.3E-05	-4.0E-04	0.0E+00
CAS	0.0028 (10.96)	0.0159	0.0000	0.0031	0.0151	0.0000	3.0E-04	-8.0E-04	0.0E+00
SAS	0.0025 (15.35)	0.0093	0.0000	0.0030	0.0113	0.0000	4.4E-04	2.0E-03	0.0E+00

c. From Wast to East, v component

	20CE			A1B			A1B-20CE		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	0.0133 (0.52)	0.1297	0.0000	0.0026	0.0897	0.0000	-1.1E-02	-4.0E-02	0.0E+00
CAS	0.0025 (10.02)	0.1410	0.0000	0.0028	0.0983	0.0000	2.5E-04	-4.3E-02	0.0E+00
SAS	0.0027 (12.14)	0.1445	0.0000	0.0029	0.1154	0.0000	2.0E-04	-2.9E-02	0.0E+00

d. From East to West, v component

	20CE			A1B			A1B-20CE		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	0.0023 (4.89)	0.2039	0.0000	0.0025	0.1404	0.0000	2.7E-04	-6.4E-02	0.0E+00
CAS	0.0022 (7.56)	0.2039	0.0000	0.0027	0.1408	0.0000	4.7E-04	-6.3E-02	0.0E+00
SAS	0.0024 (7.97)	0.1411	0.0000	0.0027	0.1485	0.0000	3.4E-04	7.4E-03	0.0E+00

Oceanic temperatures in the 20CE versus the A1B climate scenario are shown in table B7. Also for the sea, temperatures increase under the A1B scenario over the three regions. Both the maximum and the minimum values increase more or less at the same extent (from 1.86 °K for the minimum in the south to 3.97 °K increase in the maximum temperature in the north). The variability is less enhanced than it was observed for the atmosphere.

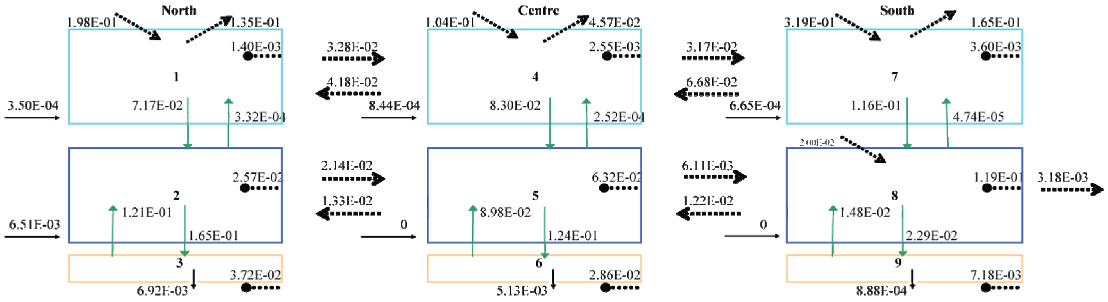
Table B7. Ocean temperatures (u.m. °K) are shown here for the 20CE and A1B climate scenarios defined by the University of Belgrade RCM. In the third column the difference A1B-20CE is shown for the arithmetic mean, maximum and minimum values. Cfs are shown in parenthesis.

	20CE			A1B			A1B-20CE		
	Mean	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**Max**	**Min**
NAS	288.0 (1.78)	298.9	278.1	290.2	302.8	281.7	2.2	4.0	3.6
CAS	288.2 (1.64)	299.5	279.8	290.3	303.2	282.8	2.1	3.7	3.0
SAS	288.1 (1.43)	300.3	283.5	289.5	303.5	285.3	1.4	3.3	1.9

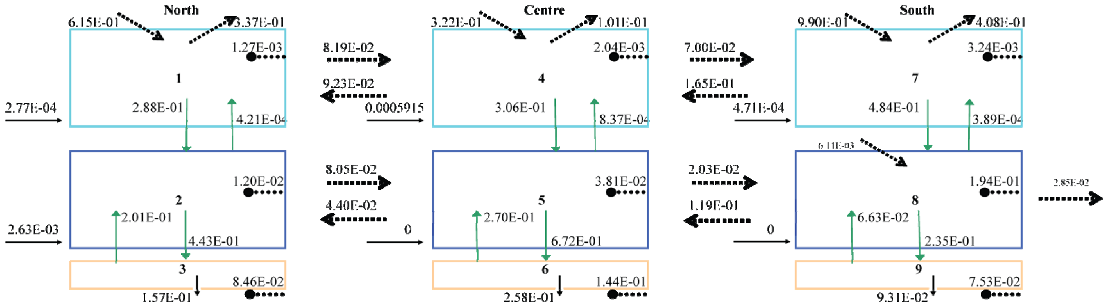
B.5 Mass balance diagrams

Figure B2 shows the mass balance diagrams for a. PCB 52, b. PCB 138 and c. PCB 153. Mass balance diagrams are reported here because they are an useful tool to evaluate which is the most important income in each region, and which processes play an important role in driving the inputs into one region and the removals from the region. This Figure is discussed in chapter 5.

a. PCB 52 mass balance diagram



b. PCB 138 mass balance diagram



c. PCB 153 mass balance diagram

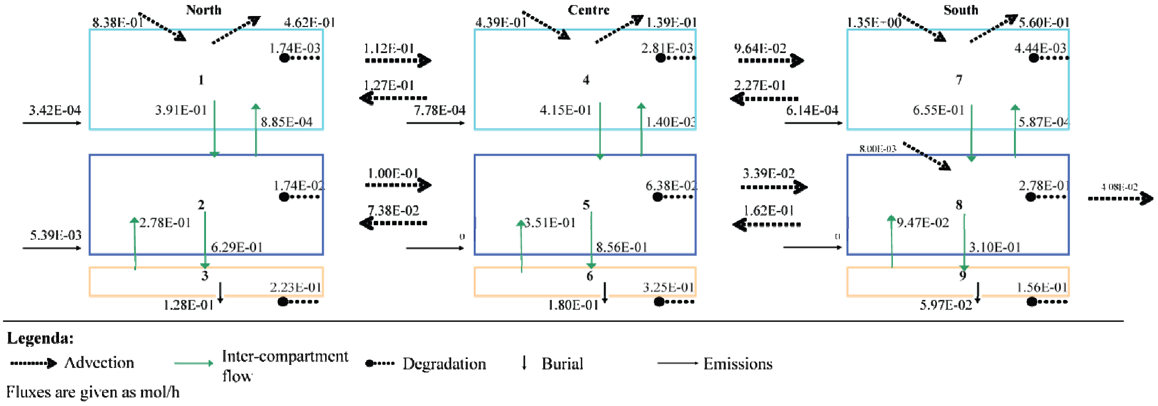


Figure B2. Mass Balance diagrams for a. PCB 52, b. PCB 138, c. PCB 153. Fluxes are given as mol/h.

B.6 Sensitivity analysis

Figures B3 and B4 show the sensitivity analysis results for PCB 52 and 138. these plots are discussed in chapter 5 of this thesis.

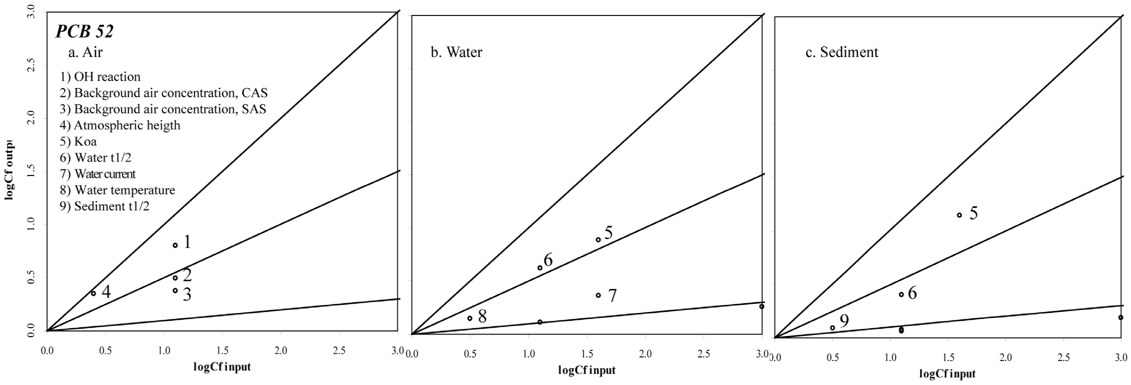


Figure B3. Graphical analysis of contribution to uncertainty in steady state fugacity of PCB 52 in the CAS. Analysis for a. atmosphere, b. water and c. sediment. The most important individual input parameters in terms of contribution to uncertainty in total steady state fugacity of PCB 52 are Koa for water and sediment, and background air concentration and aerosol solids fraction and dry deposition are important in determining the output fugacity for air. In water and sediment water half life is important in determining the results, and in water also water currents and temperature are also influential. Sediment half life play an important role in determining the fugacity in sediment. Lines corresponding to sensitivity S=1, 0.5 and 0.1 are shown.

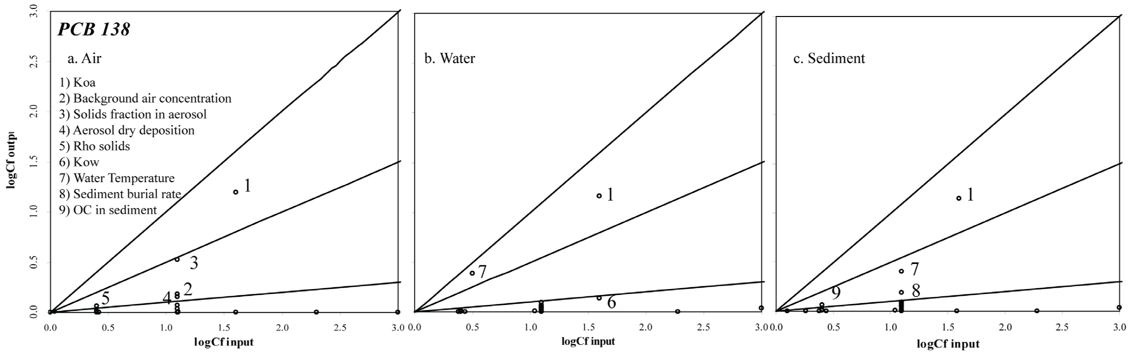


Figure B4. Graphical analysis of contribution to uncertainty in steady state fugacity of PCB 138 in the CAS is shown here. Analysis for a. atmosphere, b. water and c. sediment. The most important individual input parameters in terms of contribution to uncertainty in total steady *state fugacity of PCB 138 are* K_{oa} *for all compartments, and background air concentration and aerosol solids fraction and dry deposition and solids density are important in determining the output fugacity for air, whereas for water and sediment temperature,* K_{ow}*, OC content and sediment burial are more influential. Lines corresponding to sensitivity S=1, 0.5 and 0.1 are shown.*

*B.*7 Experiments results

Climate experiments results are shown here for PCB 52 and 138. These plots are discussed in chapter 5.

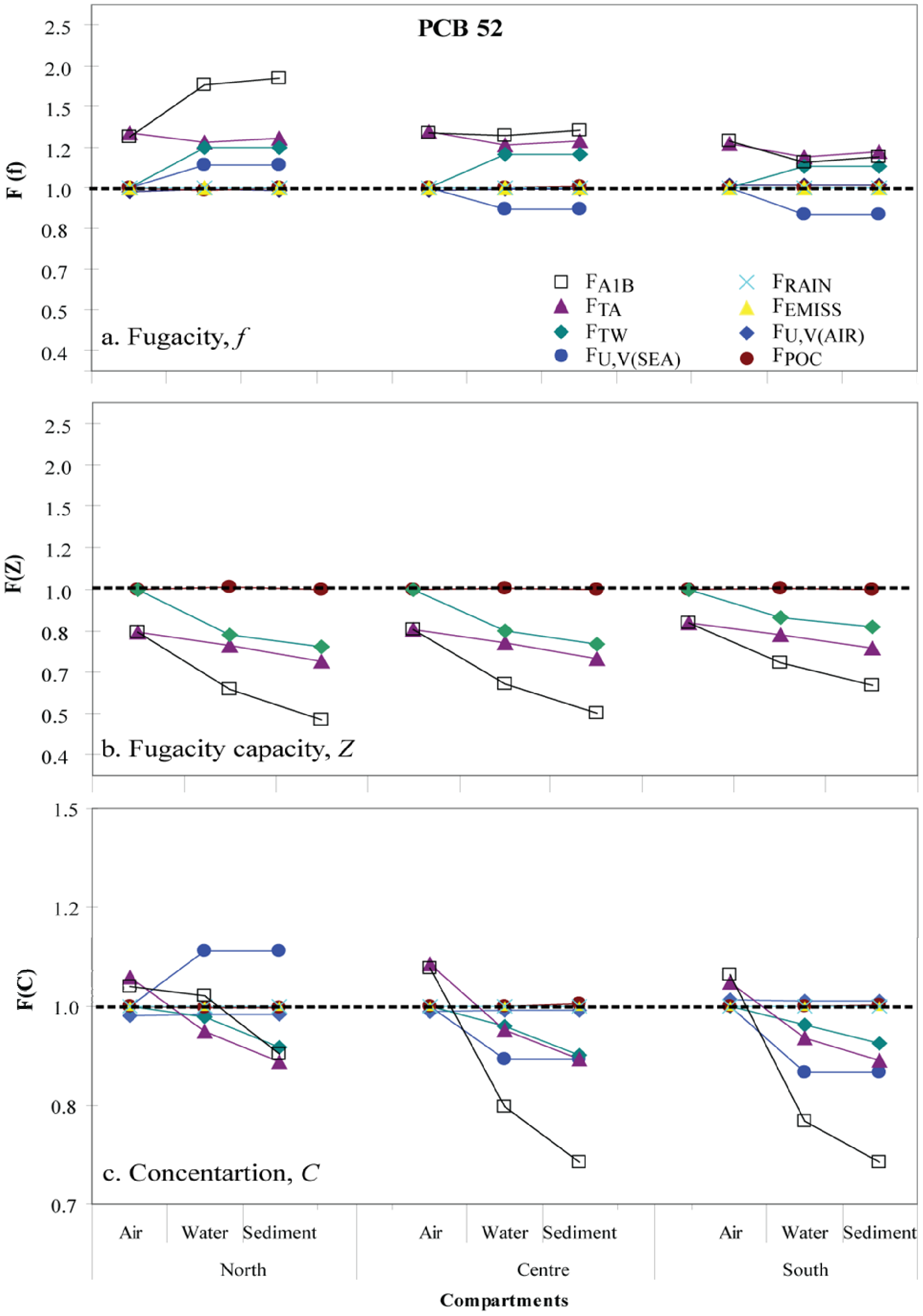


Figure B5. Experiments results are shown here for PCB 52. a: F – factor of change – for fugacities in the different compartments and regions is *shown; b: the F values for Z are shown (only* T_A*, POC,* T_W *and* $u,v_{(SEA)}$ *contribute to determine a change in Z); c: F for concentration in all compartments 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_{EMISS}*,* F_{RAIN}*,* F_{POC}*,* F_{TW}*,* $F_{U,V(SEA)}$*, stand respectively for atmospheric temperature increase, air velocity, temperature effect on emissions, precipitation, particulate organic carbon, sea temperature and sea currents factor of change.*

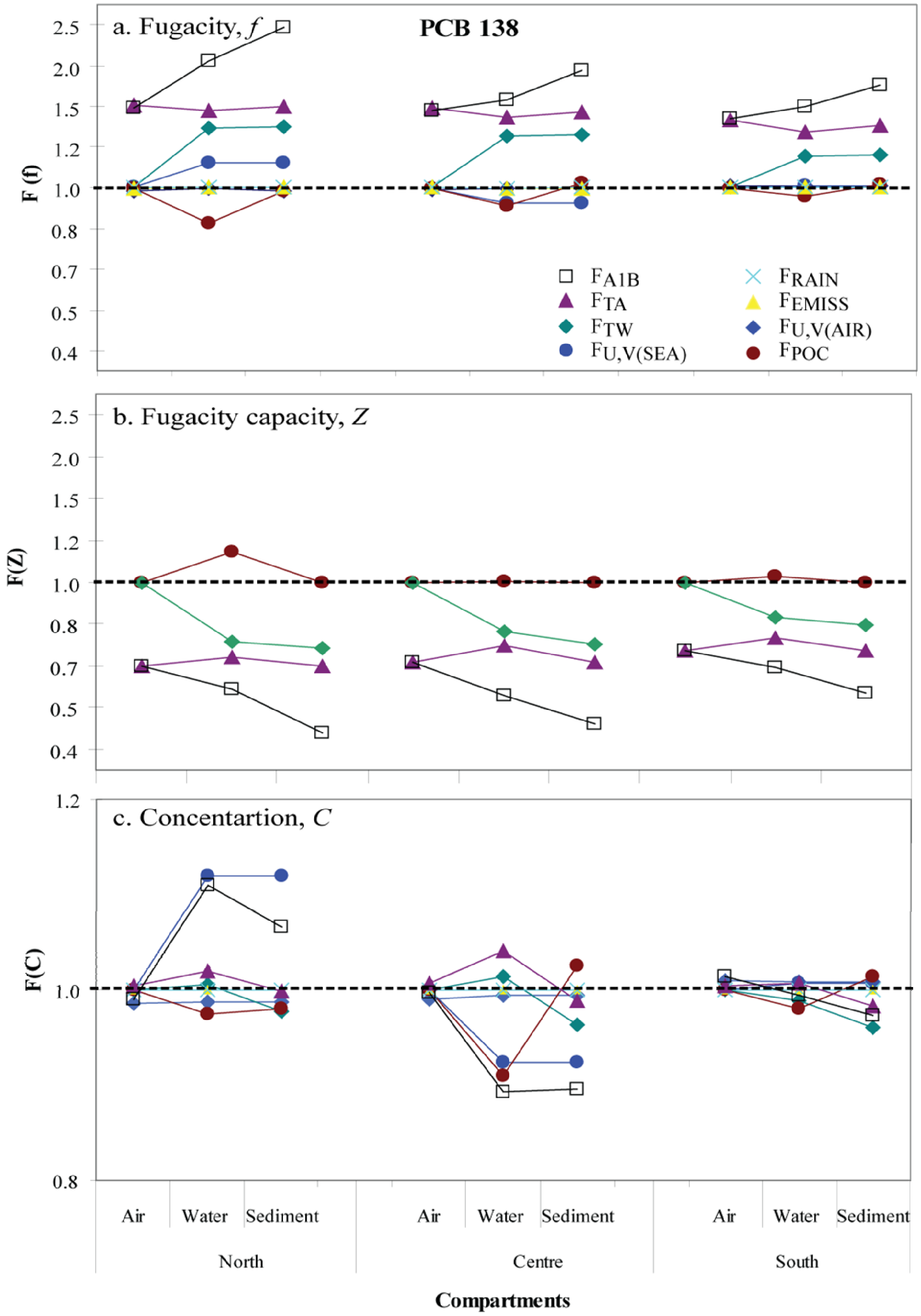


Figure B6. Experiments results are shown here for PCB 138. a: F – factor of change – for fugacities in the different compartments and regions is shown; b: the F values for Z are shown (only T_A, POC, T_W and $u,v_{(SEA)}$ contribute to determine a change in Z); c: F for concentration in all compartments 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_{EMISS}, F_{RAIN}, F_{POC}, F_{TW}, $F_{U,V(SEA)}$, stand respectively for atmospheric *temperature increase, air velocity, temperature effect on emissions, precipitation, particulate organic carbon, sea temperature and sea currents factor of change.*

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Synergy —
the bonus that is achieved when things work together harmoniously.
(*Mark Twain*)

This Ph.D. thesis was possible thanks to the collaborative personalities that I encountered during these three years. Therefore, I would like to gratefully acknowledge all the scientists with whom I had the pleasure and the honor to collaborate during my Ph.D., and these are:

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Dr. Stefano Foramiti for the collaboration in data management in the Adriatic Sea case study;

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Dr. Martin Scheringer and Ph.D. student Harald von Waldow for the support and the interesting comments and directions in the global case study presented in this thesis;

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Estratto per riassunto della tesi di dottorato

Studente: Lara Lamon matricola: 955349

Dottorato: Scienze Ambientali

Ciclo: XXII

Titolo della tesi: Influence of climate change on the environmental behavior and distribution of persistent organic pollutants (POPs)

Estratto:

Ricostruzioni temporali dell'andamento climatico dimostrano come esso sia in continuo cambiamento. Sono numerose le osservazioni sperimentali a scala regionale e globale a favore della teoria del cambiamento climatico. Anche i microinquinanti organici (POP, Persistent Organic Pollutants) costituiscono una questione di interesse sopranazionale. Questa tesi di dottorato ha l'obiettivo di studiare in quale modo il cambiamento climatico possa influenzare il comportamento ambientale dei POP, sostanze prioritarie il cui comportamento ambientale dipende anche dalle variabili climatiche.

Nella prima parte della tesi saranno introdotte le tematiche di cambiamento climatico, POP e la metodologia che sarà poi sviluppata nella sezione applicativa seguente, ed è presentata una analisi delle conseguenze che il cambiamento climatico può avere sui vari aspetti connessi ai POP (in particolare sul monitoraggio, sulle attività modellistiche e sulle applicazioni legislative).

Nella seconda sezione saranno applicati modelli di fugacità per sviluppare le considerazioni di cui sopra attraverso due casi di studio. Il primo esercizio modellistico consiste nell'applicazione di un modello esistente a scala globale adattato a due scenari climatici, di cui uno presente a rappresentare lo stato attuale, ed uno scenario di cambiamento climatico A2 come definito dal Pannello Intergovernativo sul cambiamento climatico (IPCC). Il secondo consiste nella costruzione di un modello di fugacità di III livello a scala regionale i cui risultati sono confrontati con valori provenienti da osservazioni sperimentali, e poi è parametrizzato in modo da rappresentare lo senario A1B come definito dall'IPCC in modo da valutare quali fattori influenzino significativamente la distribuzione ambientale dei composti organici considerati.

Firma dello studente

Ph.D. thesis abstract

Student: Lara Lamon identification number: 955349
Ph.D. in: Environmental Sciences
Cycle: XXII

Title of the thesis: Influence of climate change on the environmental behavior and distribution of persistent organic pollutants (POPs)

Abstract:

The climate temporal reconstruction shows how the Earth’s climate is in continuous change. Evidence of climate change has been observed at both the global and regional scales. The environmental contamination caused by Persistent Organic Pollutants (POPs) is also a global concerning issue. This Ph.D. thesis aims at investigating which effects climate change would exert on the environmental distribution of POPs, priority pollutants which behavior is affected by climate variables.

First, the concepts about climate change and POPs are introduced, the methods which will be used in the applicative part are described, and a review on the consequences of climate change on POPs behavior and on POPs-related activities (i.e. monitoring, modeling and regulation) is presented.

In the application section, multimedia fate and transport models are applied in order to investigate the climate change effect on POPs environmental behavior through the development of two case studies. The first model exercise aims at understanding which factors are more effective in determining POPs environmental behavior under a climate change scenario through the application of a global fate and transport model (BETR Global) to two climate scenarios, a present climate scenario and the A2 climate change scenario, a reference climate change scenario defined by the Intergovernmental Panel on Climate Change (IPCC). The second case study consists on the creation of a level III fugacity model for the Adriatic Sea, and is evaluated and then is parameterized following the A1B climate change scenario as it is defined by the IPCC in order to investigate which is the effect of climate change on POPs environmental distribution and concentration.

Student’s signature